土壌の汚染除去と回収･固化技術-1

水熱分解法による汚染土壌･焼却灰処理技術

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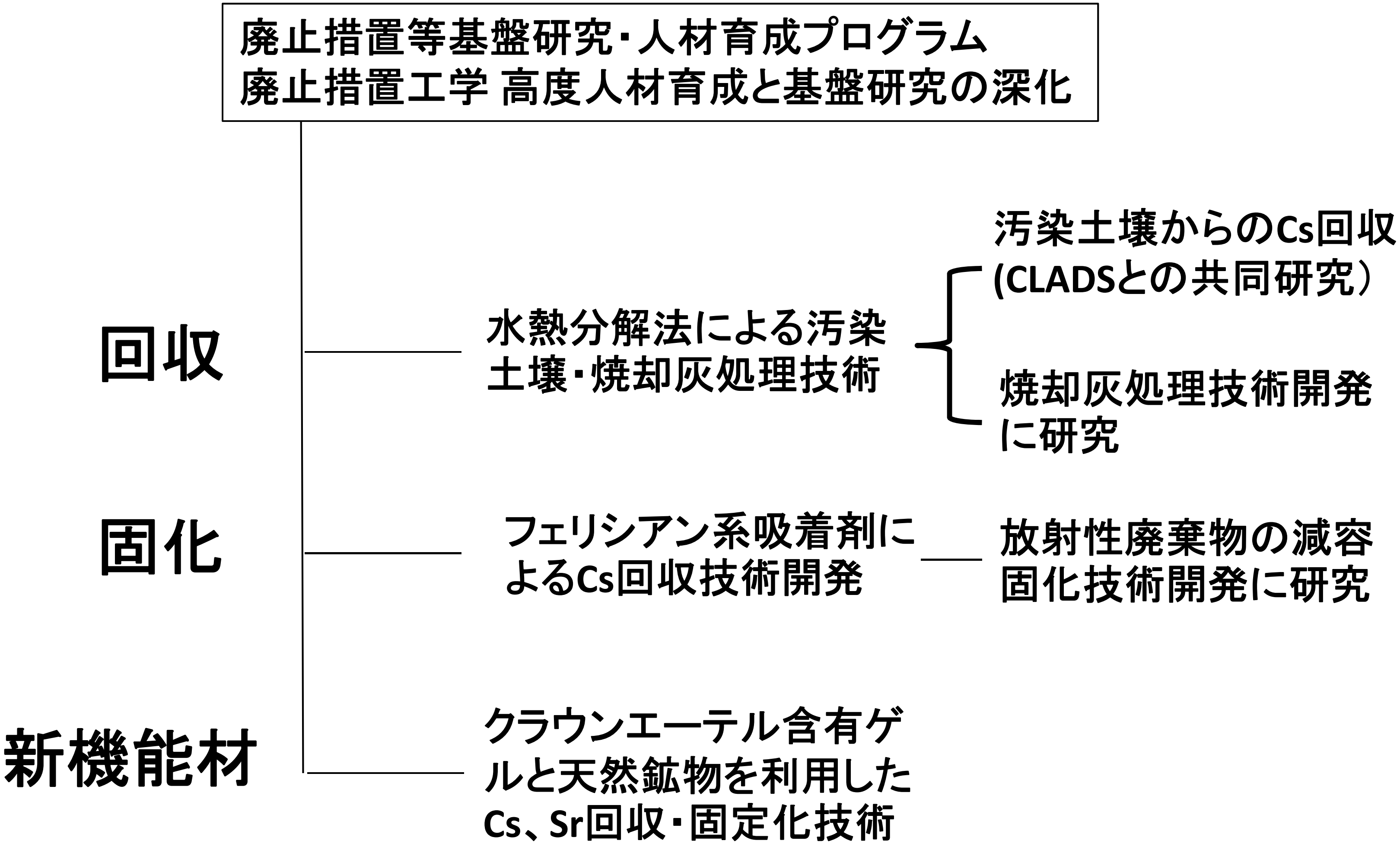
廃止措置技術･人材育成フォーラム
2017年1月20日

現在進めている研究



廃止措置等基盤研究・人材育成プログラム
廃止措置工学 高度人材育成と基盤研究の深化

回収

水熱分解法による汚染土壌・焼却灰処理技術

汚染土壌からのCs回収(CLADSとの共同研究）

焼却灰処理技術開発に研究

固化

フェリシアン系吸着剤によるCs回収技術開発

放射性廃棄物の減容固化技術開発に研究

新機能材

クラウンエーテル含有ゲルと天然鉱物を利用したCs、Sr回収・固定化技術

現在進めている研究

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- **回収**
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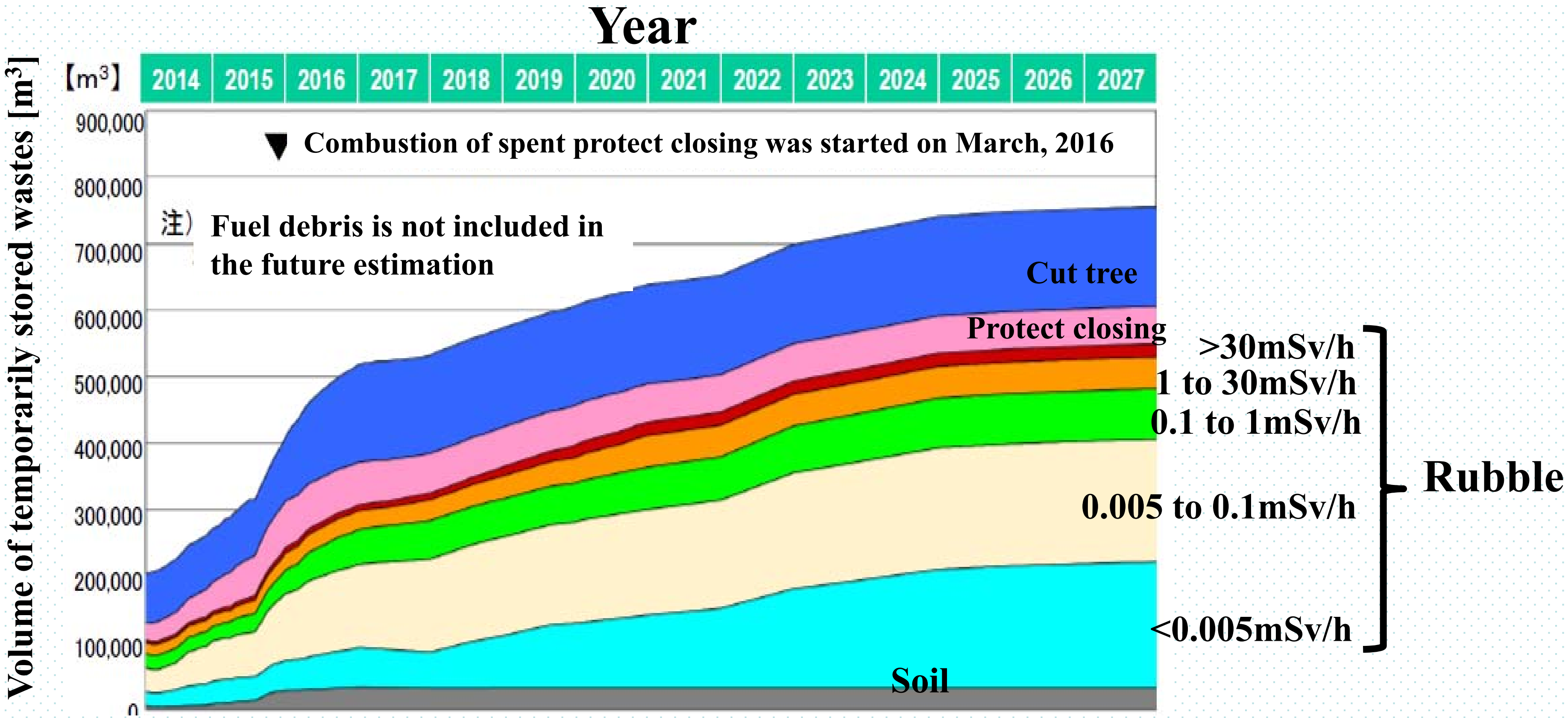
Estimation of Solid Waste Generation

- This figure shows the time change of the volume of solid waste in temporary storage facility.
- If any measures to volume-reduce the solid wastes are not taken, total volume of solid wastes will be increased to about 750,000 m^3 by 2028.

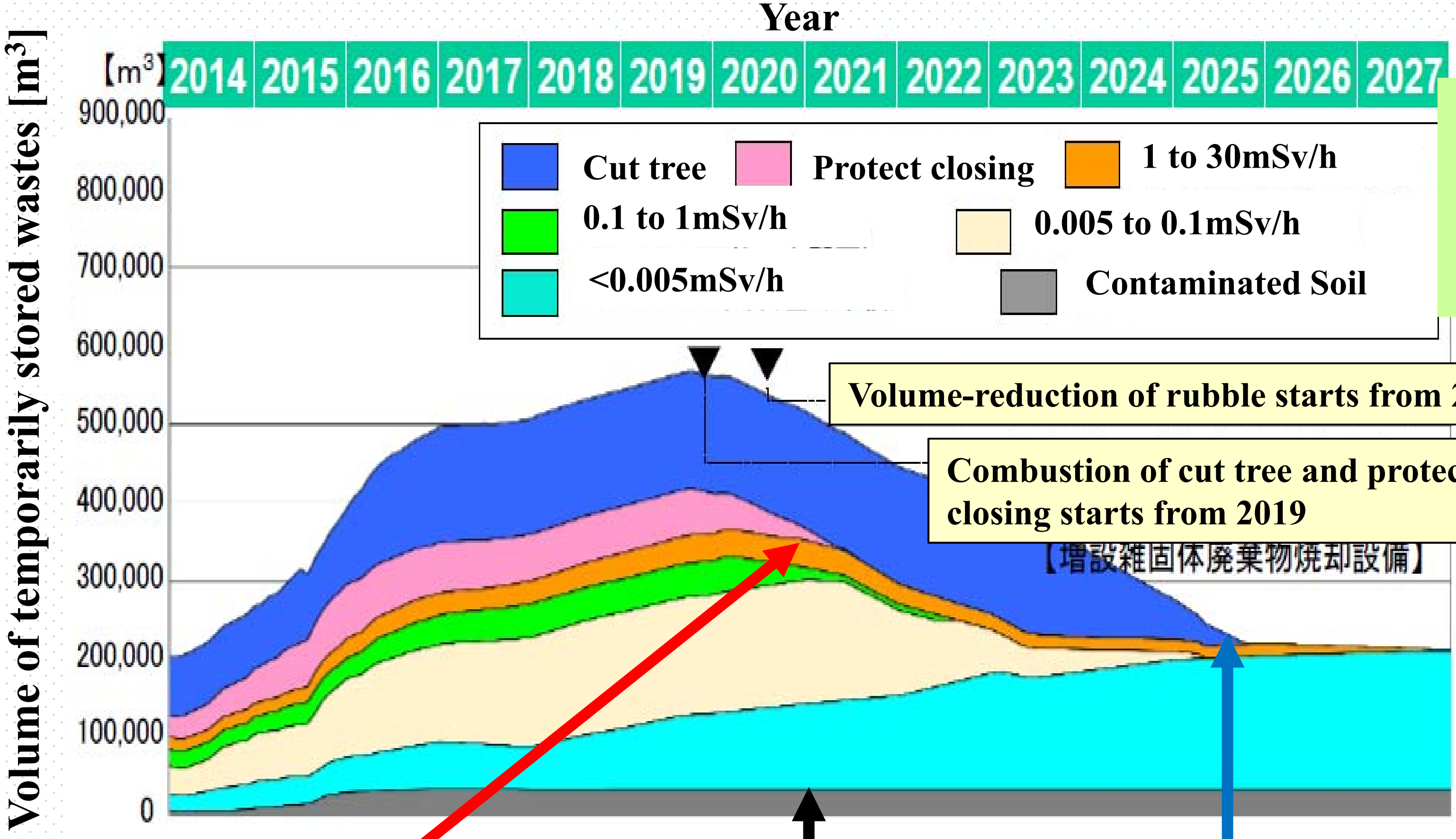


*** Rubble means solid wastes including contaminated metal, concrete and soil**

Ref. 東京電力　福島第一原子力発電所（1F）の廃止措置で発生する固体廃棄物の管理について （2016年4月）

Estimation of Solid Waste Generation with Volume-reduction Measures

- Several volume-reduction measures such as combustion of cut tree and protective closing and the volume reduction of rubble, are considered. If these measures are attained, the volume of solid waste in temporary storage facility can be reduced. The temporary storage of solid wastes except low-radiation rubble will be ended by 2026.



Volume-reduction of rubble starts from 2020

Combustion of cut tree and protect closing starts from 2019

We need volume-reduction technology of solid wastes

The storage of spent protect closing will be ended until 2021

Development of contaminated soil treatment technology

The storage of cut tree will be ended until 2026

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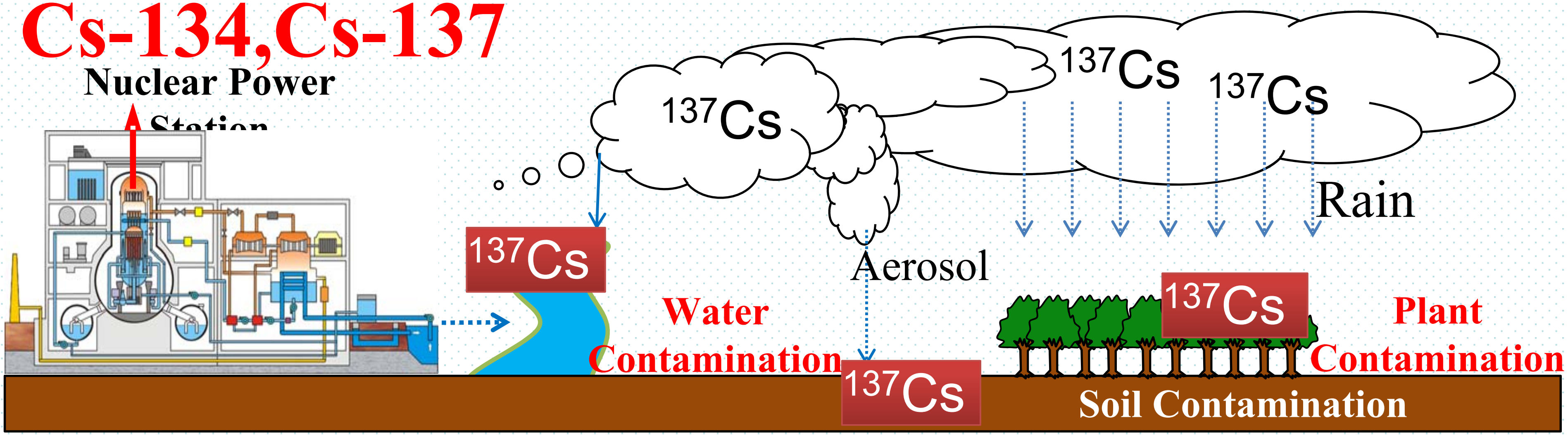
Release of Radioactive Nuclides to Environment

Release to atmosphere
Cs-134,Cs-137

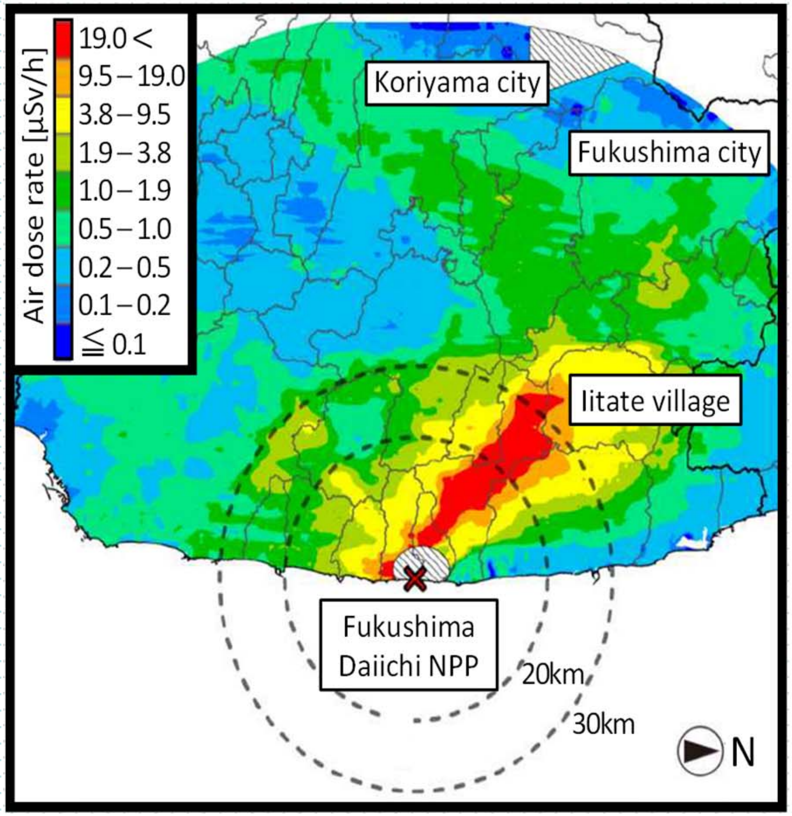


- Cs and I were released to the atmosphere by the explosion of reactor buildings and fallouts of radioactive elements contaminated widely in Eastern Japan.
- A short-lived nuclide, I-131, has already decayed. Nowadays Cs-134 and Cs-137 are main radioactive nuclides of environmental pollution.

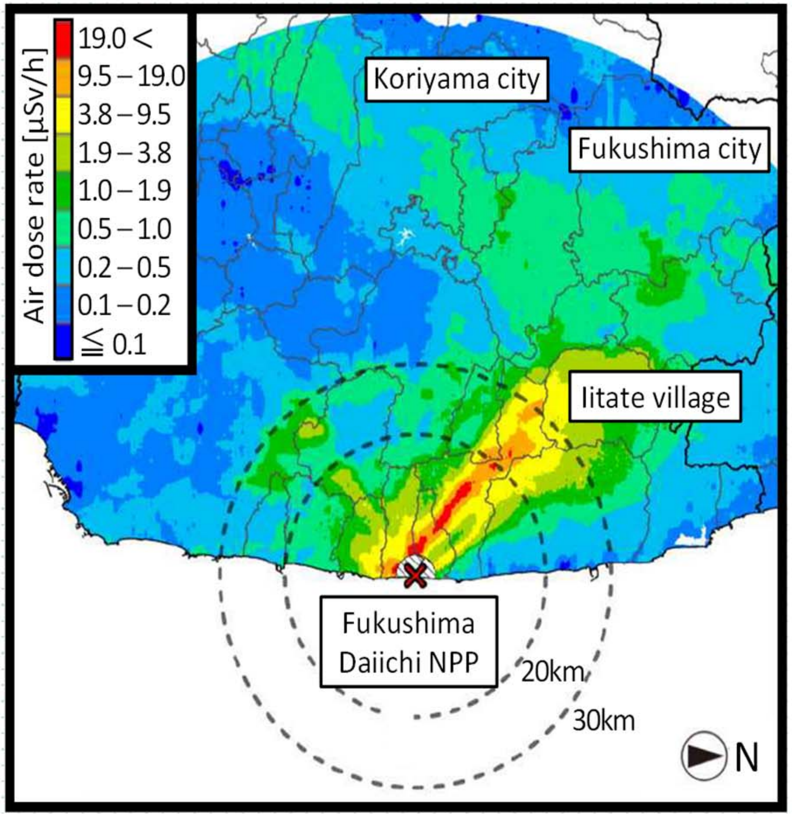
Total amount of released ^{137}Cs : 15 PBq ^{134}Cs : 18 PBq
Data By Nuclear and Industrial Safety Agency (2011)

1PBq=10^{15}Bq

Circumstance of Cs deposition in Eastern Japan



April 29, 2011



September 28, 2013

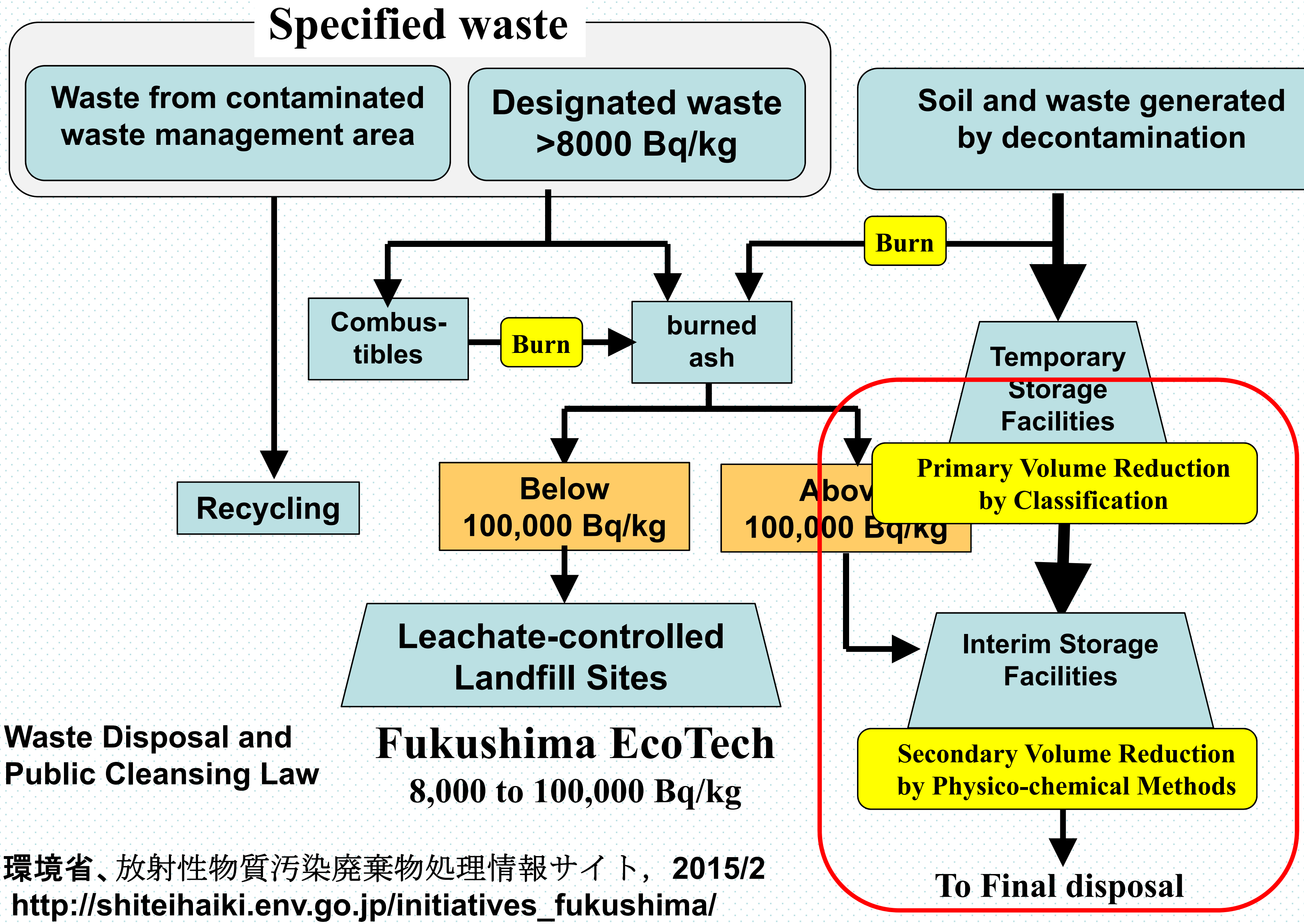
The width of plume becomes narrower as time elapses Radioactivity of ^{137}Cs and ^{134}Cs is reduced by not only the physical decay, but also the weathering effect such as wind and rain. The decreasing rate of the radioactivity is faster than that by the physical decay.

