Overview of chemical treatments for radioactive waste

- Estimation of stability of Cs in soils by chemical treatment -

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Caesium Workshop

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