Classification of Contaminated Waste (2011)

	Fukushima Pref.			Outside Fukushima Pref.	
Classification of Waste	Specified Waste		Soil and waste generated by decomtamination	Specified Waste	Soil and waste generated by decomtamination
	Waste from Contaminated waste management area (Wastes from restricted areas and deliberate evacuation areas)	Designated Wastes (Paddy straw and wastes generated from water and sewage facilities and waste incineration facility, whose radiation doses are above 8000 Bq/kg.)		Only designated waste	
Weight of generated waste	about 500,000 ton	about 60,000 ton/yr	about 15 to 31 million m^3	about 80,000 ton/yr	about 1.4 to 13 million m^3

Contaminated waste is classified as three categories, waste from contaminated waste management area, designated waste (> 8000 Bq/kg) and soil and waste generated by decontamination. In 2011, Ministry of the Environment estimated weights of the wastes. These values are very large.

Flow Diagram of Specified Waste and Contaminated Soil



Specified waste

Waste from contaminated waste management area

Designated waste >8000 Bq/kg

Soil and waste generated by decontamination

Burn

Combus-tibles

Burn

burned ash

Temporary Storage Facilities

Recycling

Below 100,000 Bq/kg

Above 100,000 Bq/kg

Primary Volume Reduction by Classification

Leachate-controlled Landfill Sites

Interim Storage Facilities

Secondary Volume Reduction by Physico-chemical Methods

To Final disposal

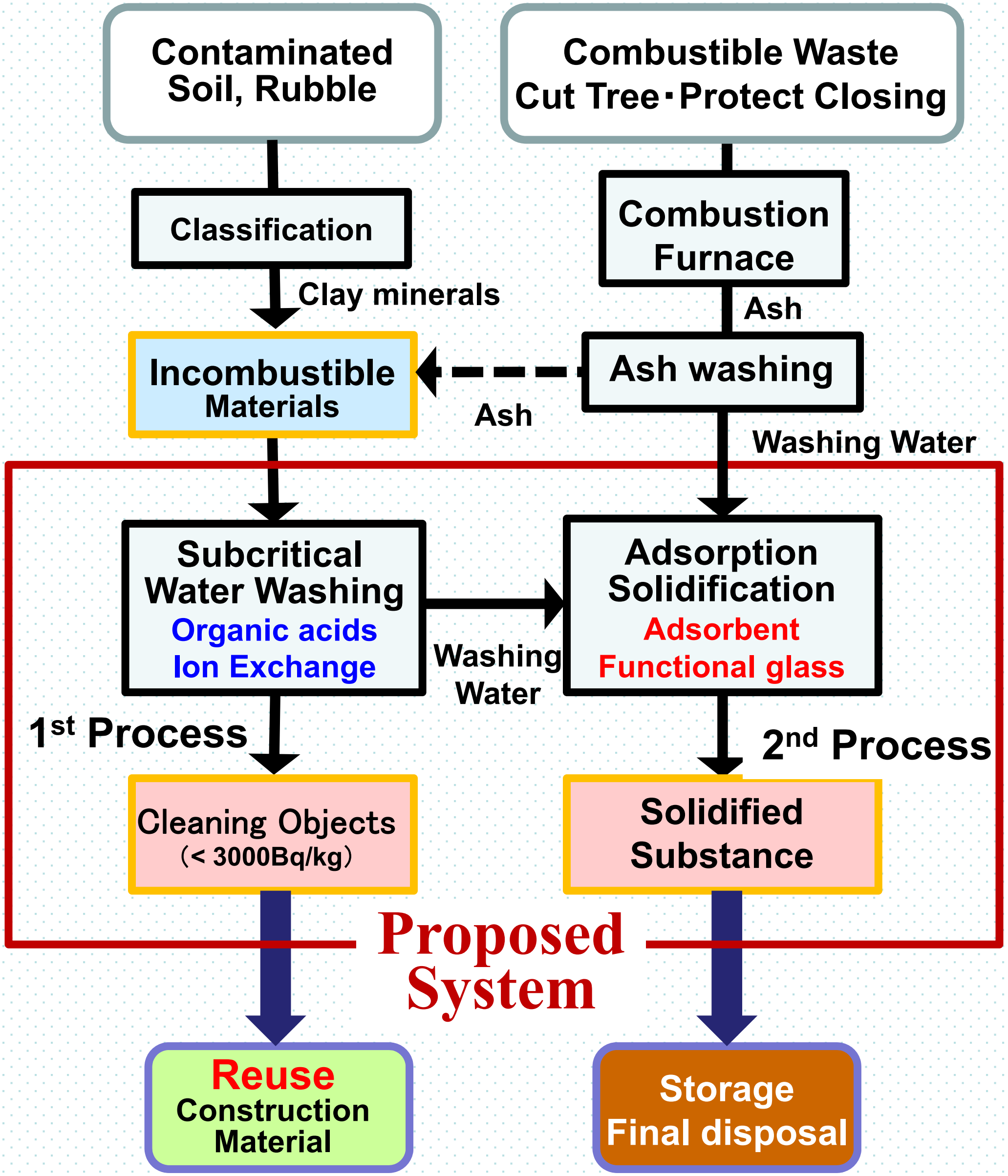
Waste Disposal and Public Cleansing Law

Fukushima EcoTech

8,000 to 100,000 Bq/kg

環境省、放射性物質汚染廃棄物処理情報サイト，2015/2
http://shiteihaiki.env.go.jp/initiatives_fukushima/

Proposal of Solid Waste Treatment System



We propose a new solid waste treatment system with two processes to realize the concept of solid waste treatment.

1st Process (HTT process)

①Radioactive elements (Cs) in solid waste are recovered in subcritical water with organic acids or alkaline and alkaline earth ions.

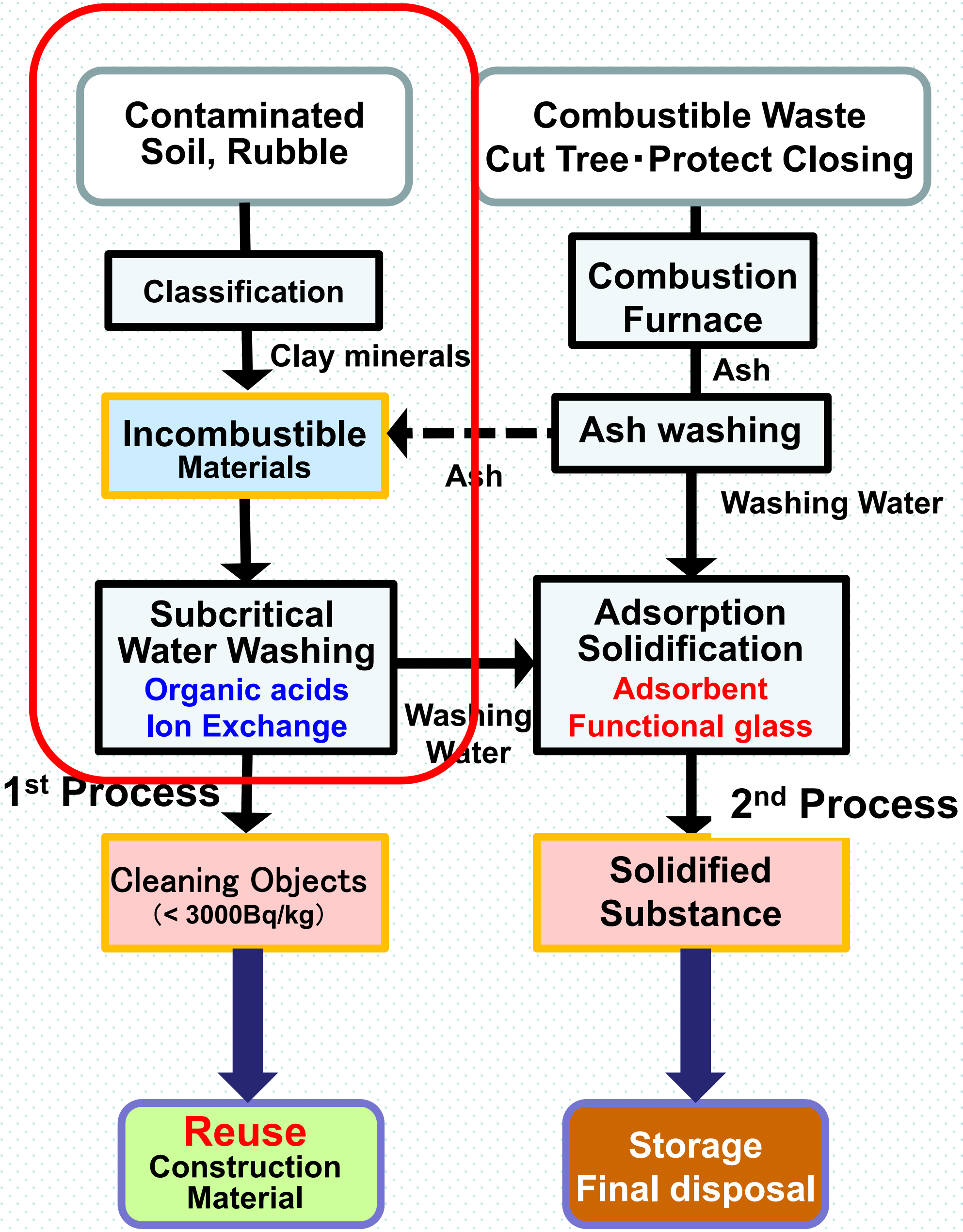
②Cleaning objects can be reused industrially (e.g. construction material)

2nd Process

①Radioactive elements (Cs) in washing water are concentrated in highly selective adsorbent or functional glass.

② Radioactive elements (Cs) are solidified in stable inorganic materials (e.g. glass, heteropoly acid). A small amount of radioactive waste is stored finally.

Proposal of Solid Waste Treatment System



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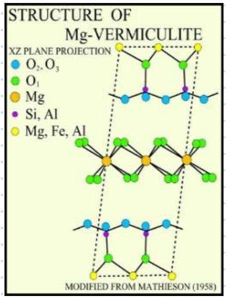
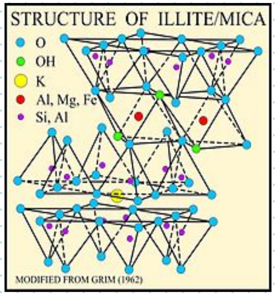
Cs Adsorption in Various Clays

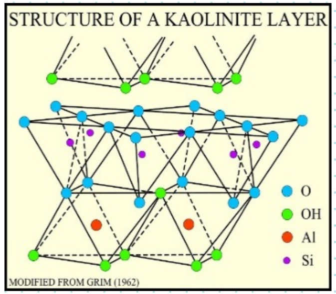
Clay Minerals

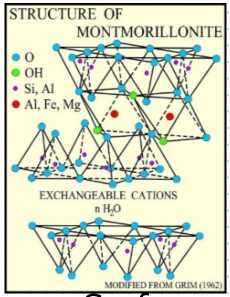
- Montmorillonite: 2:1 type, high expansion
- Vermiculite: 2:1 type, intermediate expansion
- Illite: 2:1 type, non-expansion
- Kaolinite: 1:1 type, non-expansion

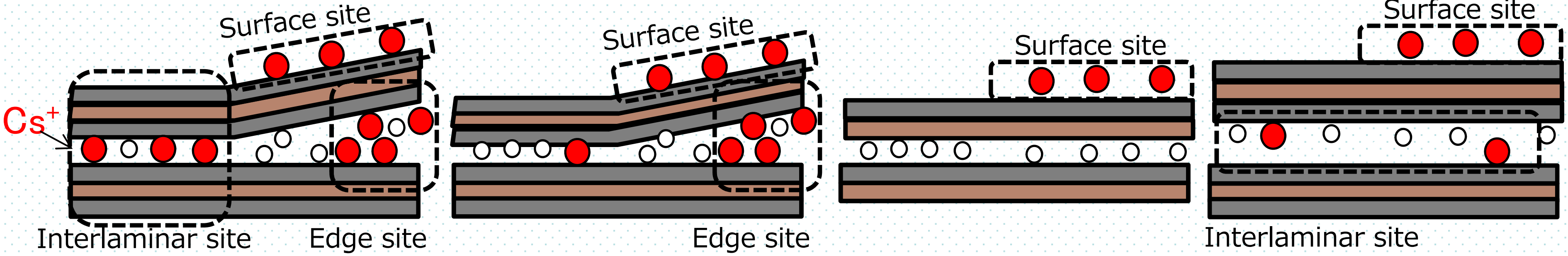


▬ :Silica layer
▬ :Alumina layer
● :Cs⁺
○ :Na⁺, K⁺ **or** Mg²⁺, Ca²⁺ (Competitive cation)









Vermiculite
(intermediate expansion)

Illite/micas
(non-expansion)

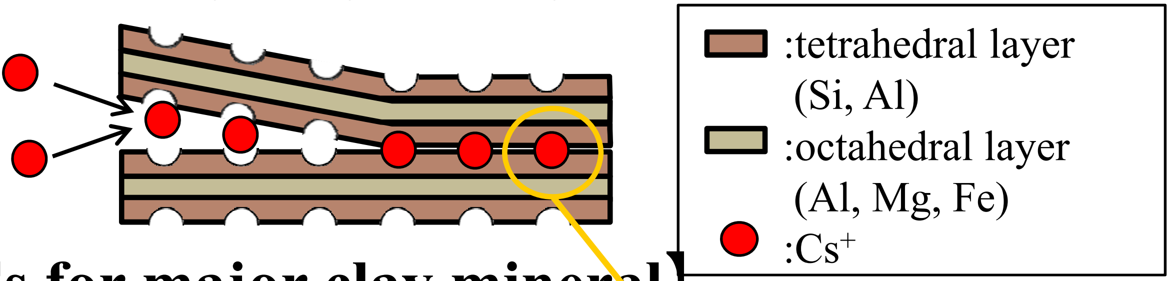
Kaolinite
(non-expansion)

Montmorillonite
(high expansion)

Adsorption of Cs(I) into Clay Mineral

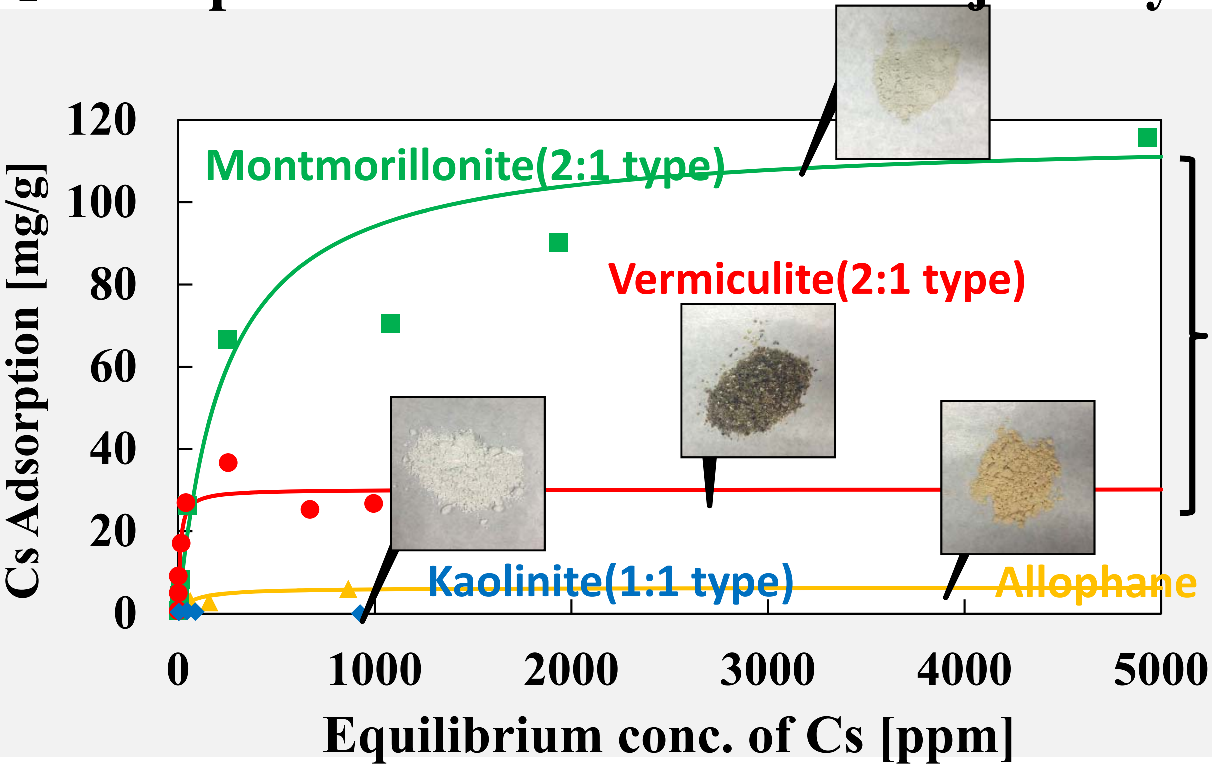
Contaminated soil with Cs-137($t_{1/2}$=30yr)

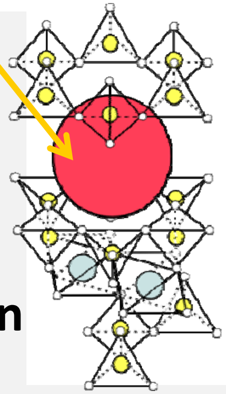
Cs is adsorbed strongly into 2:1 type layered clay mineral of soil



2:1 type layered clay mineral

【Adsorption Isotherm of Cs for major clay mineral】





Montmorillonite：

Adsorbed Cs is recovered easily.

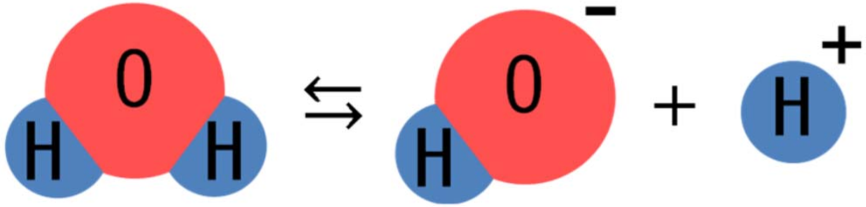
Vermiculite：

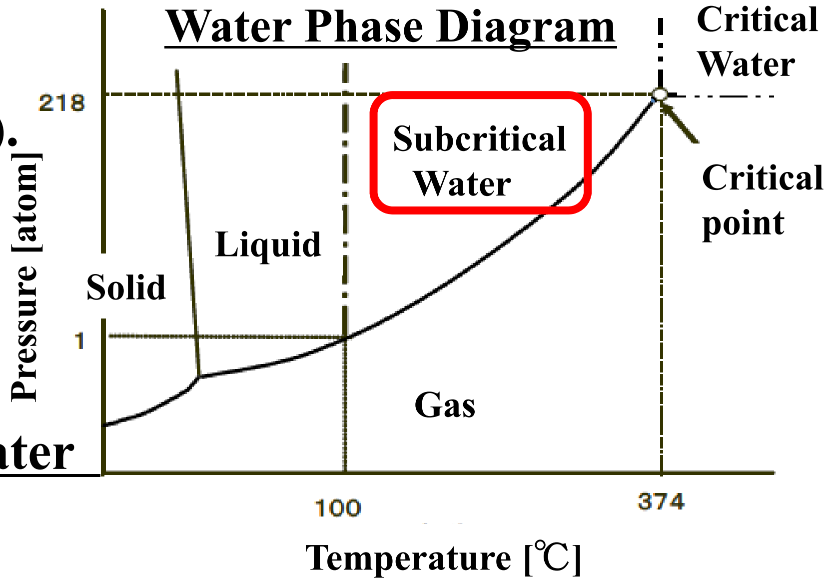
Desorption of Cs is very difficult.

If Cs is desorbed from vermiculite, the recovery of Cs from soil is improved

Subcritical Water

Ionic product of water becomes larger in subcritical condition under high temperature (about 200℃) and high pressure (about 3MPa).





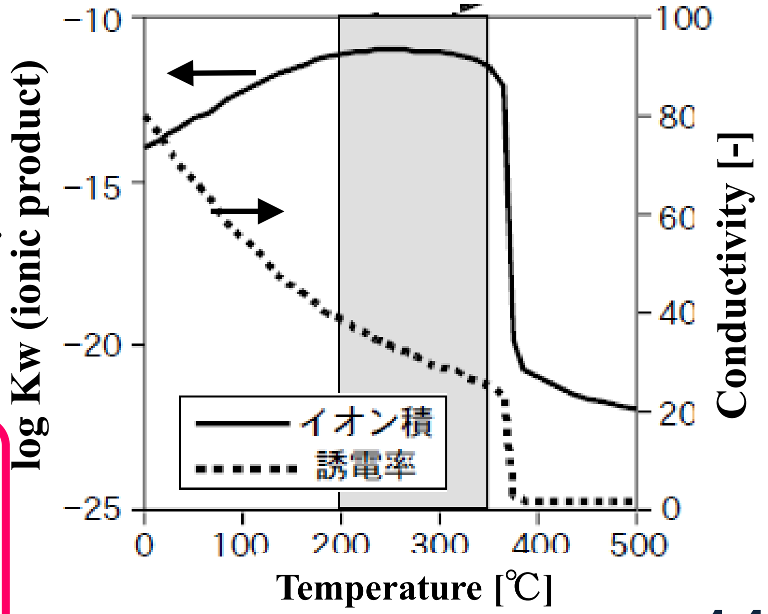
Specific Chemical Properties of Subcritical Water

① **High-speed Hydrolysis Effect**

- **Cs adsorbed in organic materials can be recovered to water phase by the decomposition of organic materials.**
- **Cs adsorbed in inorganic materials is also recovered by the high-speed decomposition of inorganic materials by subcritical water with organic acids.**

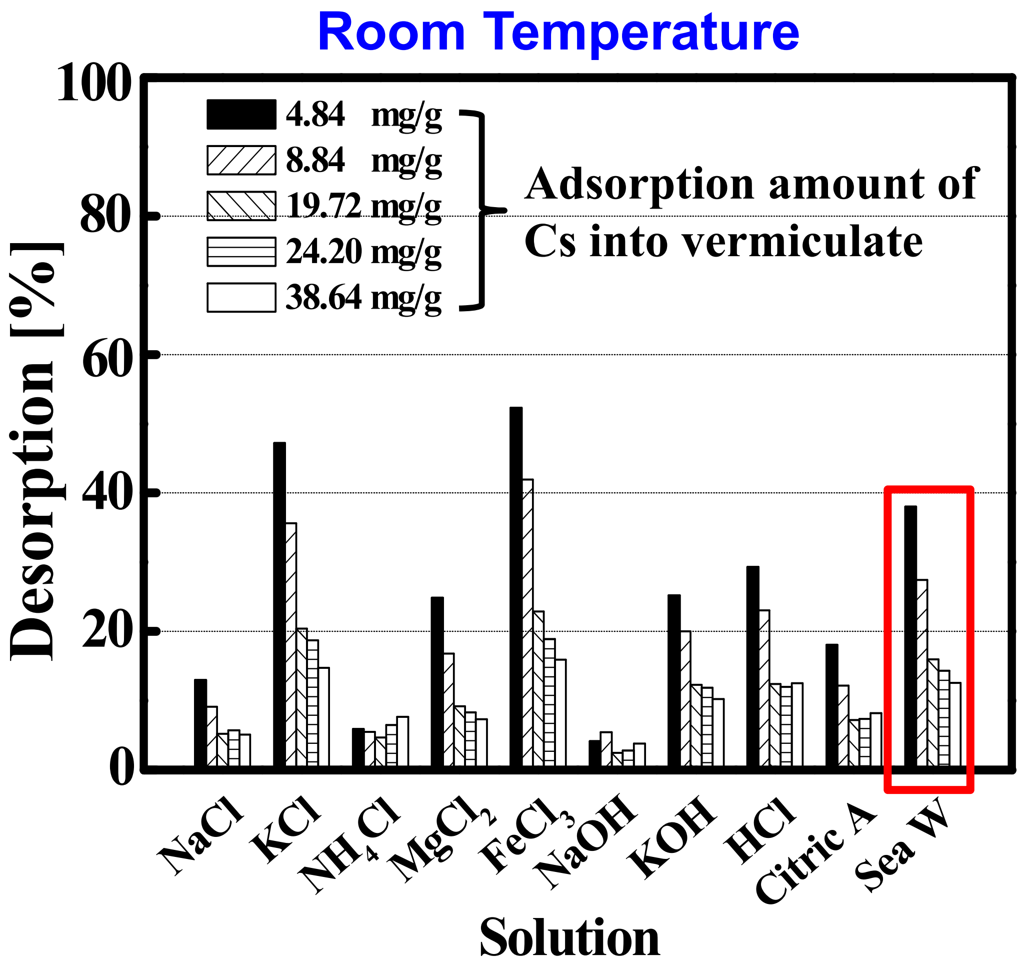
② **High-speed Ion Exchange Effect**

Cs adsorbed in inorganic materials can be recovered to the aqueous phase by subcritical water with alkaline and alkaline earth ions.



Ionic Product and Conductivity of Water

Ion-exchange Recovery of Cs from Vermiculate at Room Temp.

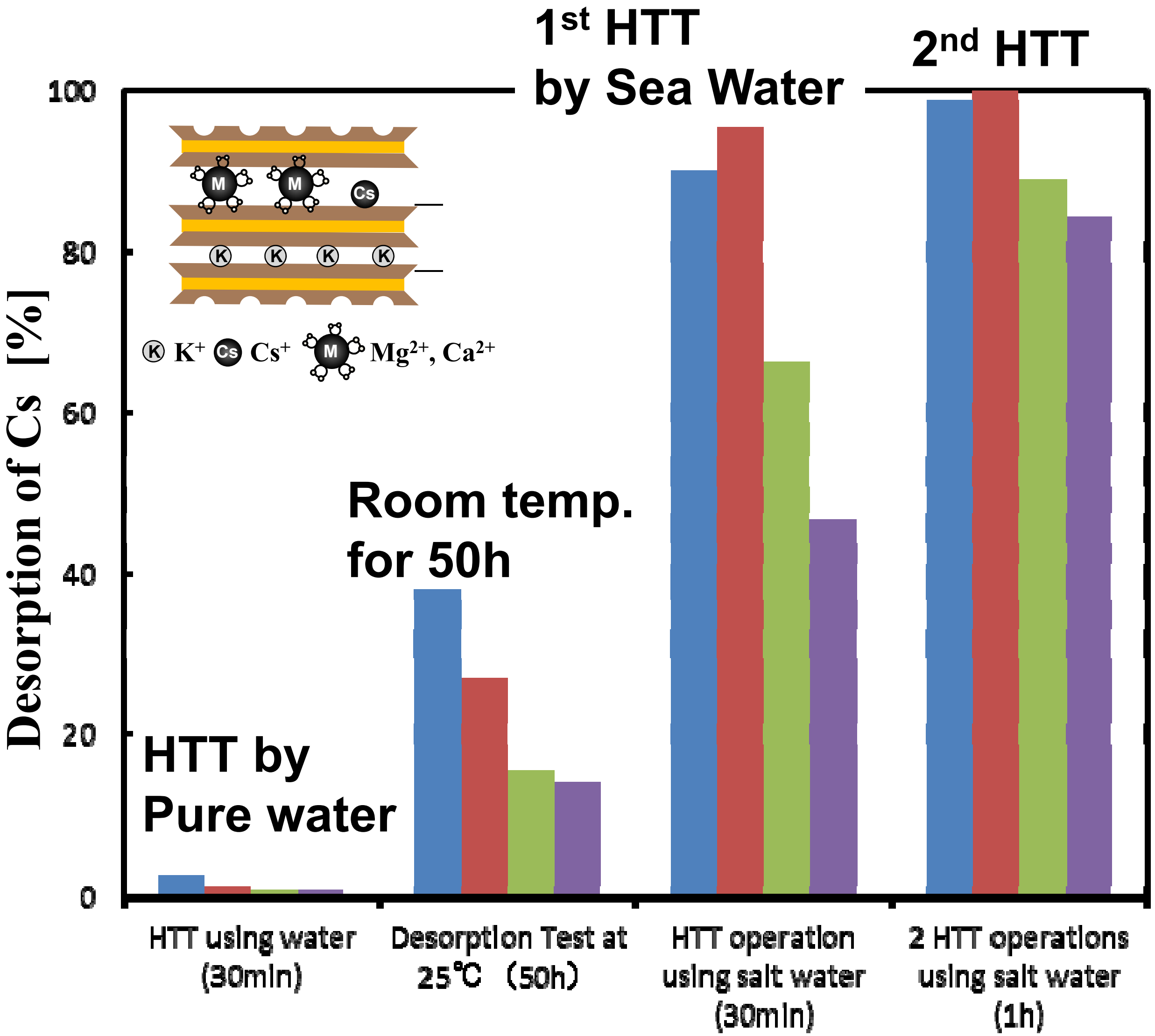


Experimental Conditions

Volume of salt solution =10ml
Weight of Vermiculate=100mg
Conc. of salt= 0.1M
Temperature =25 ℃
Operation time=24h.

- **Ability**: Fe^{3+} ＞ K^+ ＞**S.W** ＞ H^+ ＞ Mg^{2+} ＞ Citric Acid ＞ Na^+ ＞ NH_4^+ .
- **Sea water** has a relative high ion exchange ability.
- **Ion-exchange technique** is useful for the recovery of Cs from Vermiculate.

Ion Exchange of Cs Adsorbed into Vermiculite



Experimental Conditions

Volume of solution=50ml
Weight of Vermiculite =0.5g
Temperature =250℃
Operation Time= 30 min
Conc. of salt -0.5 M

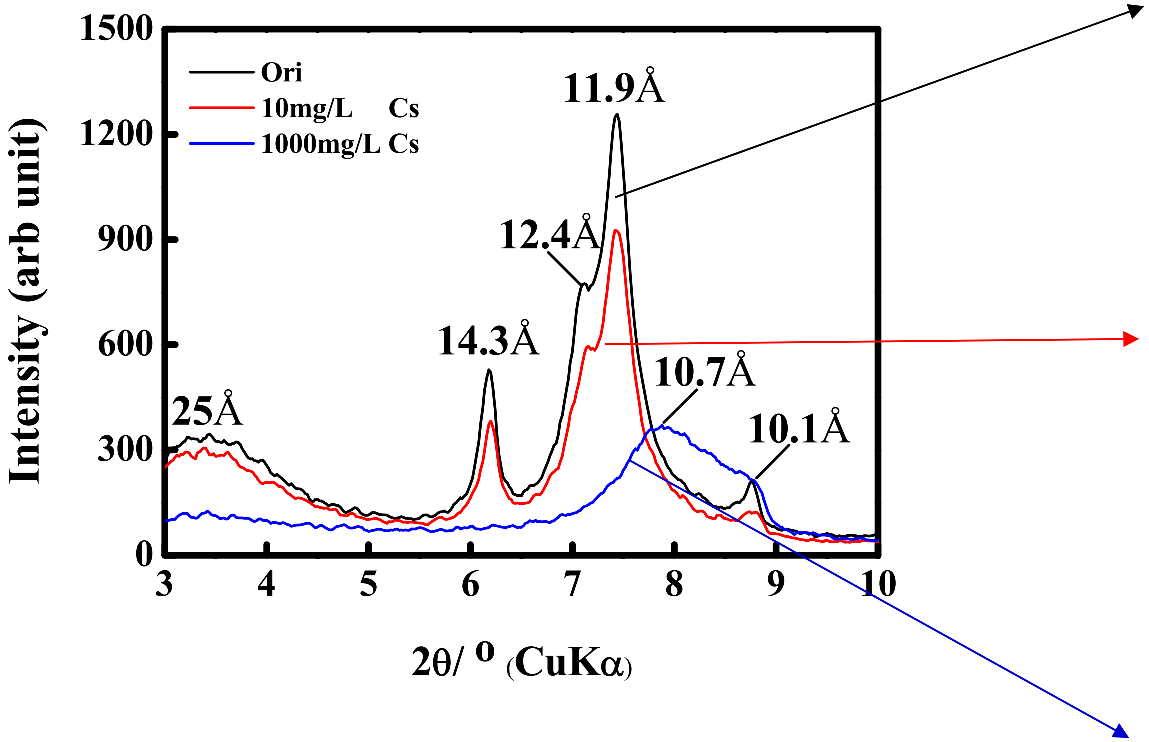
Adsorption amount
of Cs into Vermiculite

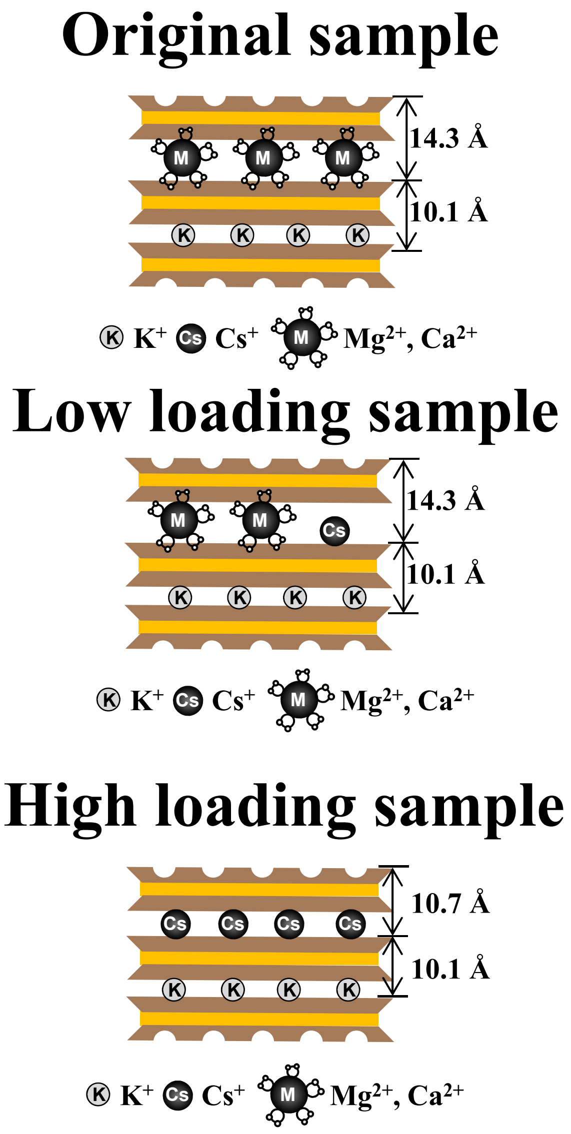
🟦 4.84 mg/g
🟥 8.84 mg/g
🟩 19.7 mg/g
🟪 24.2 mg/g

**Conc. of ^{133}Cs in soil
= 10mg/kg**

- HTT using water is not useful for the desorption of Cs
- Desorption rate of Cs with salt solution at 25℃ is very slow.
- Sea water+HTT promotes the desorption of Cs.

XRD Analysis of Cs-Vermiculite




Original sample

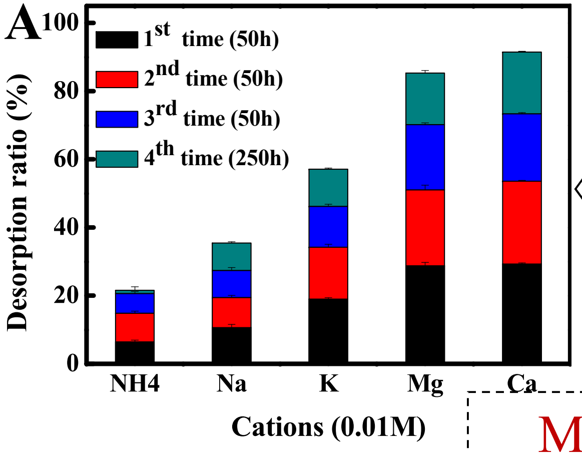
Low loading sample

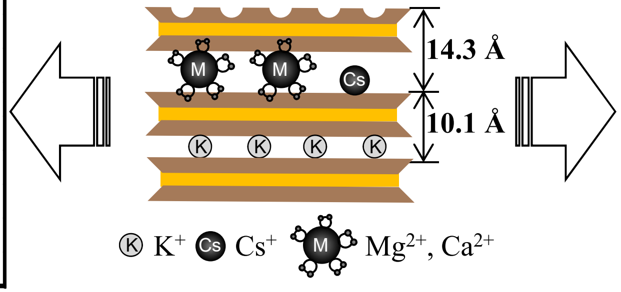
High loading sample

- 25 Å: Regular interstratification of Mg and K layer
- 14.3 Å: Hydrous Mg^{2+} layer
- 12.3 Å: Partial hydrous Mg^{2+} layer
- 11.9 Å: Random interstratification of Mg and K layer
- 10.7 Å: Cs collapsed layer
- 10.1 Å: Biotite K^+ layer

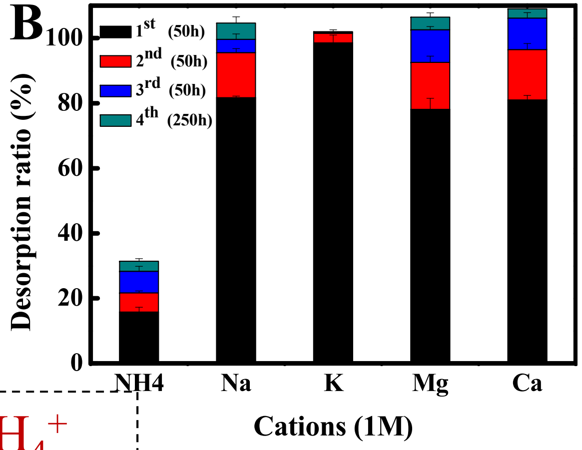
Cs Desorption from Vermiculite with low Cs loading (25℃)

Low ionic strength (0.01M)





High ionic strength (1M)

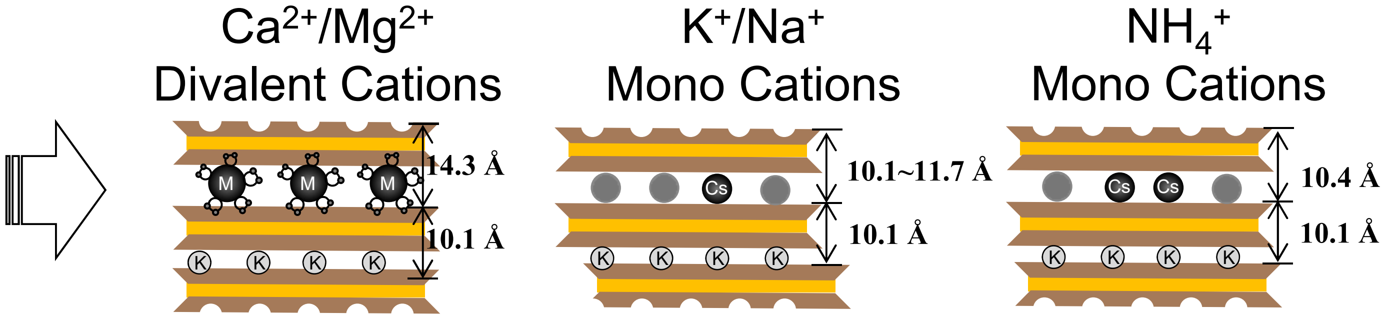


$Mg^{2+} \approx Ca^{2+} > K^{+} > Na \gg NH_4^{+}$

Hydrous radius: Mg(Ca)＞ Na＞ K(NH_4)
Hydration energy: Mg(Ca)＞ Na＞ K(NH_4)
Ion valence : Mg(Ca)＞ Na= K(NH_4)

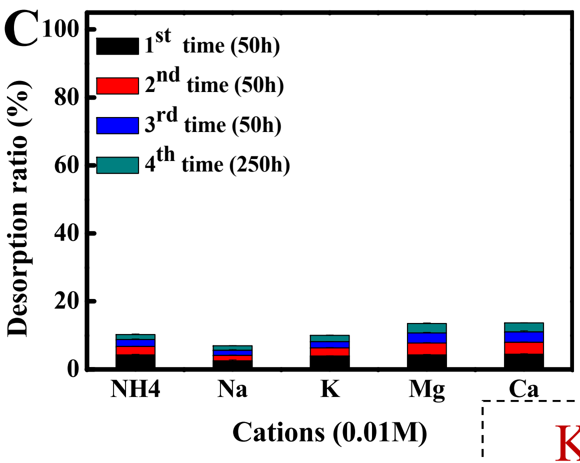
- Cs is desorbed more easily by divalent cation.
- High concentrated K^+(Na^+) desorbs Cs easily.
- NH_4^+ desorb the least Cs^+.

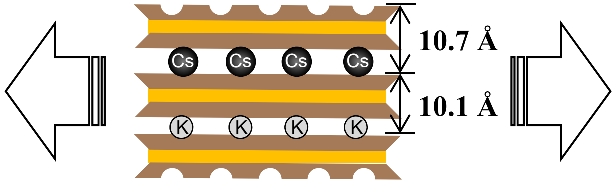
After Cs desorption



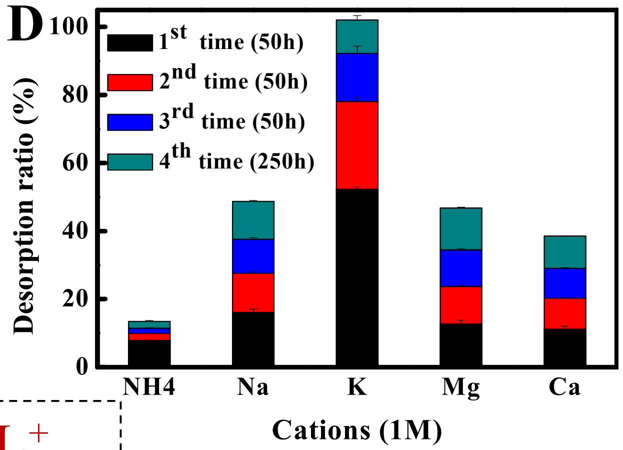
Cs Desorption from Vermiculite with High Cs Loading (25℃)

Low ionic strength (0.01M)





High ionic strength (1M)



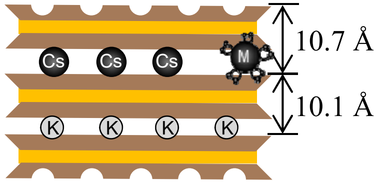
$K^+ > Na^+ \approx Mg^{2+} \approx Ca^{2+} \gg NH_4^+$

Radius: Mg(Ca) > Na > K(NH_4)
Energy: Mg(Ca) > Na > K(NH_4)
Valence : Mg(Ca) > Na = K(NH_4)

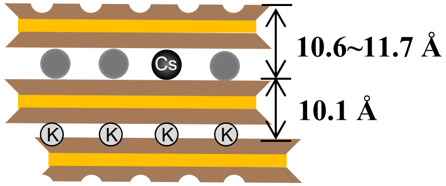
- Cs is rarely desorbed by each cation in dilute solution.
- Cs is desorbed more easily by high concentration of K^+.
- High concentrations of Na^+, and Mg^{2+}/Ca^{2+} are useful for desorption.
- Cs^+ is rarely desorbed by NH_4^+ .

After Cs desorption

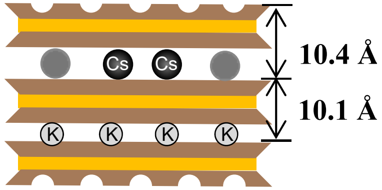
Ca^{2+}/Mg^{2+}
Divalent Cations



K^+/Na^+
Mono Cations

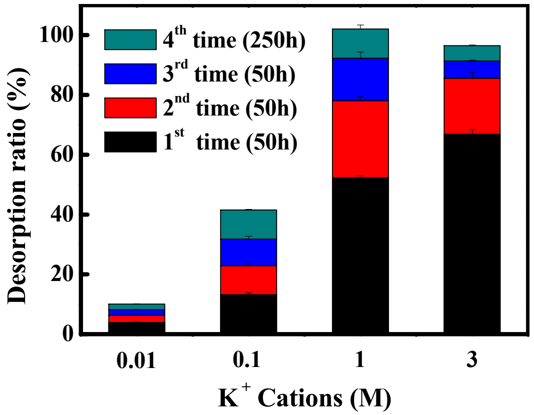


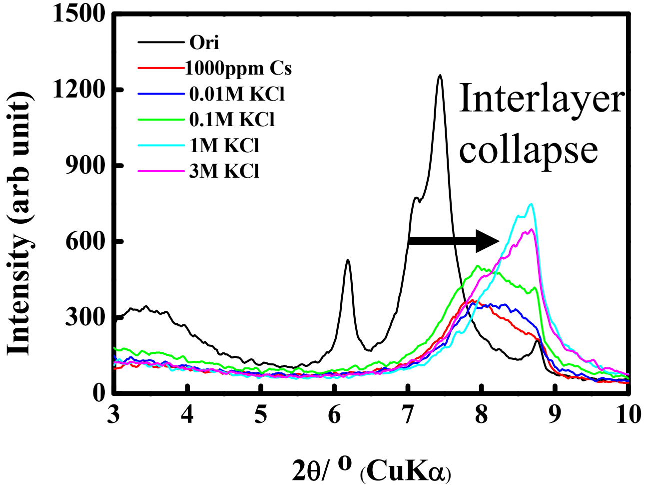
NH_4^+
Mono Cations



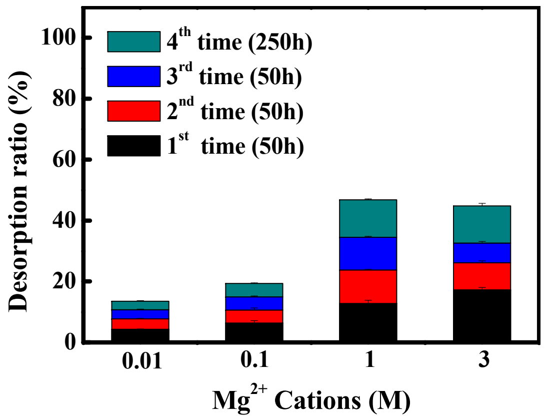
Cs Desorption from Vermiculite with High Cs Loading (25℃)

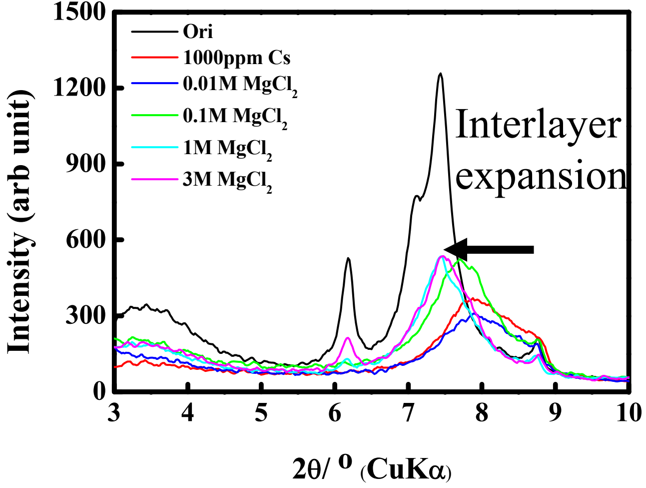
Effect of K^+ conc.





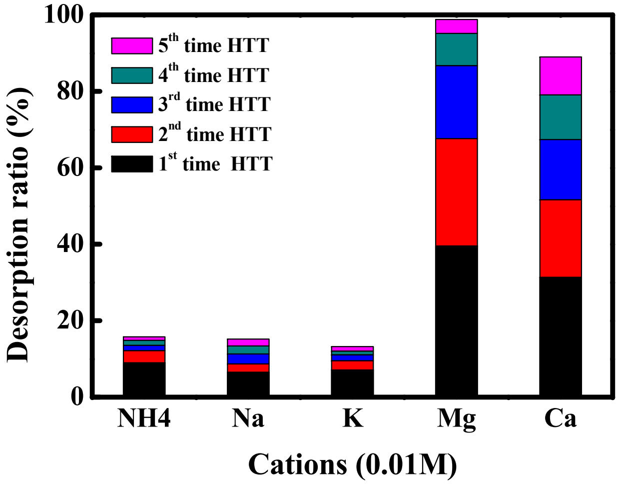
Effect of Mg^{2+} conc.



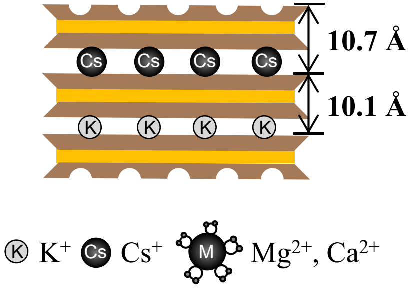


- Cs desorption is promoted by the high concentration of cation.
- Diffusion ability of divalent cations to the collapsed interlayer is very weak at room temperature due to their larger ionic radius.

Cs Desorption from Vermiculite with High Cs Loading (250℃)



High Cs loading

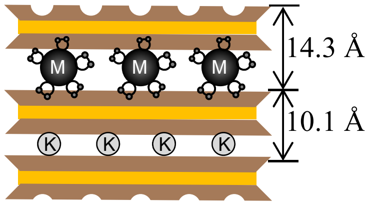


- ➢ The results are contrary to those at 25 ℃.
- ➢ The Cs desorption is promoted by the subcritical water washing with divalent cations.
- ➢ The use of monovalent cations is not useful for the desorption of Cs.
- ➢ Both Cs and original K are desorbed by Mg^{2+}.

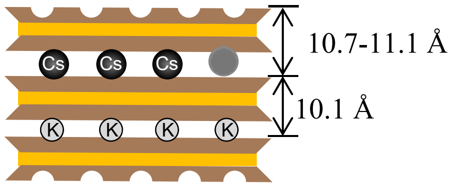
$Mg^{2+} \approx Ca^{2+} \gg K^{+} \approx Na^{+} \approx NH_4^{+}$

After Cs desorption

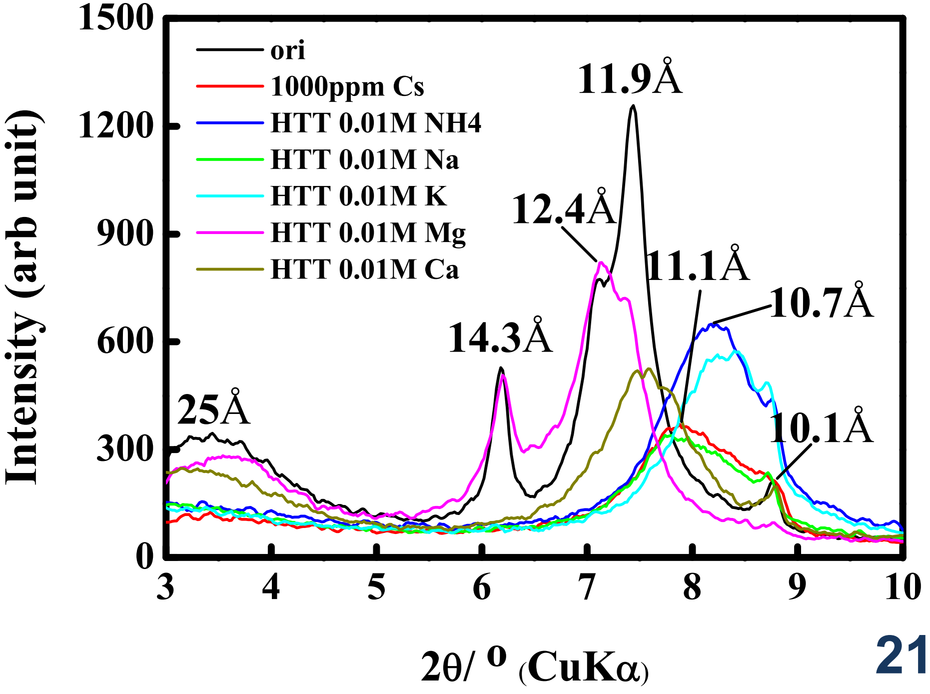
Mg^{2+} /Ca^{2+}
Divalent Cations



K^{+}/Na^{+}/NH_4^{+}
Mono Cations

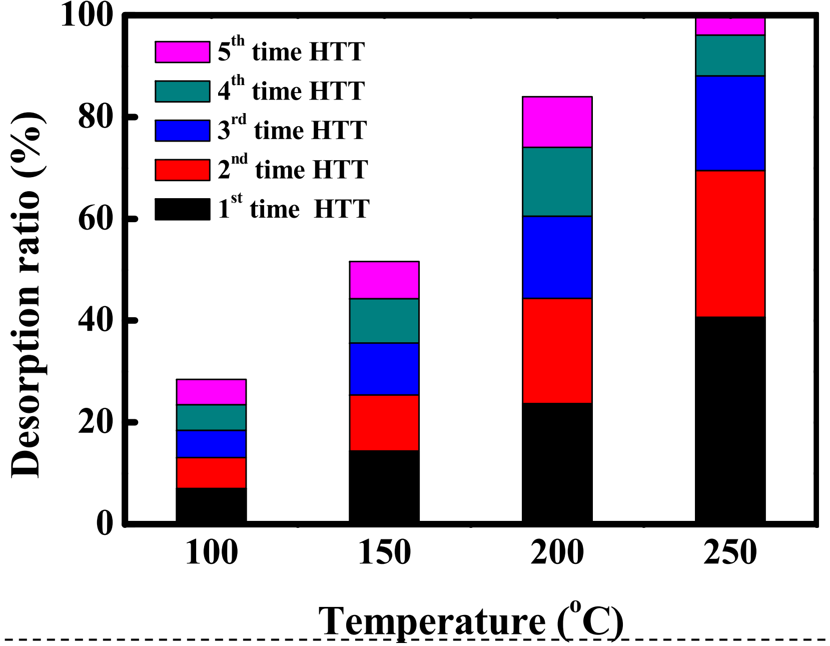


XRD analysis



Cs Desorption from Vermiculite with High Cs Loading (250℃)

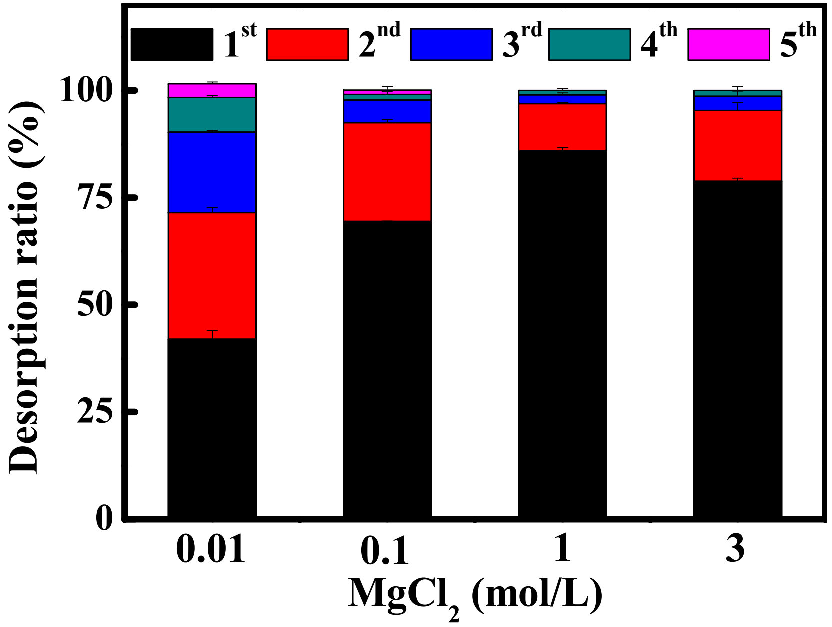
Effect of temperature



(100-250℃), S/L=0.5g/50ml

- Mg²⁺濃度0.01M、L/S=50ml/0.5g
- 亜臨界水温度の増加→高速イオン交換

Effect of ionic strength

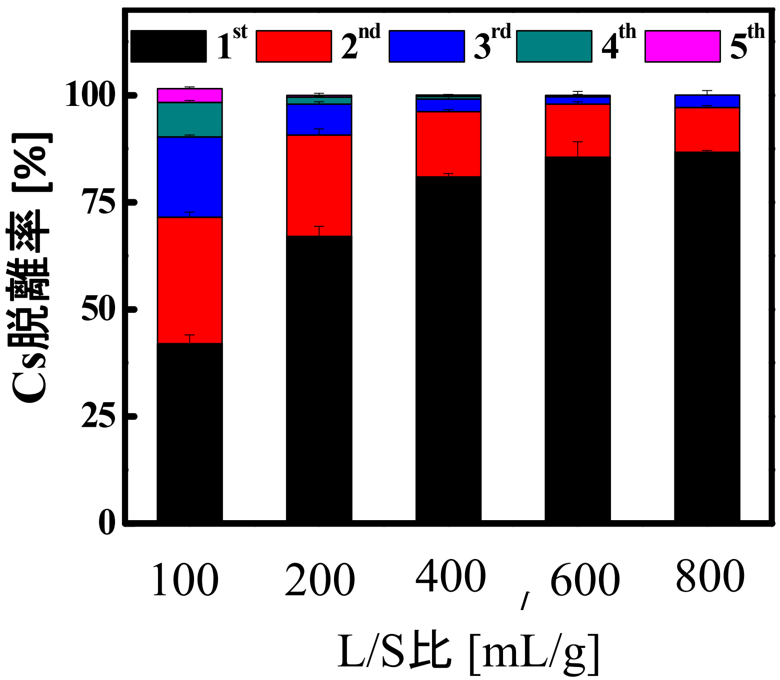


HTT(250℃), S/L=0.5g/50ml

- Mg²⁺濃度の増加に従ってイオン交換速度が増加し、Cs脱離率増加
- 1M程度で最大。高濃度にし過ぎるとむしろCs脱離率低下。
- 1M程度の濃度では1回の洗浄でCs脱離率80%程度が期待できる。

Cs Desorption from Vermiculite with High Cs Loading (250℃)

Effect of L/S ratio



HTT (250℃), Mg^{2+}=0.01M

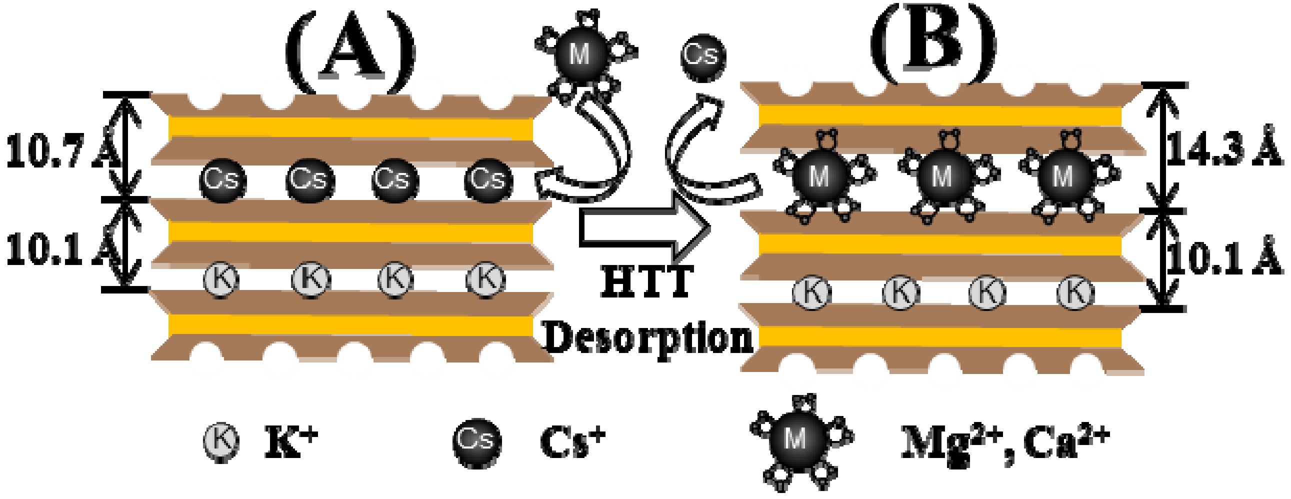
$Mg^{2+} + 2Cs\text{-}Verm \leftrightarrows Mg\text{-}Verm_2 + 2Cs^+$

Enhanced Cs Desorption ⇨

1. Mg^{2+} concentration ⇧
2. Cs^+ concentration ⇩
3. Temperature ⇧

- L/S比が増加するに従ってイオン交換速度が増加し、Cs脱離率増加
- 0.01Mの低イオン強度においても、L/S比が大きくなると、2回程度の洗浄で100%のCs脱離が可能になる。

Cs Desorption from Vermiculite with High Cs Loading (250℃)



採取土壌について

三菱マテリアル那珂エネルギー開発研究所内（茨城県那珂市）にて土壌を採取

雨樋の排水口周辺など、
雨水により環境中の放射性セシウムの
流入が見込まれる場所から採取

汚染
土壌

非汚染
土壌

採取した土壌を2mm未満に
分級後、混合

- 約3kg所有
- 混合した土壌の放射能濃度
  1.55×10^4 Bq/kg

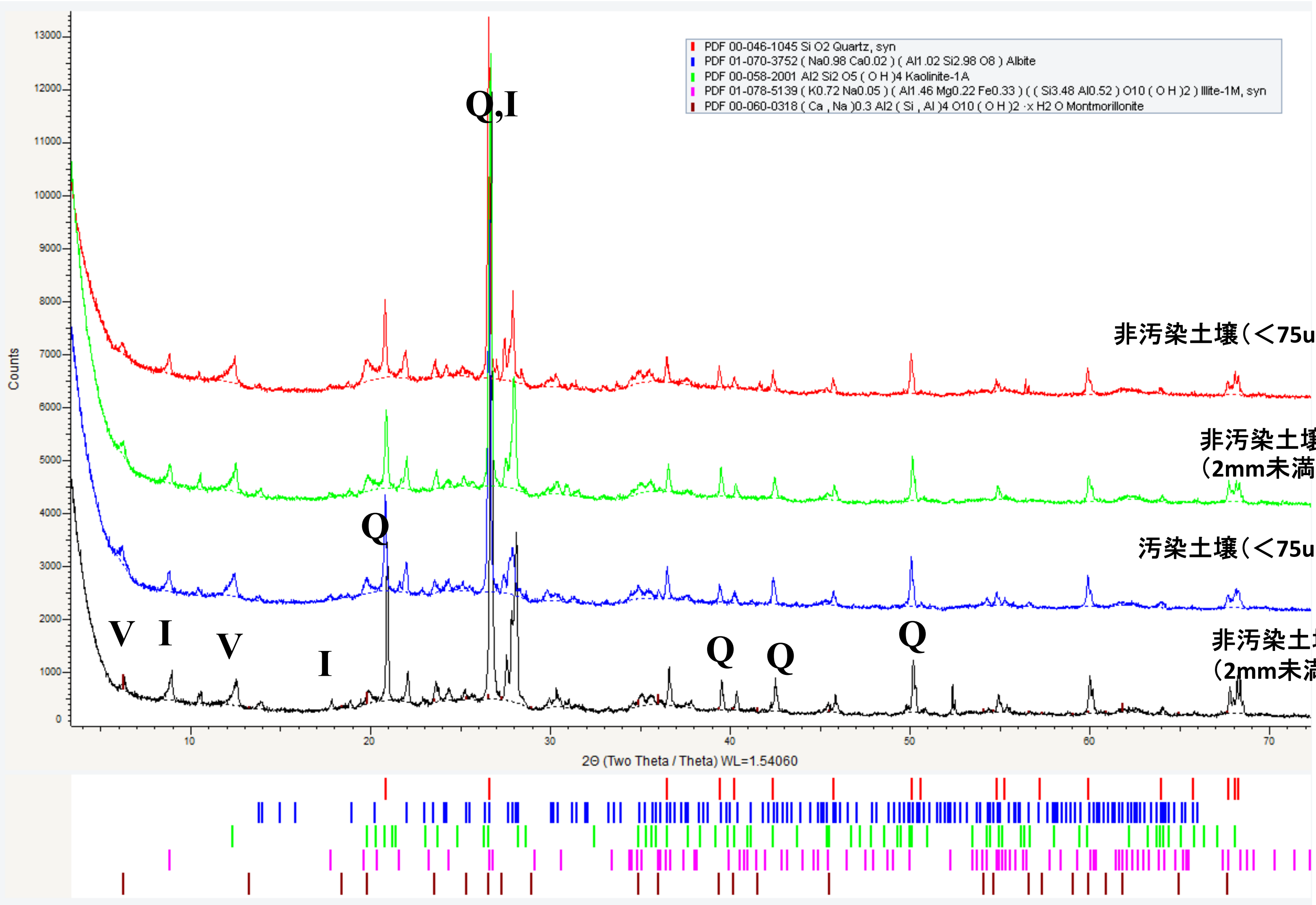
採取した土壌を2mm未満に
分級後、混合

- 約8kg所有
- 混合した土壌の放射能濃度
  2.12×10^2 Bq/kg

細粒分を念頭にさらに<75μmに分級

土壌（<75μm未満）

汚染土壌と非汚染土壌のXRD分析結果（<75μm分級前後の比較）



分級後土壌（<75μm）においても鉱物組成に大きな差異はない。

（２）イオン含有亜臨界水によるCs脱離試験（ホット）

・実施条件例：

試験回数	対象物	添加イオン または添加物	添加イオン 濃度[M]	液固比 [ml/g]	保持温度 [℃]
全3回程度	ホット試験用試料 （汚染土壌の細粒物）	Mg^{2+} or Mg^{2+}+ 0.3M Citric Acid	0.01 ～ 0.5	5 ～ 100	250

※コールド試験の結果から設定する。試験結果によっては同条件による繰り返し再現性試験をすることもある。

試験方法：

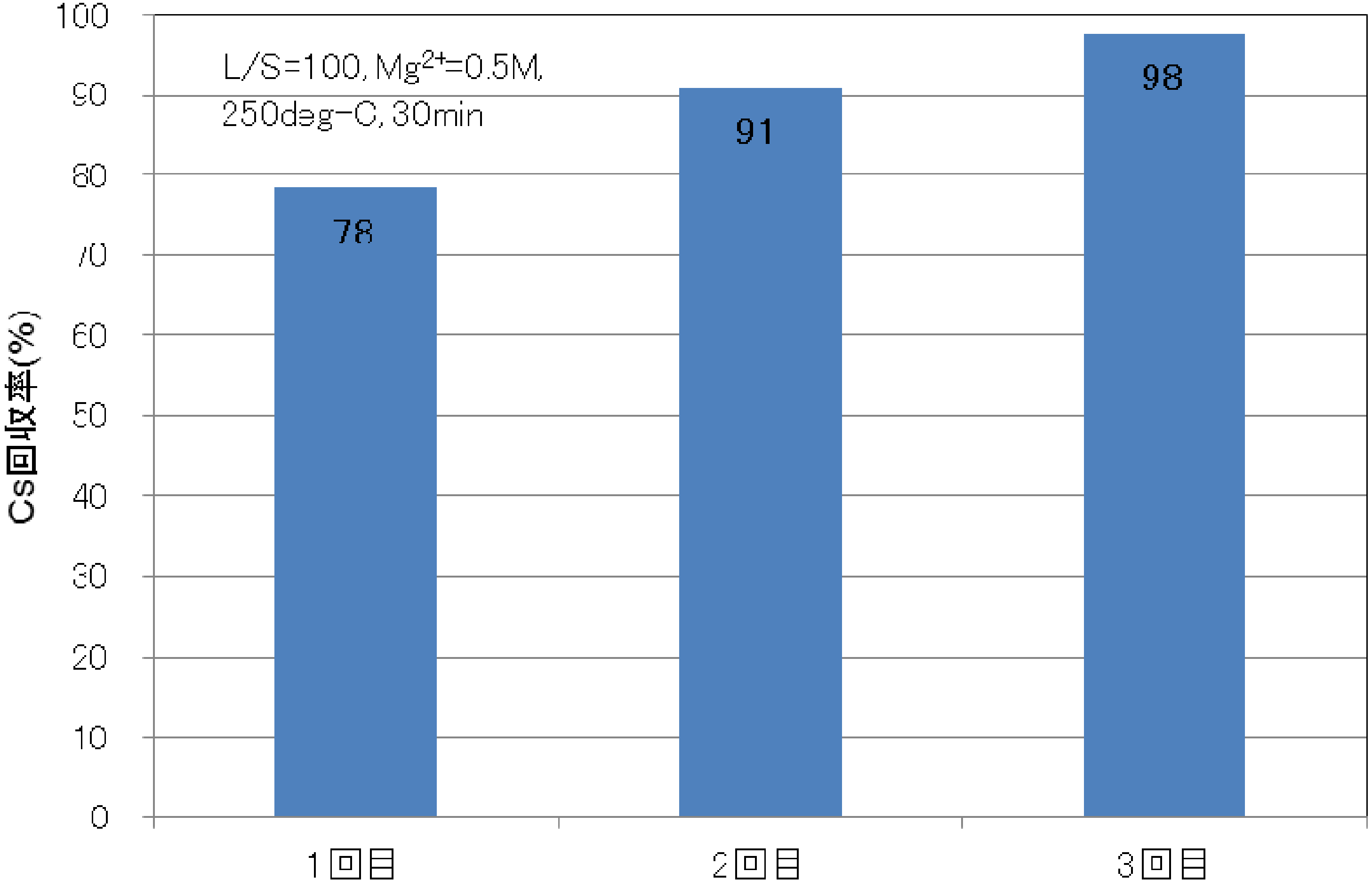
- コールド試験の結果から得られたCs脱離の最適条件（添加イオン組成、濃度、液固比、保持温度）を中心に、ホット試験用試料を用いて小型水熱処理装置で脱離試験を行う。
- 試験後の試料とイオン水の放射能量をGe半導体検出器で測定し、Cs脱離率を求める。
- さらにコールド試験と同様に繰り返し試験を行い、Cs脱離率の変化を調べる。

評価項目：

・Cs脱離率、及び物質収支の評価を行う。

（2）イオン含有亜臨界水によるCs脱離試験（ホット）

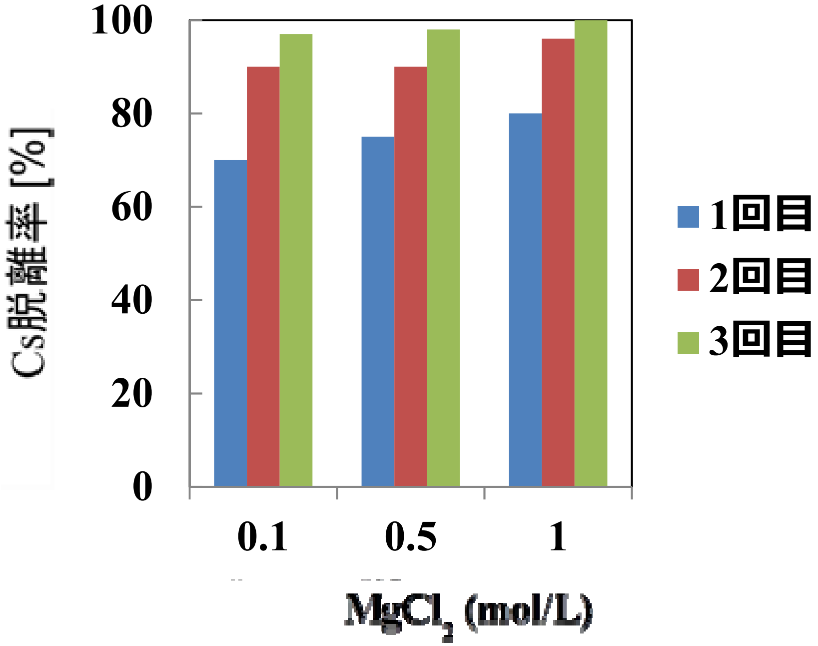
溶離液のMg^{2+}濃度0.5Mにおいて2回の亜臨界水洗浄でほぼ90%、3回で96%のCs回収率を達成できた。本法により10万Bq/kg程度の汚染物であれば、十分に8000Bq/kg以下にできる見通しを得た。



L/S=100で0.5 M Mg^{2+}溶離液を用いた場合の繰り返し試験

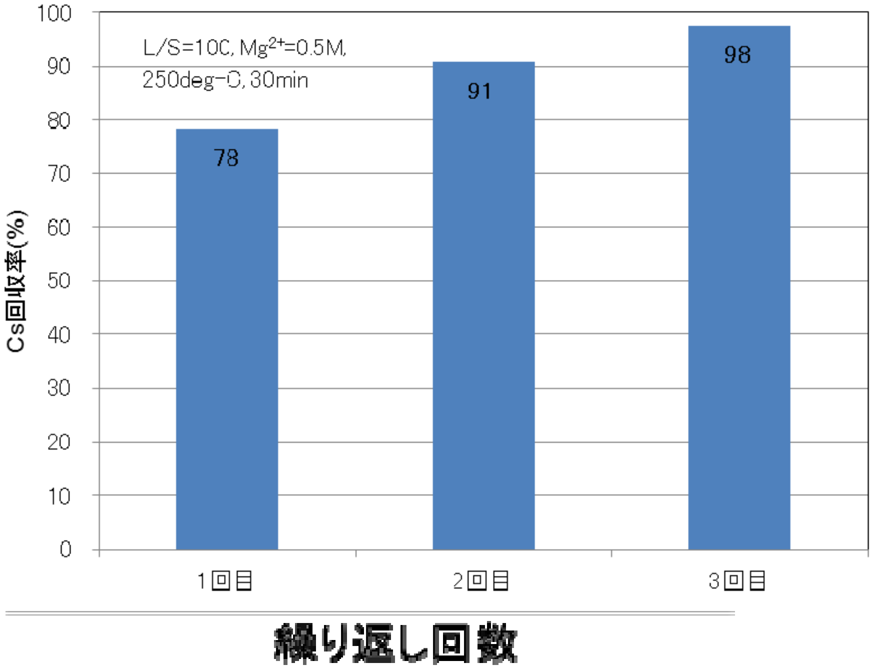
Comparison between cold test and hot test (250℃)

Temp.250℃, L/S=100,
$[Mg^{2+}]$=0.01-3M

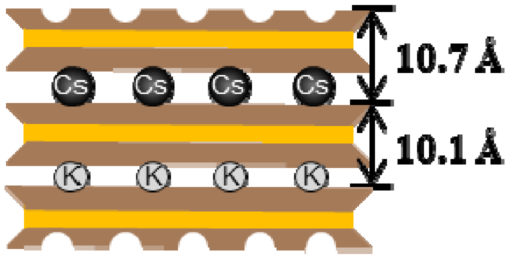


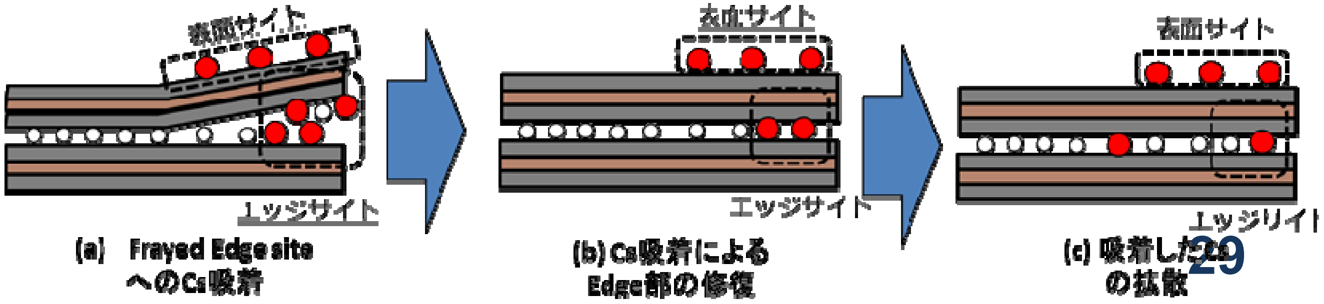
(a)コールド試験（Mg^{2+}濃度の影響）

Temp.250℃, L/S=100,
$[Mg^{2+}]$= 0.5M

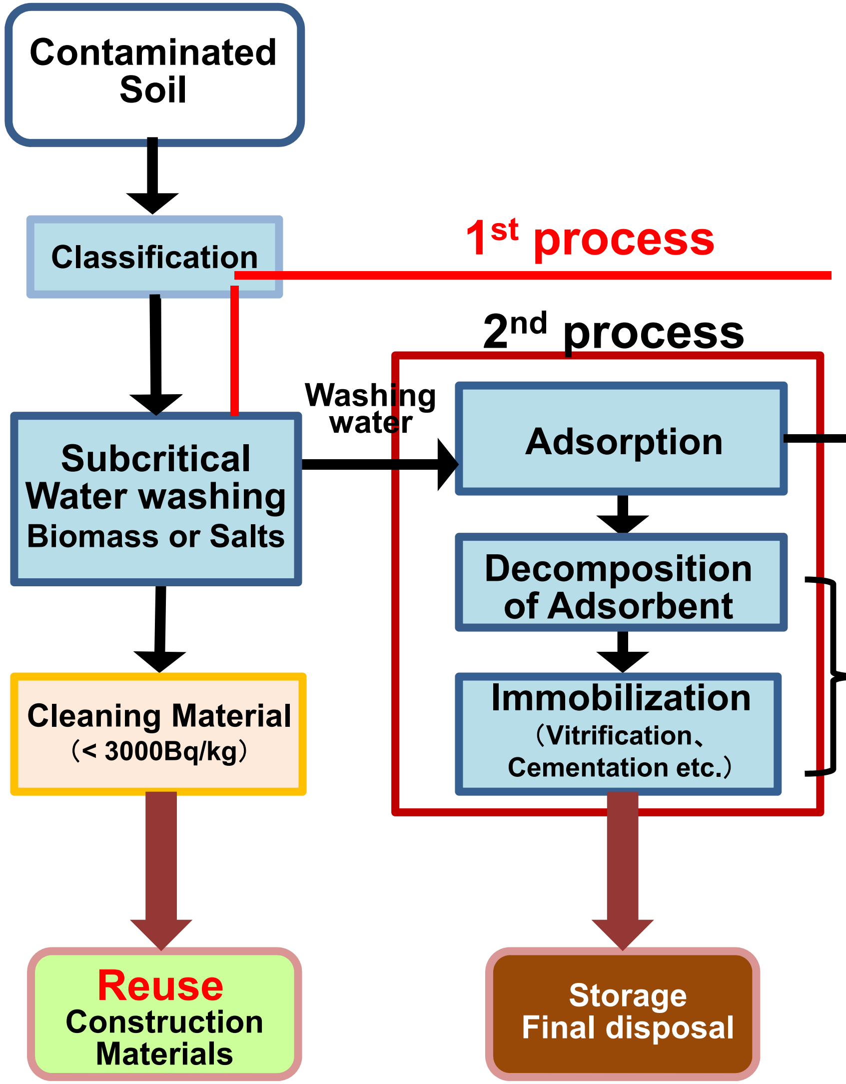


(b)ホット試験（Mg^{2+}濃度固定）





Volume Reduction Technology of Cs-ccontaminated Soil



Contaminated Soil

Classification

1^{st} process

Subcritical Water washing
Biomass or Salts

Washing water

2^{nd} process

Adsorption

Decomposition of Adsorbent

Immobilization
（Vitrification、Cementation etc.）

Cleaning Material
（< 3000Bq/kg）

Reuse
Construction Materials

Storage
Final disposal

In the 2^{nd} process, Cs in washing water is concentrated by an adsorbent, ferric ferrocyanide and solidified into glass

（1）Subcritical water washing

Release of Cs from Soil to water

（2）Adsorption

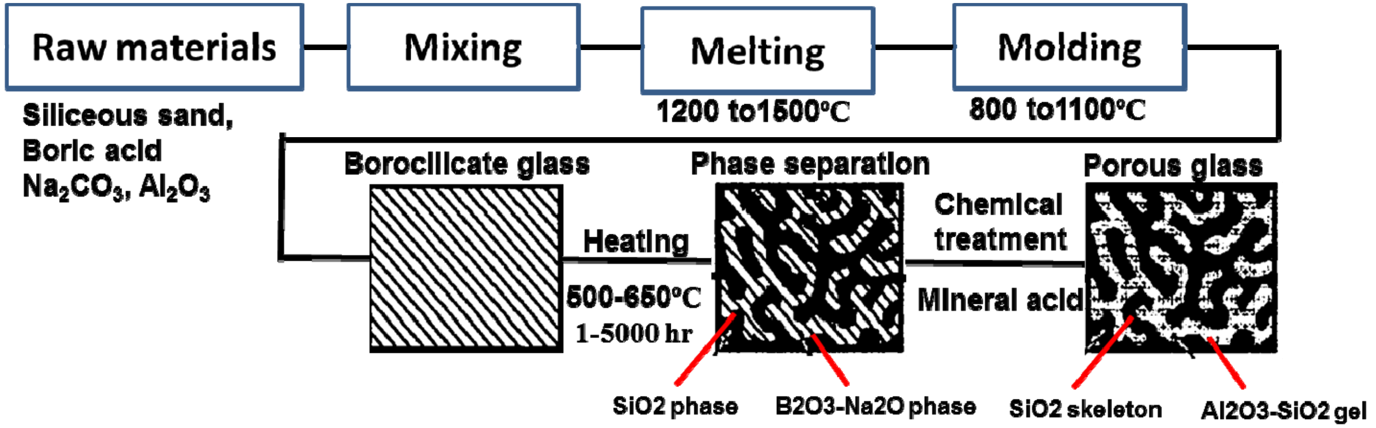
Selective recovery of Cs from washing water by ferric ferrocyanide

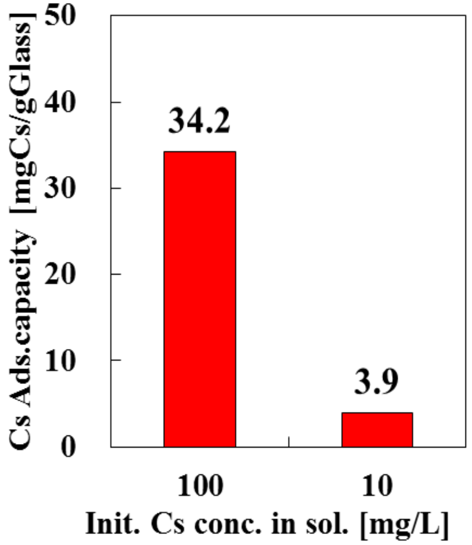
（3）Solidification

- Thermal Decomposition of ferric ferrocyanide
- Leaching of Cs from residue to water and diluted HNO_3
- Immobilization of Cs in glass

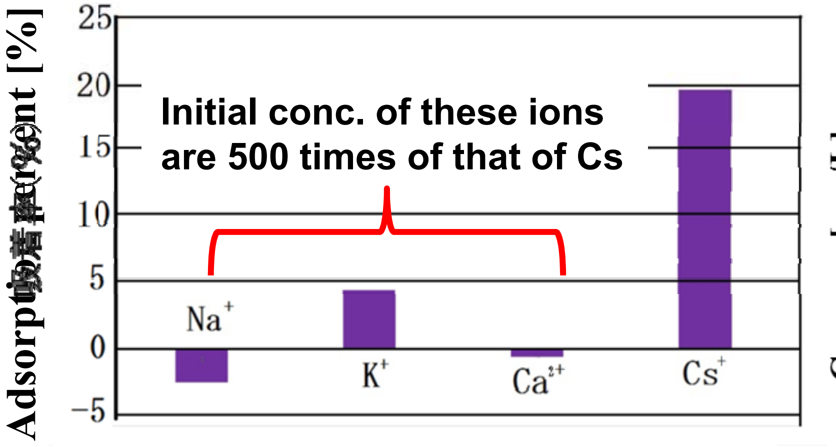
Future Adsorbent --- Porous Glass with Alminosilicate Gel

1. Synthesis of porous glass with aluminosilicate gel


Raw materials
Siliceous sand,
Boric acid
Na_2CO_3, Al_2O_3
Mixing
Melting
1200 to1500°C
Molding
800 to1100°C
Borocilicate glass
Heating
500-650°C
1-5000 hr
Phase separation
Chemical treatment
Mineral acid
Porous glass
SiO2 phase
B2O3-Na2O phase
SiO2 skeleton
Al2O3-SiO2 gel



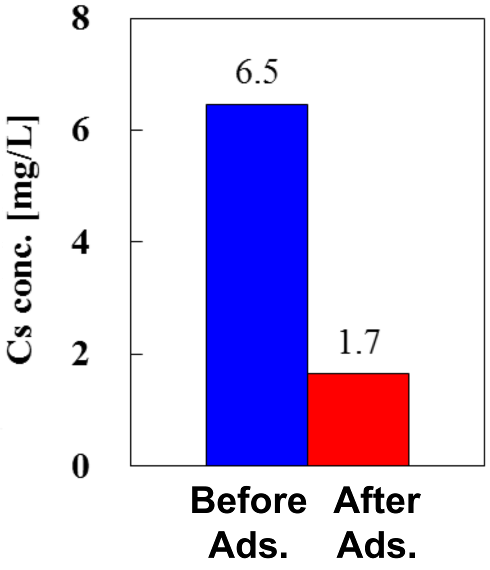
2. Selectivity



Initial conc. of these ions are 500 times of that of Cs

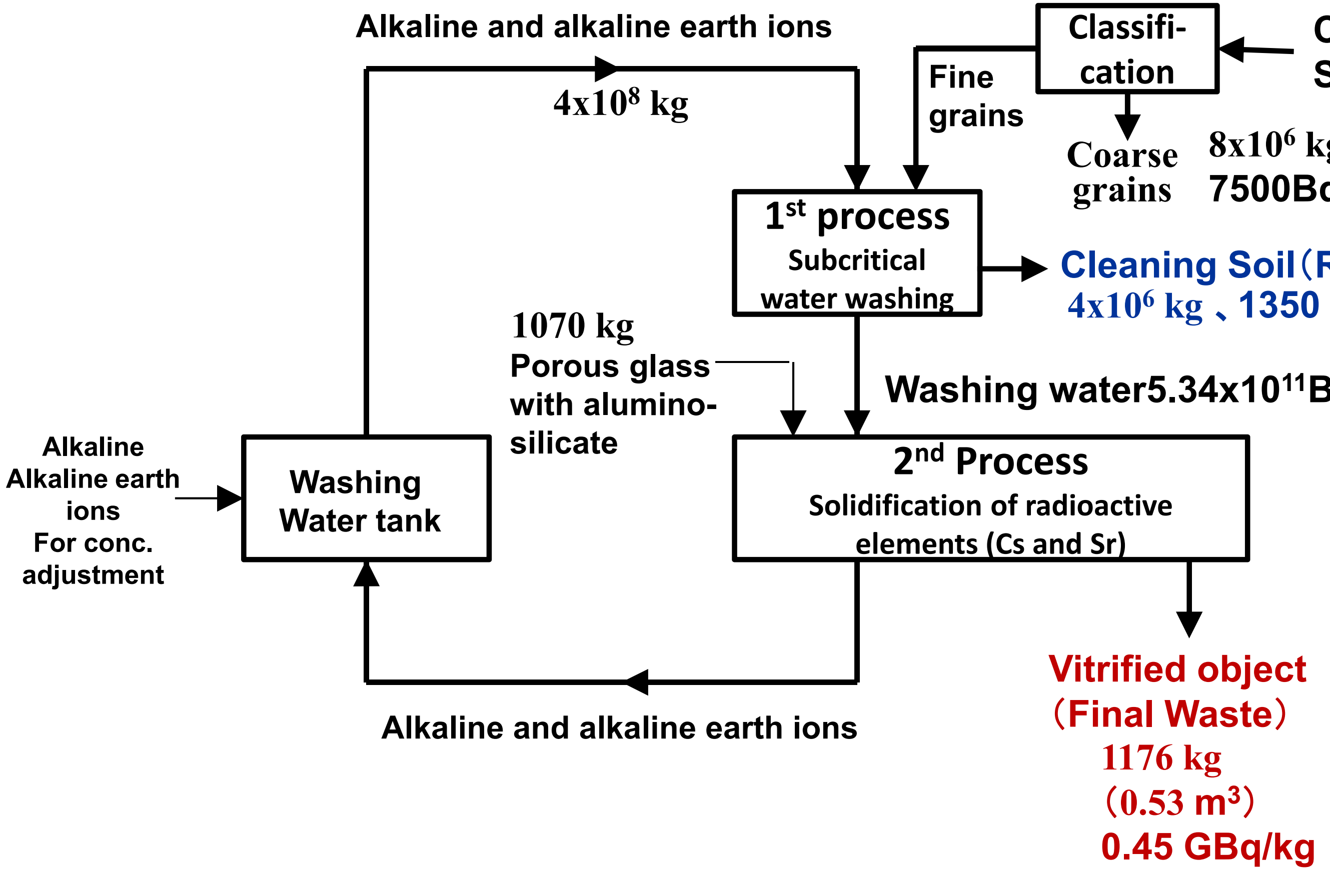
Cs is adsorbed selectively compared with Na, K and Ca.

3. Adsorption performance



- Washing solution after subcritical water washing was used for the Cs adsorption test.
- The content of alminosilicate gel is 3 wt%. The concentration of Cs in the washing solution is 6.5 mg-Cs/L.
- 1g of the porous glass was added to 100mL of the washing solution.
- Cs was adsorbed selectively and the adsorption capacity is 0.6mg/g-Glass.

Mass and Radioactive Balances of Future Treatment System



Contaminated Soil (Feed)

Classifi-cation

Fine grains

Coarse grains

$8x10^6$ kg

7500Bq/kg

1^{st} process

Subcritical water washing

Cleaning Soil（Reuse）

$4x10^6$ kg 、1350 Bq/kg

Alkaline and alkaline earth ions

$4x10^8$ kg

Washing water$5.34x10^{11}$Bq

1070 kg
Porous glass with alumino-silicate

2^{nd} Process

Solidification of radioactive elements (Cs and Sr)

Alkaline
Alkaline earth ions
For conc. adjustment

Washing Water tank

Alkaline and alkaline earth ions

Vitrified object
（Final Waste）
1176 kg
（0.53 m^3）
0.45 GBq/kg

Volume-reduction ratio of glass to soil
=0.53/10000
=about 1/20000

Feed Conditions （Continuous operation is assumed)

Contaminated Soil	Operating conditions
Feed :10,000m^3（$1.2x10^7$ kg)、	Processing speed：30～40ton/day
Radioactivity : 50,000 Bq/kg	Processing period：300 days

Summary

- A solid waste treatment system, which consists of two processes, subcritical water washing process and solidification process of radioactive elements, is proposed.

- Cs adsorbed strongly in clay minerals (vermiculite) was released to water effectively by the subcritical water washing process using organic acids (decomposition of clay minerals) or several salts (high-speed ion exchange).

- In the case of the immobilization of Cs into glass, the high volume reduction of contaminated soil is attained by the introduction of the proposed system (volume ratio of glass to soil = 1/20,000) .

Thank you for your attention

International collaborative Research Building

Thank you for your attention

Photo: Yomiuri Shimbun

Radioactive Wastes generated by Decommissioning of 1F NPP

- Gaseous waste, liquid waste and solid waste containing radioactive elements are generated by the decommissioning of Fukushima daiichi NPP.
- Gaseous and liquid wastes are immobilized in solid materials and the release of radioactive elements to the environment can be suppressed.

Gaseous waste

exhaust gas

PCV gas Management System
Filter

Solid waste

Radioactive elements in gaseous waste from reactor vessels is collected by filter

Liquid waste

Polluted Water Treatment Facility
Adsorbents, Sludge

Solid waste

Radioactive elements in liquid waste is recovered in polluted water treatment facility

Solid waste

Rubble etc.

Polluted metal, concrete, soil, cut tree, protective closing and filter

Secondary wastes from Treatment facility

Spent Adsorbents, Sludge

Ref. 東京電力　福島第一原子力発電所（1F）の廃止措置で発生する固体廃棄物の管理について（2016年4月）

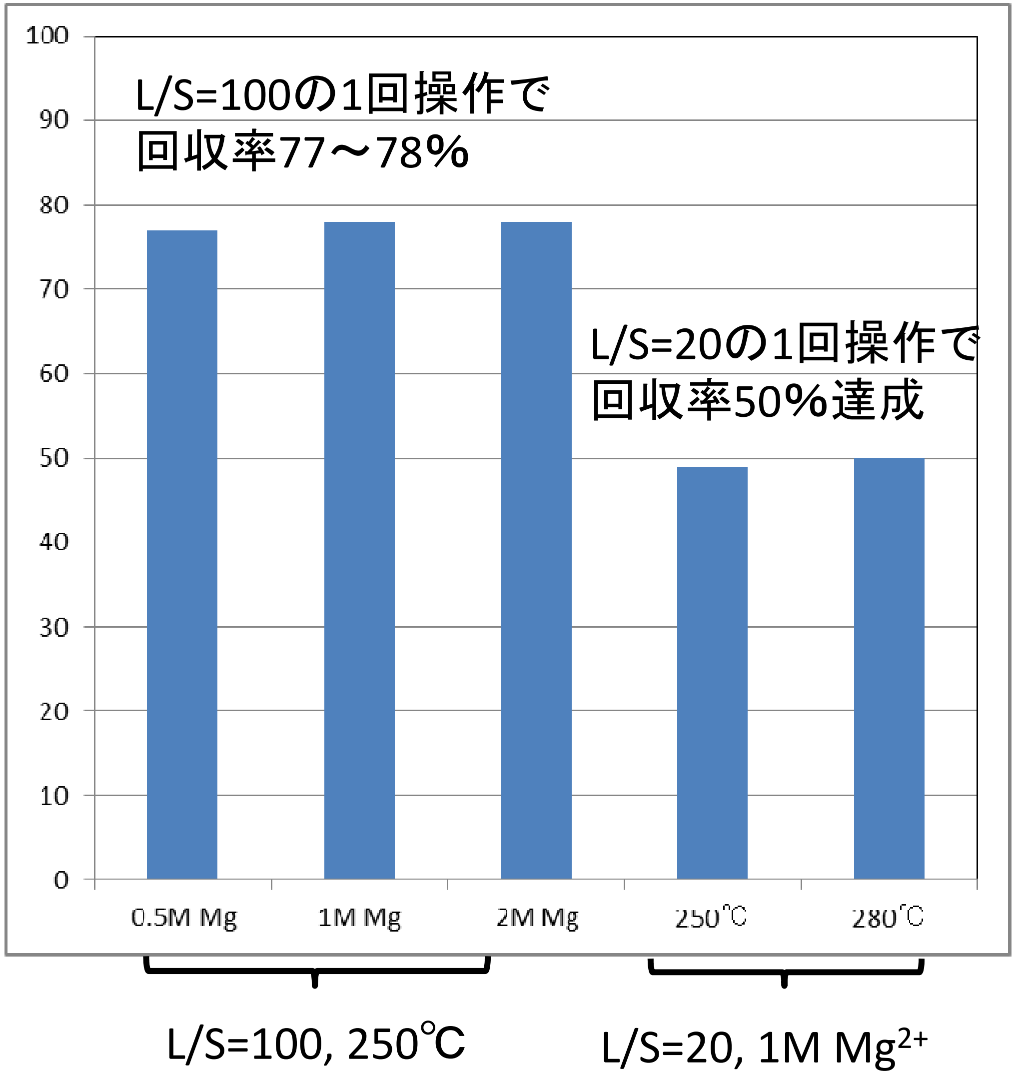
汚染土壌と非汚染土壌のXRF分析結果（ <75μm分級前後の比較）

	汚染土壌		非汚染土壌	
	分級前	分級後	分級前	分級後
SiO_2	63.1	58.7	54.9	60.9
Al_2O_3	20.0	20.8	26.6	18.1
Fe_2O_3	11.5	12.7	12.0	11.1
TiO2	1.6	1.5	1.4	2.5
MnO	0.2	0.2	－	0.1
MgO	0.9	2.7	1.9	2.1
CaO	0.9	0.7	1.0	1.0
Na_2O	0.3	0.9	0.4	1.5
K_2O	1.2	1.5	1.4	1.8
P_2O_5	0.3	0.3	0.2	0.6
合計	100	100	100	100

分級前後（<75μm）においても組成に大きな差異はない。

（2）イオン含有亜臨界水によるCs脱離試験（ホット）

- L/S=20の場合、1回の処理で50%のCsを回収できることを確認
- L/S=20における繰り返し処理の効果を確認中



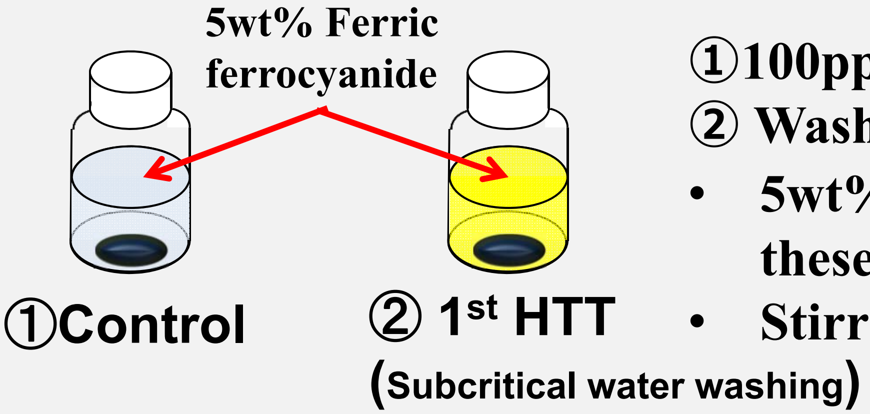
L/S=100の1回操作で
回収率77～78%

L/S=20の1回操作で
回収率50%達成

1回の亜臨界水洗浄におけるCs回収率の比較

Adsorption Tests of Cs by Ferric Ferrocyanide

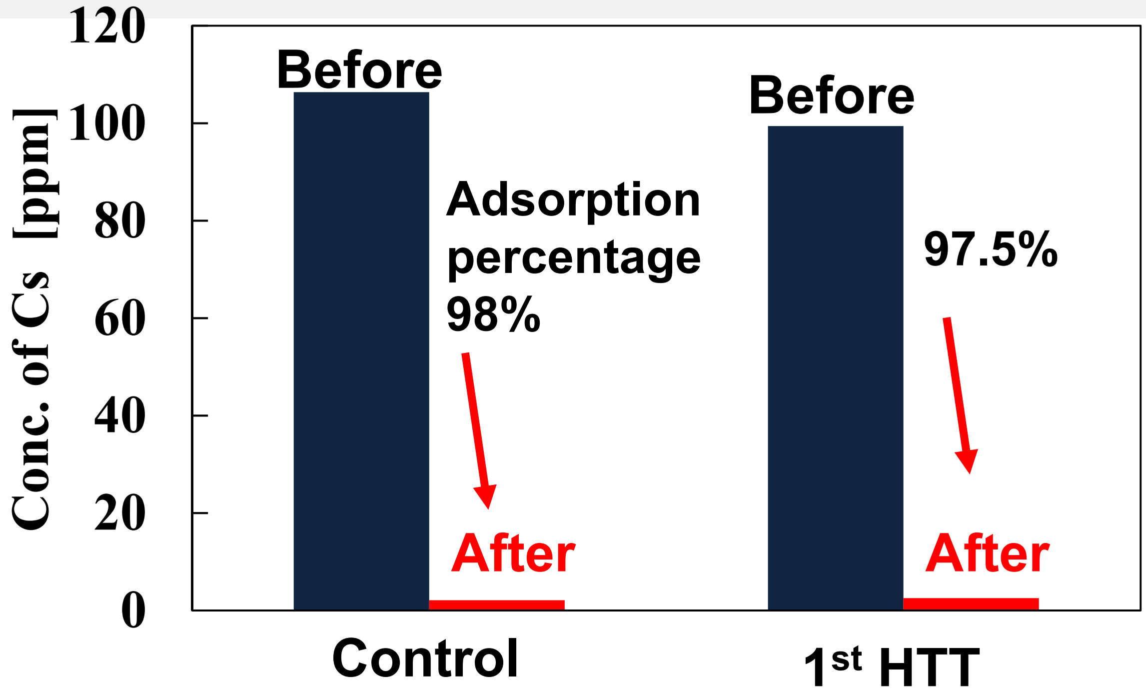
Recovery of Cs released to hydrothermal water by ferric ferrocyanide



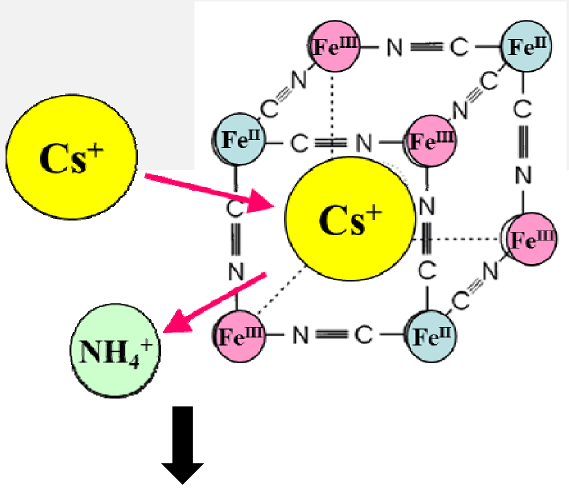
①100ppm CsCl solution (control)

② Washing water after 1st HTT

- 5wt% Ferric ferrocyanide was added in these waters
- Stirred for 24h

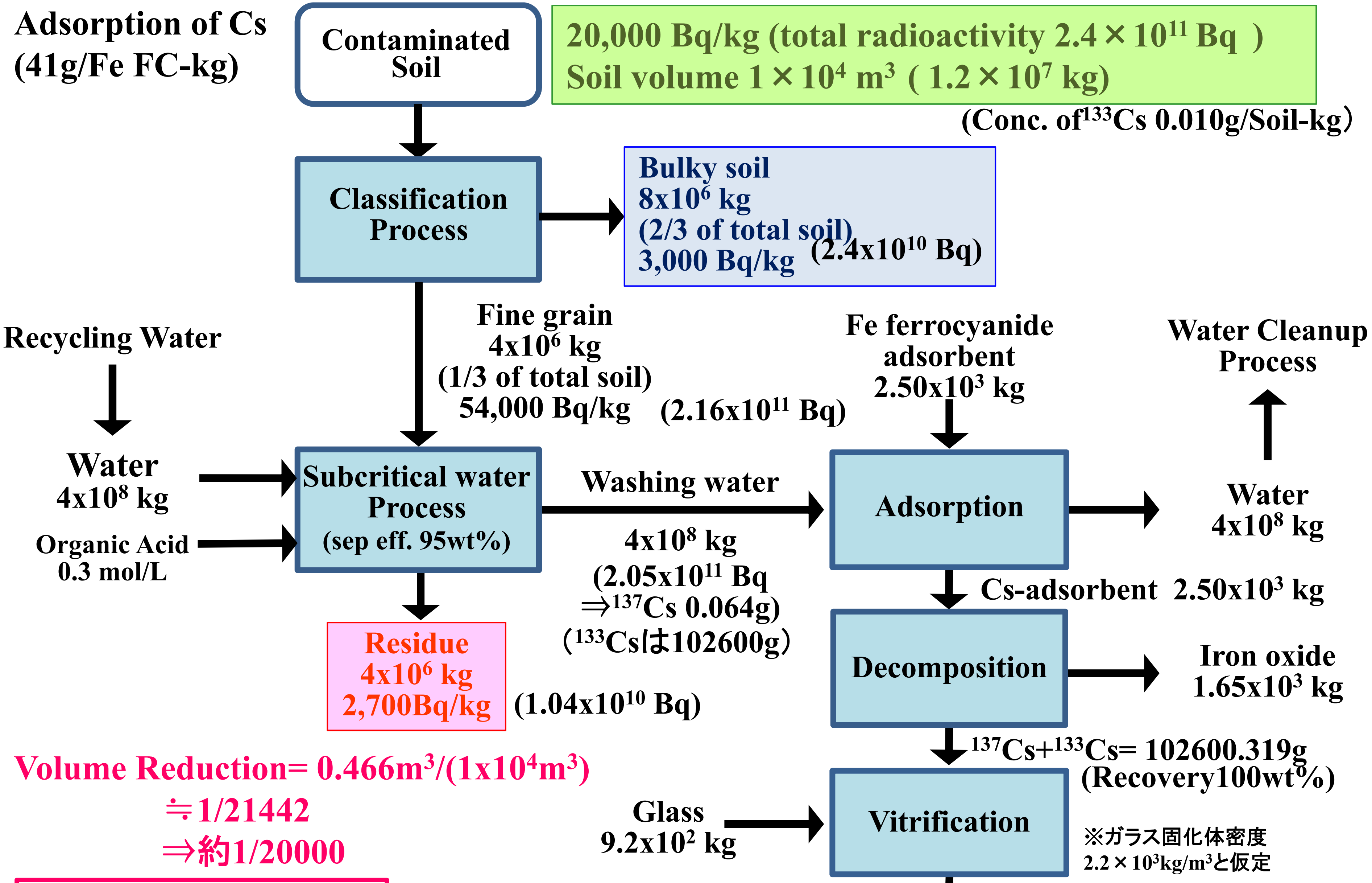


Ads. amount 1.05 mg-Cs/g-PB 0.98 mg-Cs/g-PB



- Cs in hydrothermal water was adsorbed effectively by ferric ferrocyanide.
- Easy recovery of Cs by a conventional adsorbent

Mass and Radioactive Balances of Proposed System



Adsorption of Cs
(41g/Fe FC-kg)

Contaminated Soil

20,000 Bq/kg (total radioactivity 2.4×10^{11} Bq)
Soil volume 1×10^{4} m^{3} (1.2×10^{7} kg)

(Conc. of ^{133}Cs 0.010g/Soil-kg)

Classification Process

Bulky soil
8×10^{6} kg
(2/3 of total soil)
3,000 Bq/kg (2.4x10^{10} Bq)

Fine grain
4x10^{6} kg
(1/3 of total soil)
54,000 Bq/kg (2.16x10^{11} Bq)

Recycling Water

Water
4x10^{8} kg

Organic Acid
0.3 mol/L

Subcritical water Process
(sep eff. 95wt%)

Residue
4x10^{6} kg
2,700Bq/kg (1.04x10^{10} Bq)

Washing water
4x10^{8} kg
(2.05x10^{11} Bq
⇒^{137}Cs 0.064g)
（^{133}Csは102600g）

Fe ferrocyanide
adsorbent
2.50x10^{3} kg

Adsorption

Water Cleanup
Process

Water
4x10^{8} kg

Cs-adsorbent 2.50x10^{3} kg

Decomposition

Iron oxide
1.65x10^{3} kg

^{137}Cs+^{133}Cs= 102600.319g
(Recovery100wt%)

Glass
9.2x10^{2} kg

Vitrification

※ガラス固化体密度
2.2×10^{3}kg/m^{3}と仮定

Vitrified Object (Cs:10wt%)
1.03x10^{3} kg (0.466 m^{3} =466L)

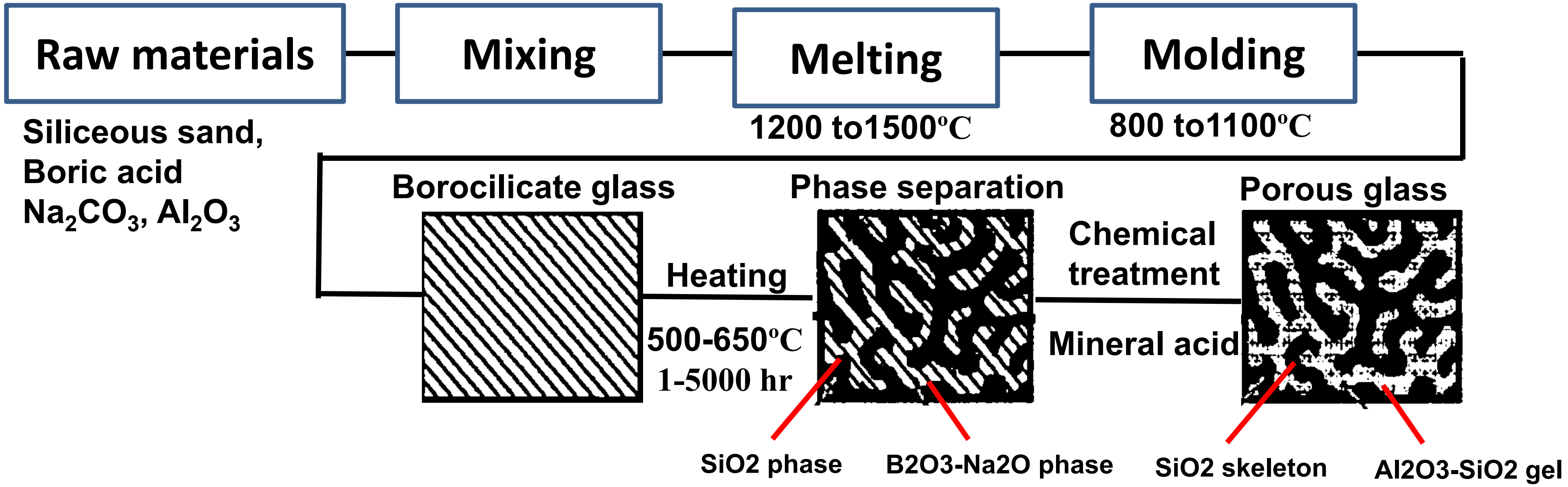
2.0x10^{8} Bq/kg
(2.05x10^{11} Bq)

Volume Reduction= 0.466m^{3}/(1x$10^{4}$$m^{3}$)
≒1/21442
⇒約1/20000

Number of Glass Rods =3
(one Glass Rod =170 L)

Adsorption of Cs by Porous Glass with Alminosilicate Gel

1. Synthesis of porous glass with aluminosilicate gel



Raw materials — **Mixing** — **Melting** — **Molding**

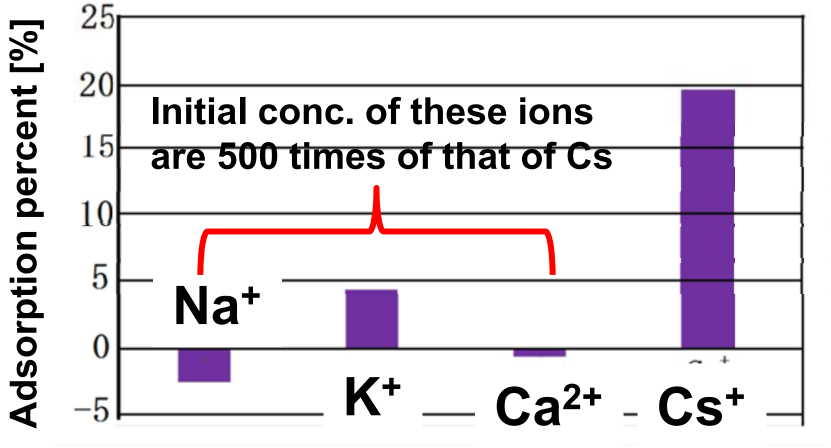
Siliceous sand,
Boric acid
Na_2CO_3, Al_2O_3

Melting: 1200 to1500°C

Molding: 800 to1100°C

Borocilicate glass → Heating (500-650°C, 1-5000 hr) → Phase separation → Chemical treatment (Mineral acid) → Porous glass

2. Metal selectivity

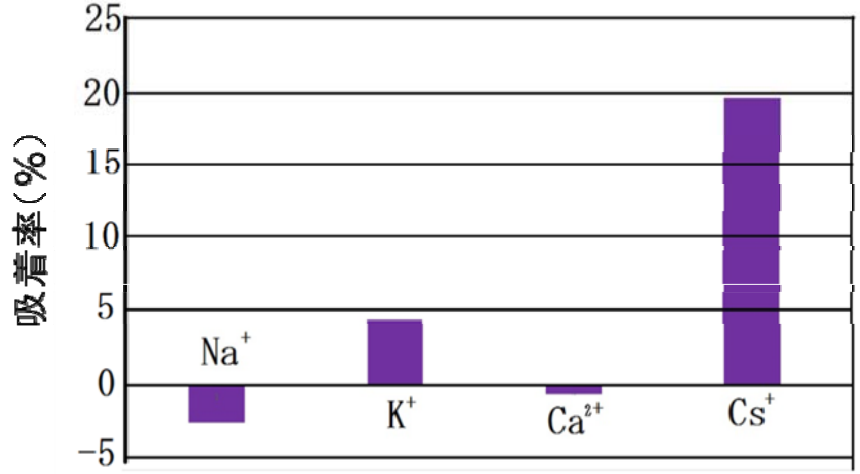


Initial conc. of these ions are 500 times of that of Cs

Cs is adsorbed selectively rather than Na, K and Cs

3. Adsorption amount

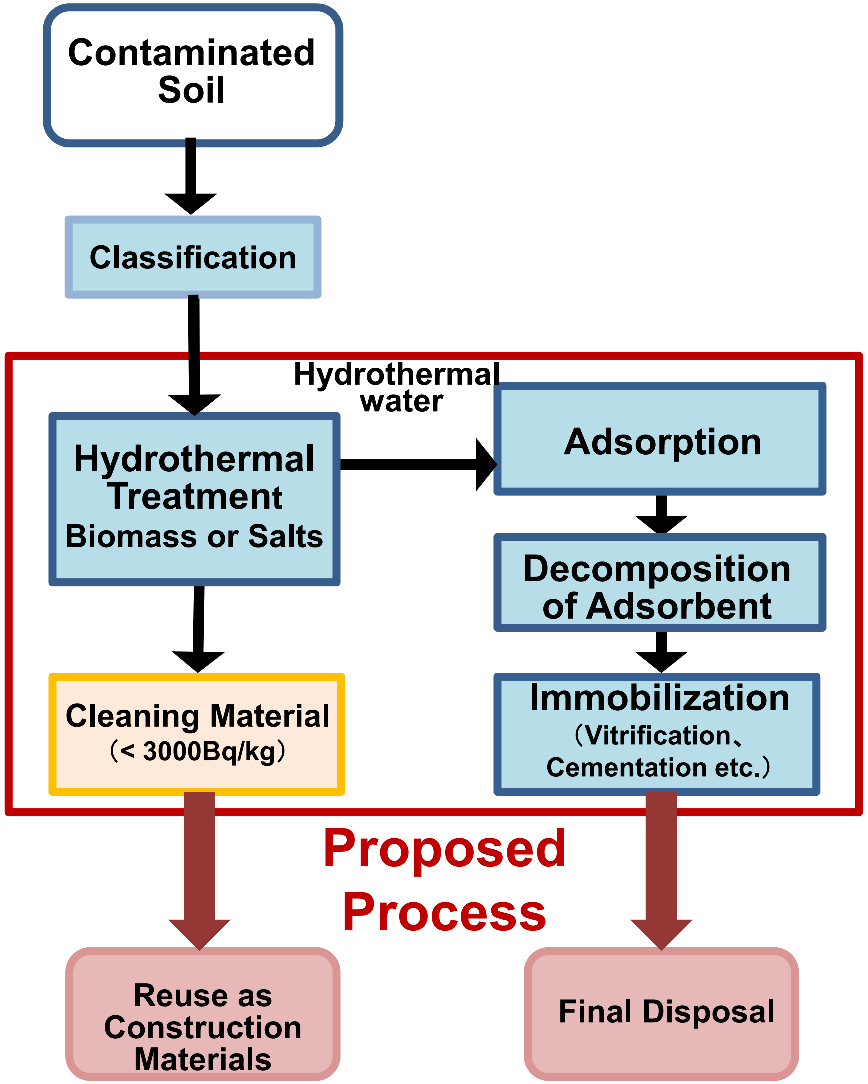
アルミノシリケートゲル堆積型高ケイ酸ポーラスガラスのCs吸着特性



混合溶液中の各イオンに対する吸着率

図6　アルミナシリケートゲル堆積型高珪酸ポーラスガラスの吸着性能

Volume Reduction Technology of Cs-ccontaminated Soil



A new volume-reduction process of Cs-contaminants is proposed for the secondary volume reduction during interim storage. This process has four steps as follow,

（1）Hydrothermal

Release of Cs from Soil to water

（2）Adsorption

Selective recovery of Cs from water

（3）Decomposition

Cs Conc. by leaching from residue

（4）Immobilization

Immobilization of Cs into glass

Conventional Volume Reduction Methods of Contaminated Soil

	Operator	Object	Volume Reduction Method	Temp. [ºC]	Initial Radioactive Cs Conc. [Bq/kg]	Cs Removal [%]
Wet Process	Toshiba Co.	Soil	Oxalic acid washing	95	5,000	93% (for 5 times washing)
	Tokyo Tech.	Soil	Hydrothermal + Coagulant settling	200	55,000	75%（85% if adding blasting)
Dry Process	Taiheyo Cement Co.	Soil	sublimation method	1300	60,000	99%

This table shows conventional volume reduction technologies of contaminated soil. Toshiba process and Tokyo Tech process are classified as wet processes. Toshiba process is a typical washing process using oxalic acid.

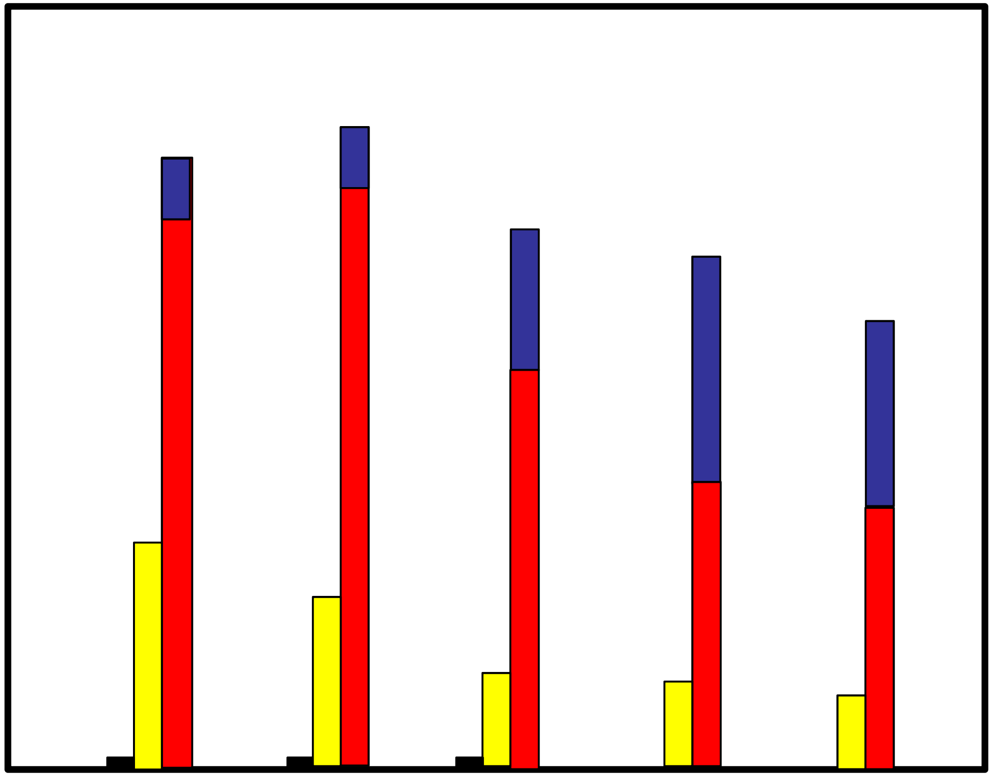
Taiheiyo cement process is classified as a dry process. This is a sublimation process. Cs in contaminated soil is transferred to gaseous phase.

Conventional Volume Reduction Methods of Contaminated Soil

	Operator	Object	Volume Reduction Method	Temp. [ºC]	Initial Radioactive Cs Conc. [Bq/kg]	Cs Removal [%]
Wet Process	Toshiba Co.	Soil	Oxalic acid washing	95	5,000	93% (for 5 times washing)
	Tokyo Tech.	Soil	Hydrothermal + Coagulant settling	200	55,000	75%（85% if adding blasting)
Dry Process	Taiheyo Cement Co.	Soil	sublim met	1300	60,000	99%

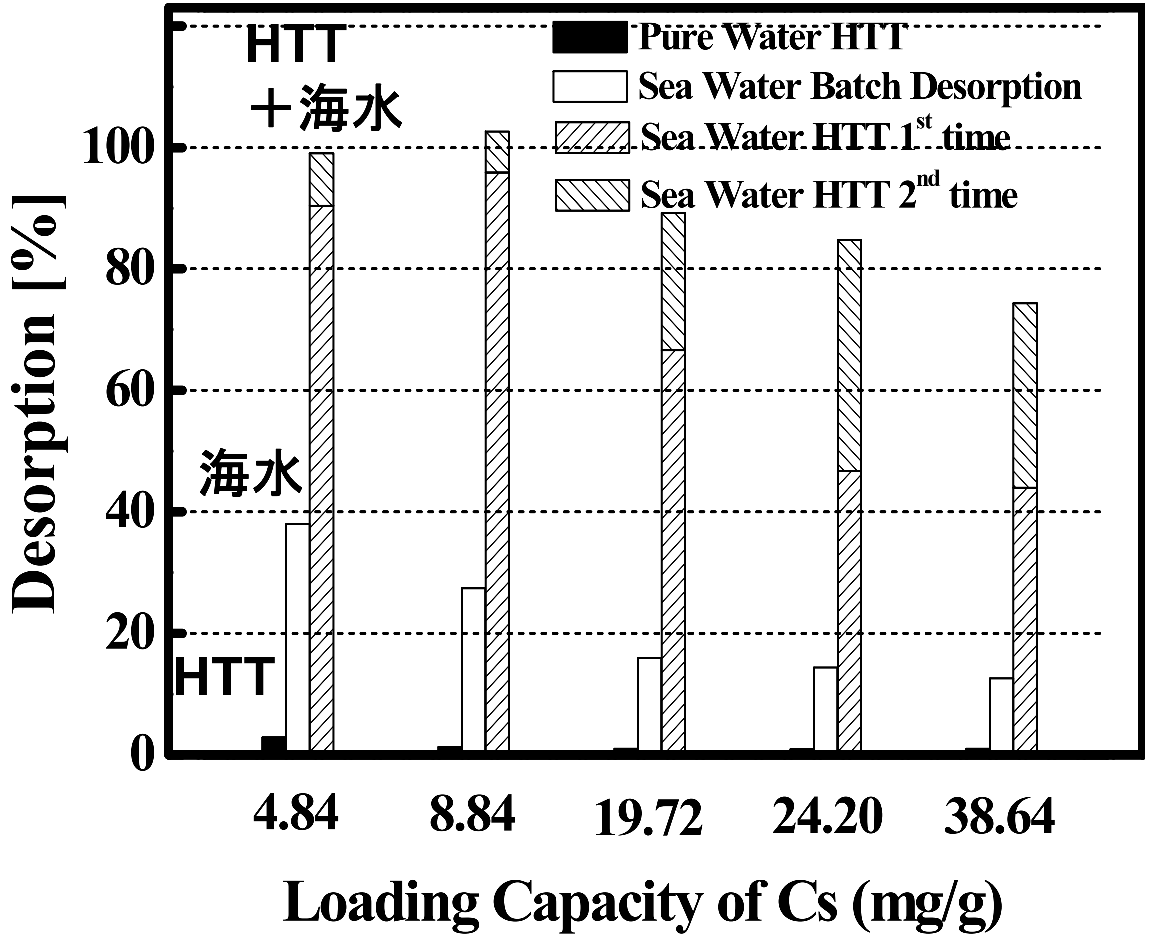
Recent Progress of Hydrothermal process for the volume reduction of contaminated soil

HTT Desorption



- Pure water is no use to desorb Cs
- Sea water HTT significantly increases the desorption.

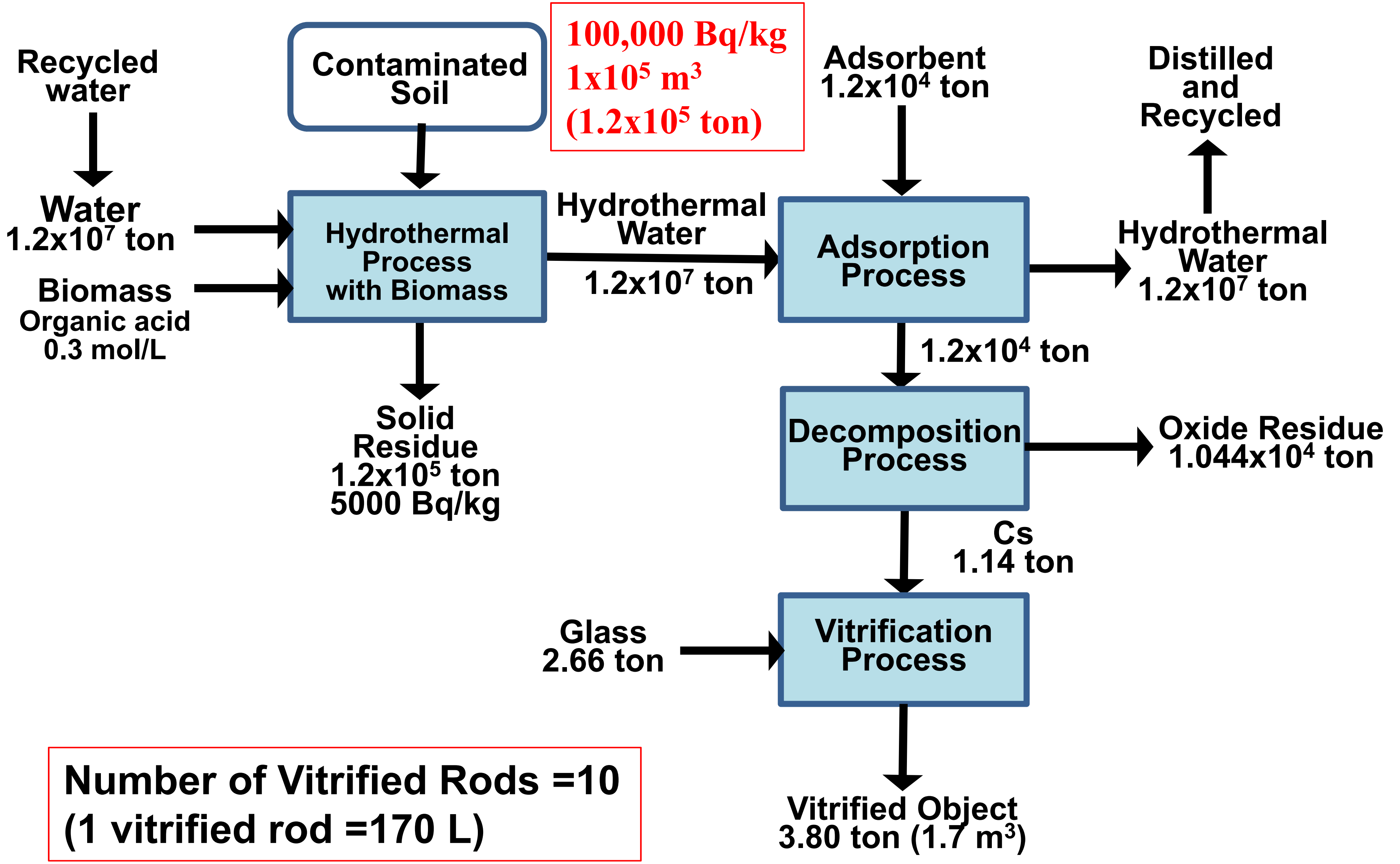
バーミキュライトのCsイオン交換性能の比較



V/m =
50ml/0.5g;
250℃，t: 30 min

- ➢**Pure water** is not useful for the desorption of Cs
- ➢**Sea water+HTT** promotes the desorption of Cs.

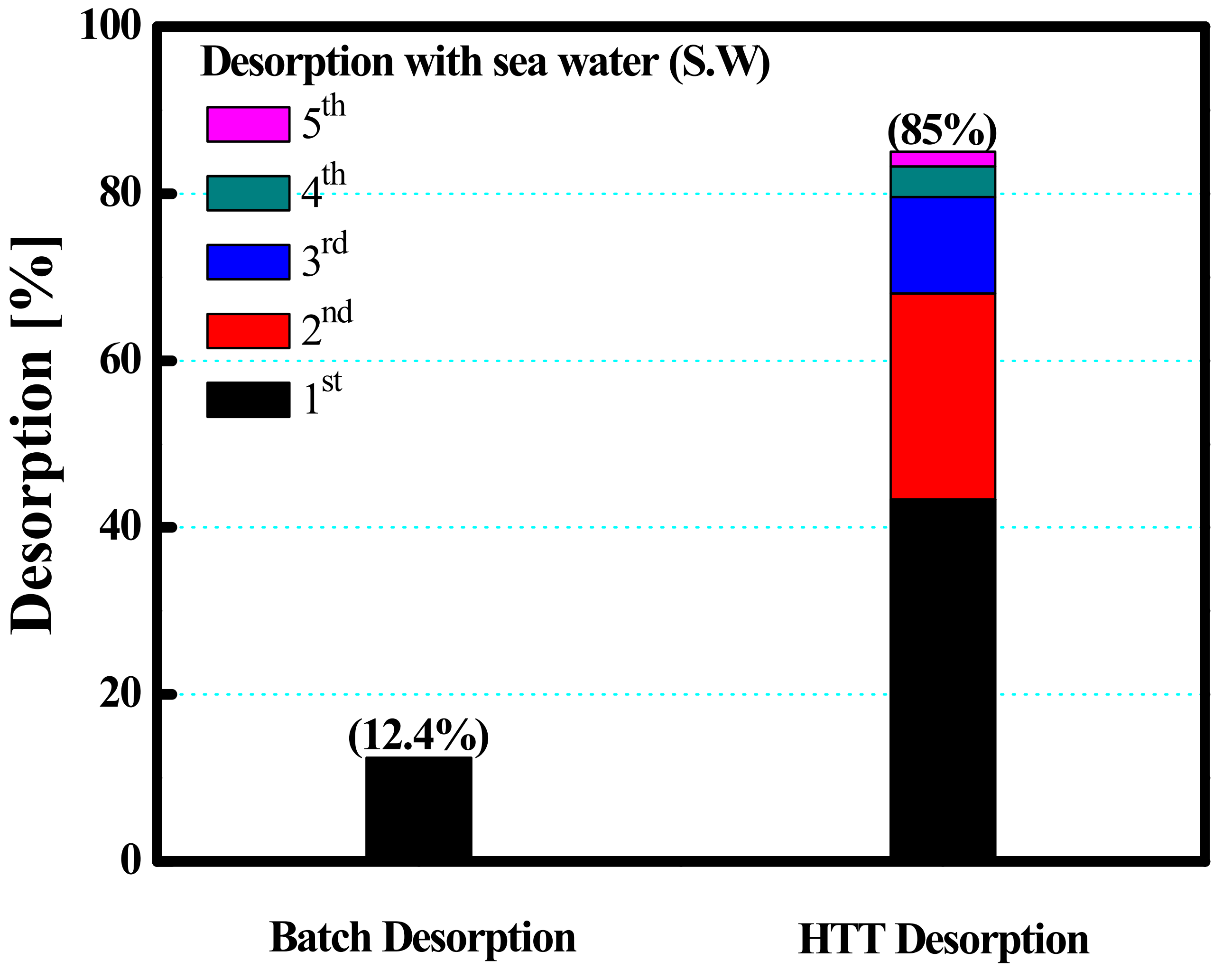
Mass Balance of Proposed Volume-reduction Process



Number of Vitrified Rods =10
(1 vitrified rod =170 L)

Volume Reduction = $1.7x10^{-5}$ =0.0017%

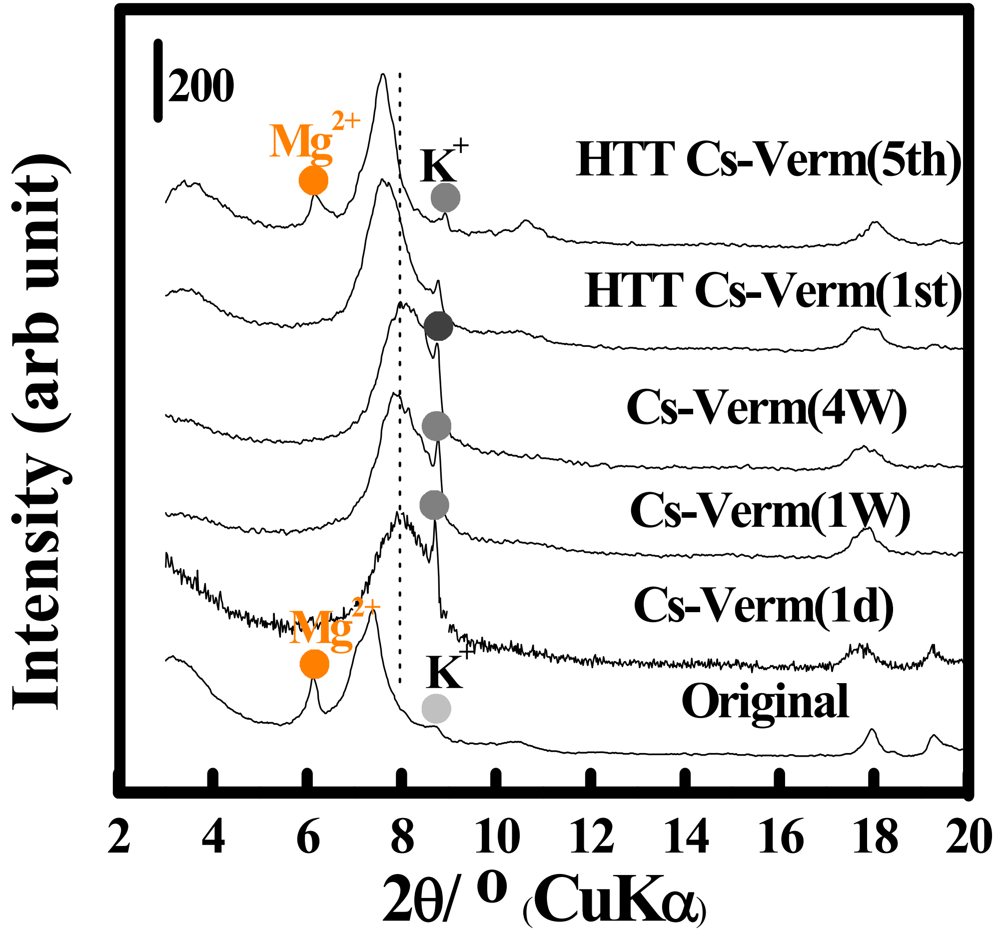
Sequential Desorption using Sea Water



Adsorption: 28d; 1
1000ppr
HTT： V/m：50ml/0.5g

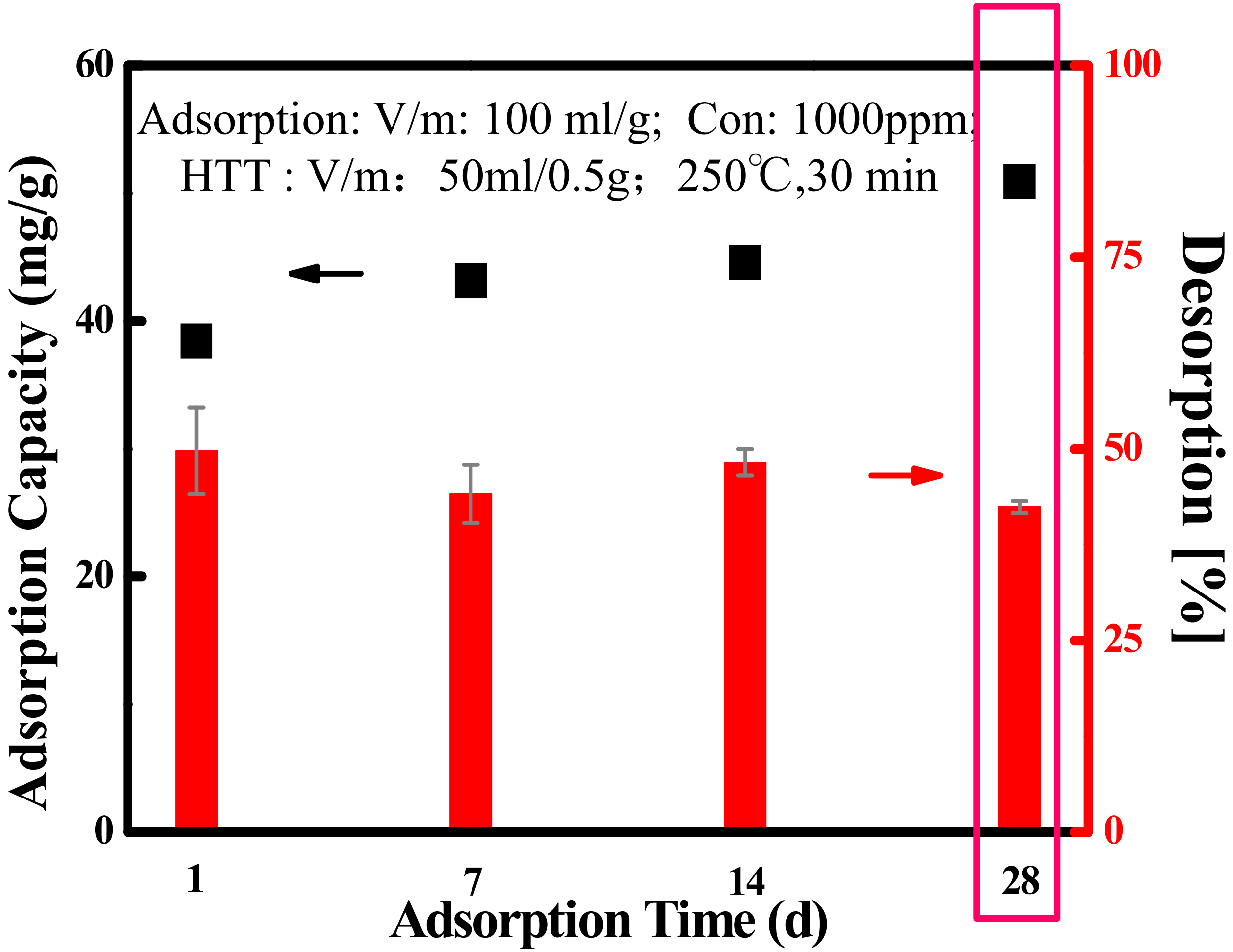
常温脱着　　HTT脱着

XRD Results With Sea Water Desorption



- ➢ The peak of Mg^{2+} **disappears** after Cs^+ adsorption.
- ➢ The peak of Mg^{2+} **appears** after HTT desorption again.

Cs吸着後のエージング時間の影響



- ➢ Adsorption is **increased** with the time.
- ➢ Desorption is **decreased** with the time.

Fukushima EcoTech

Fukushima EcoTech is located at border between Tomioka and Naraha. The leachate-controlled landfill site is on the top surface of the hardly-permeable ground. Double water barrier sheet is laid on the ground.

定できる検知システムを備えています。

フクシマエコテックは、富岡町に位置しています（搬入路は楢葉町に所在）。

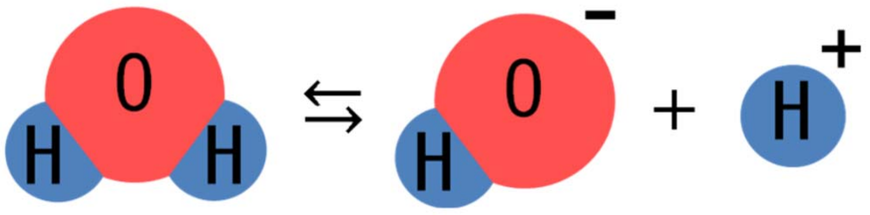
概要

処分場面積：約9.4ha
埋立地面積：約4.2ha
埋立容量　：約96万m³
残余容量　：約74万m³
［埋立可能容量：約65万m³
土堰堤：約9万m³］

環境省、特定廃棄物の埋立処分事業、2014/05
http://shiteihaiki.env.go.jp/pamphlet/pdf/landfill_disposal_pamphlet.pdf

Hydrothermal Decomposition using Subcritical Water

Promoting water solubilization of polluted materials by hydrothermal decomposition using subcritical water

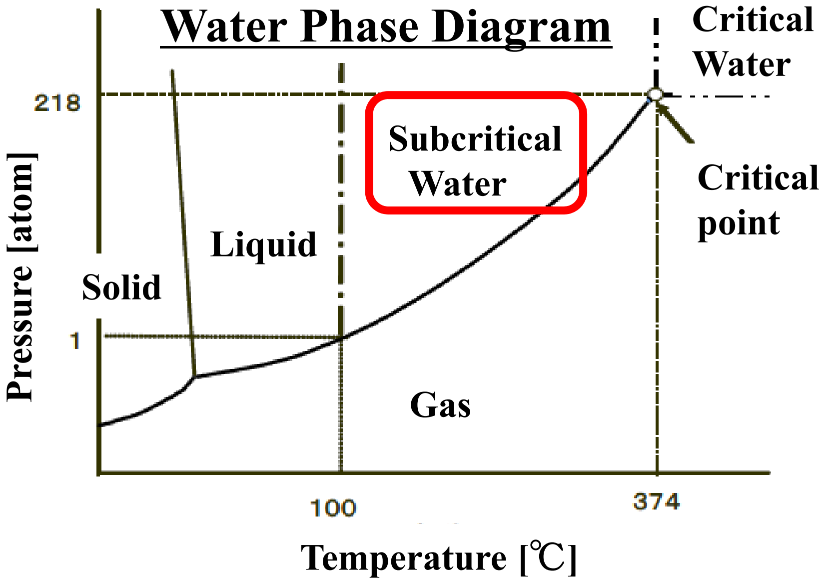


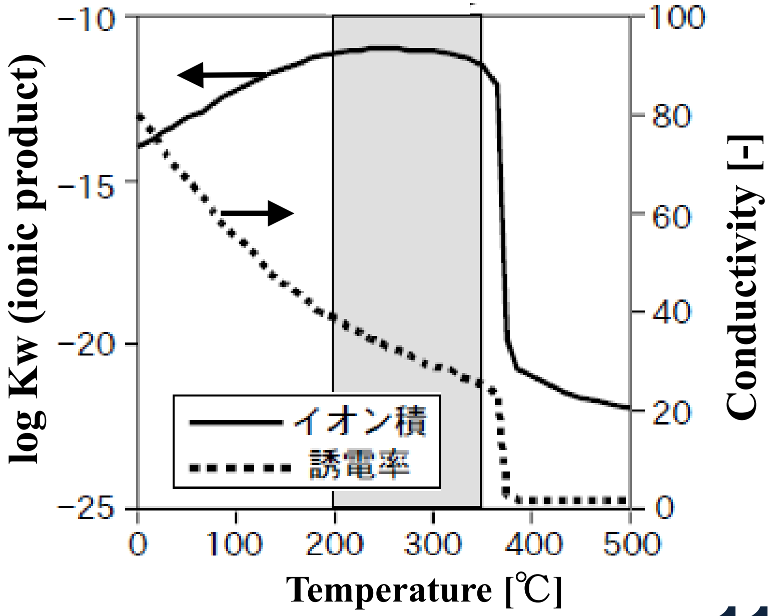
Ionic product of water becomes largest in subcritical state under high temperature (240-280℃) and high pressure (3-4 MPa).

① Cs adsorbed in organic materials is recovered to water phase by the high decomposition effect of organic materials.

② Cs adsorbed in inorganic materials is recovered to the aqueous phase by the high-speed ion exchange effect.

③ Only water is used in the decomposition process. No secondary waste is formed.





Ionic Product and Conductivity of Water

Hydrothermal Decomposition of Comtaminated Plants

Hydrothermal Operation

- **Water is added twice the sample**

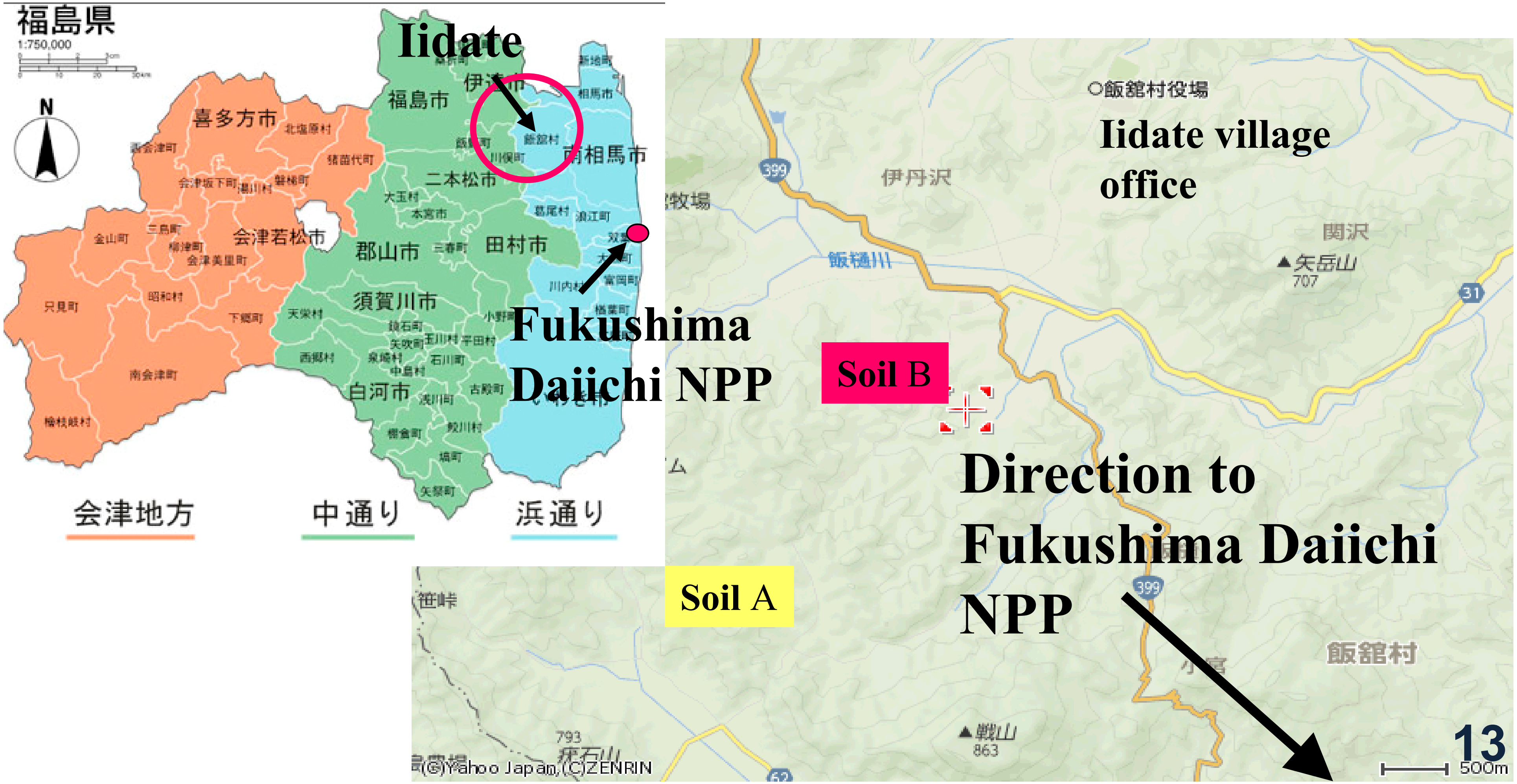
1. **Hydrothermal operation at 200ºC (14 atom) for 30 min**
2. **Gas vending at 170ºC**
3. **Sampling at 70ºC**

Organic compounds were decomposed by the hydrothermal operation. Most of solid components were decomposed to light-weight compounds, which were dissolved to water phase. Cs is also transferred to water phase.

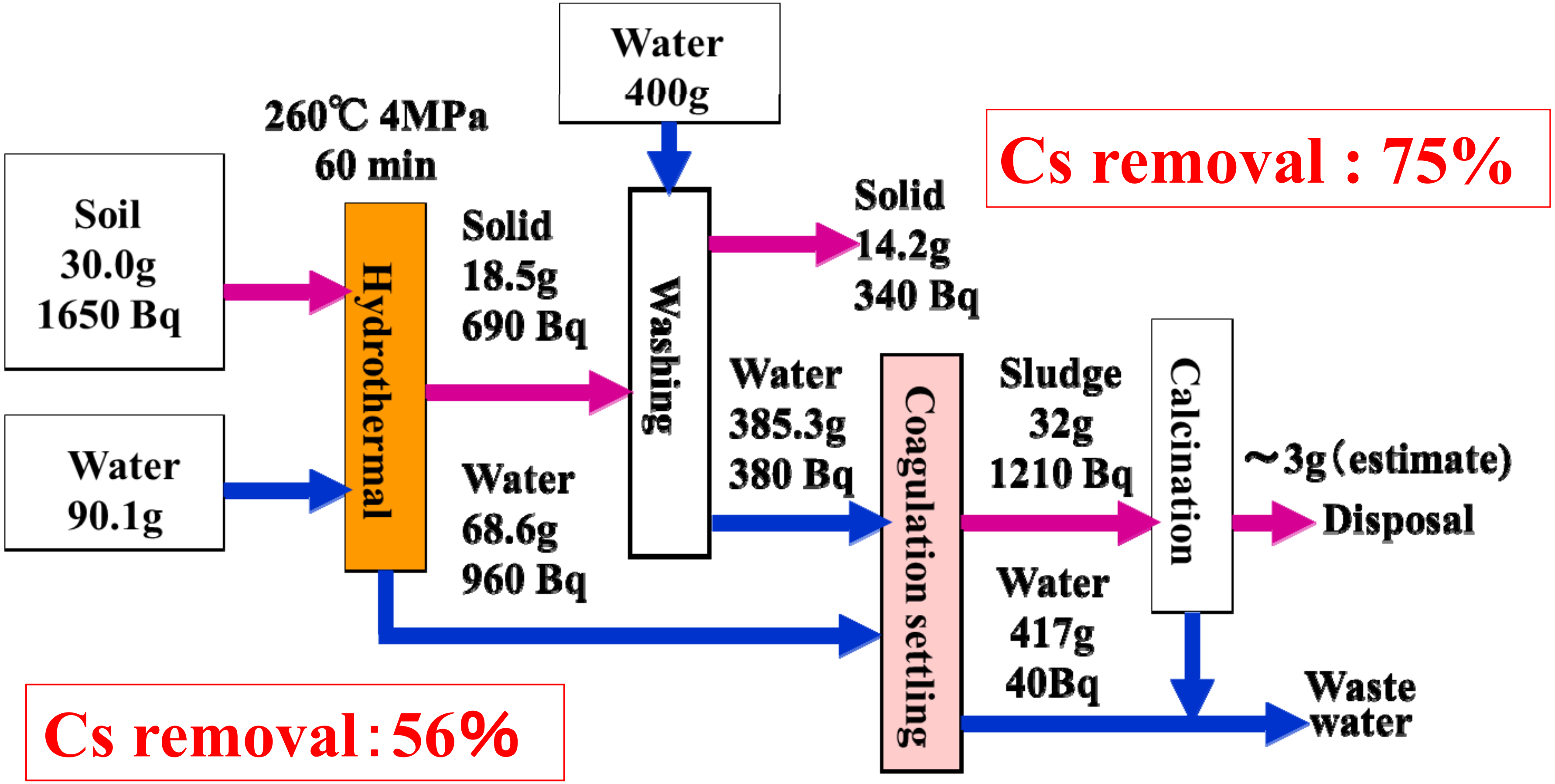
Sampling of Polluted Soil in Iidate Village

Soil A 23,600 Bq/kg

Soil B 55,000 Bq/kg



Removal Test of Cs from Soil B



Cs removal : 75%

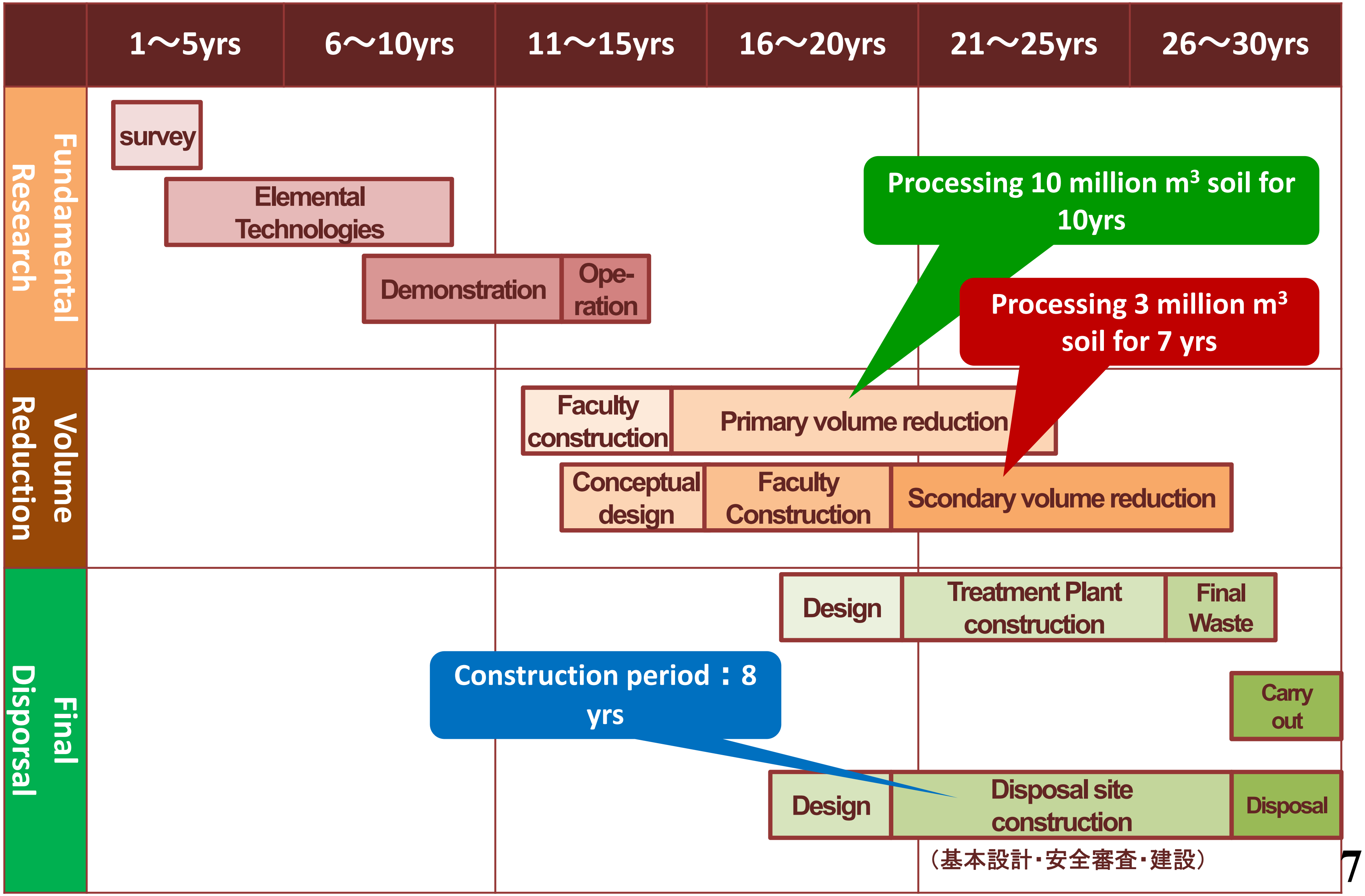
Cs removal : 56%

Ferric Ferrocyanide 0.2wt%
Ion Reaxtion P 0.2 wt%

Soil B
55,000 Bq/kg

Time Schedule of Volume-reduction of Contaminated Soil

Proposed by RANDEC (Radwaste and Decommissioning Center)



1～5yrs

6～10yrs

11～15yrs

16～20yrs

21～25yrs

26～30yrs

Fundamental Research

survey

Elemental Technologies

Demonstration

Ope-ration

Processing 10 million m^3 soil for 10yrs

Processing 3 million m^3 soil for 7 yrs

Volume Reduction

Faculty construction

Primary volume reduction

Conceptual design

Faculty Construction

Scondary volume reduction

Final Disporsal

Design

Treatment Plant construction

Final Waste

Carry out

Construction period：8 yrs

Design

Disposal site construction

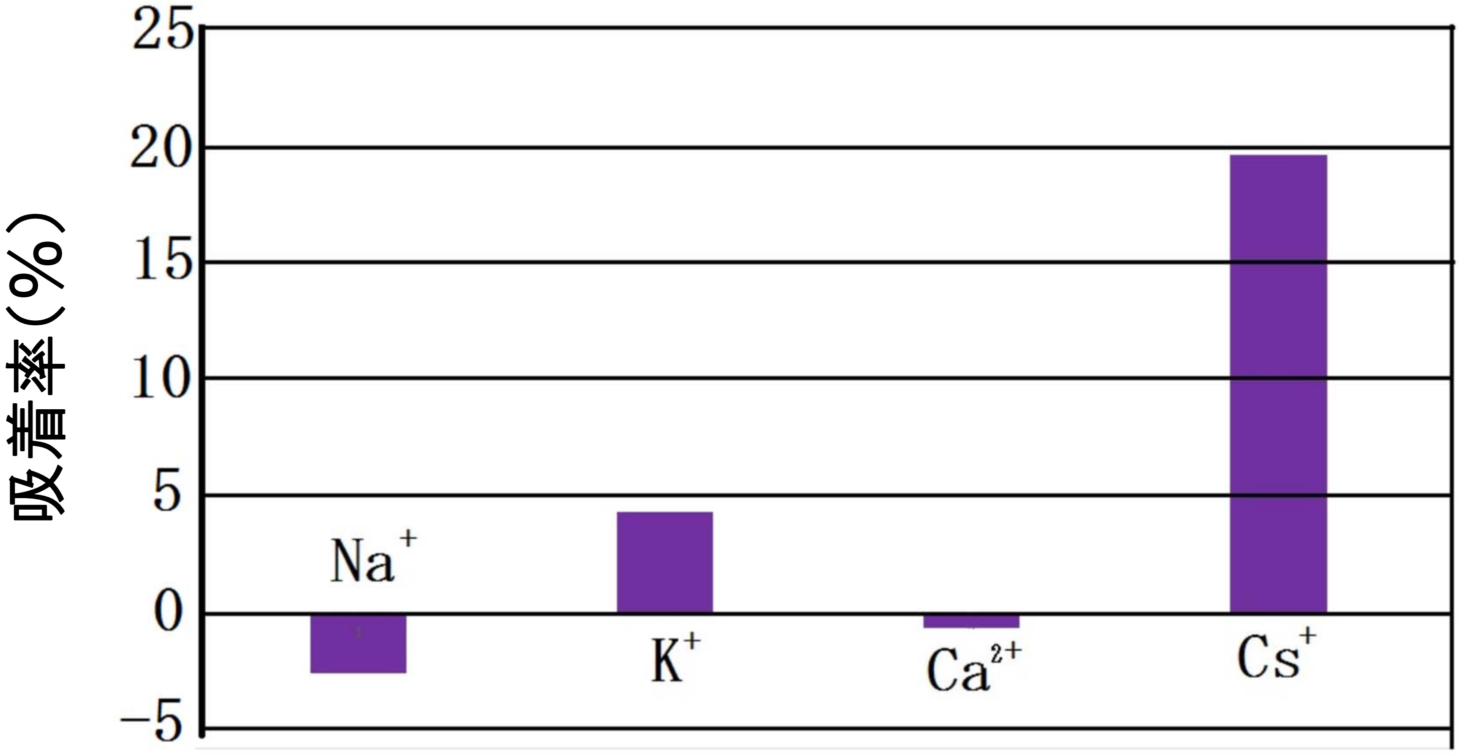
Disposal

（基本設計･安全審査･建設）

Generation of Contaminants in Fukushima Prefecture

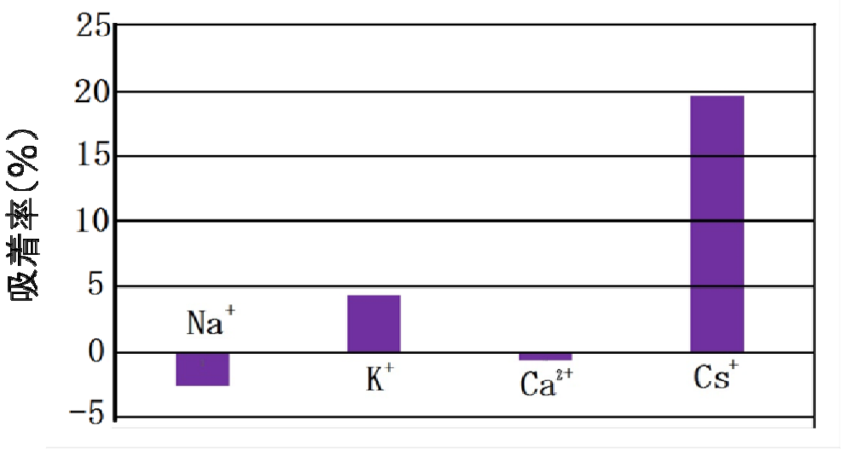
Contaminants	Volume [m^3]
Contaminated Soil below 8,000 Bq/kg	10,060,000
Contaminated Soil from 8,000 Bq/kg to 100,000 Bq/kg	10,350,000
Contaminated Soil above 100,000 Bq/kg	10,000
Ash of Combustible Decontamination Wastes	1,550,000
Decontamination Wastes above 100,000 Bq/kg	20,000

Cs+1 ppmとCs+に対しモル比濃度500倍のNa+、K+、Ca2+混合溶液に対して示す各イオンに対する吸着率



混合溶液中の各イオンに対する吸着率

Cs+1 ppmとCs+に対しモル比濃度500倍のNa+、K+、Ca2+混合溶液に対して示す各イオンに対する吸着率



混合溶液中の各イオンに対する吸着率

図3　アルミナゲル堆積型高珪酸ポーラスガラスの吸着性能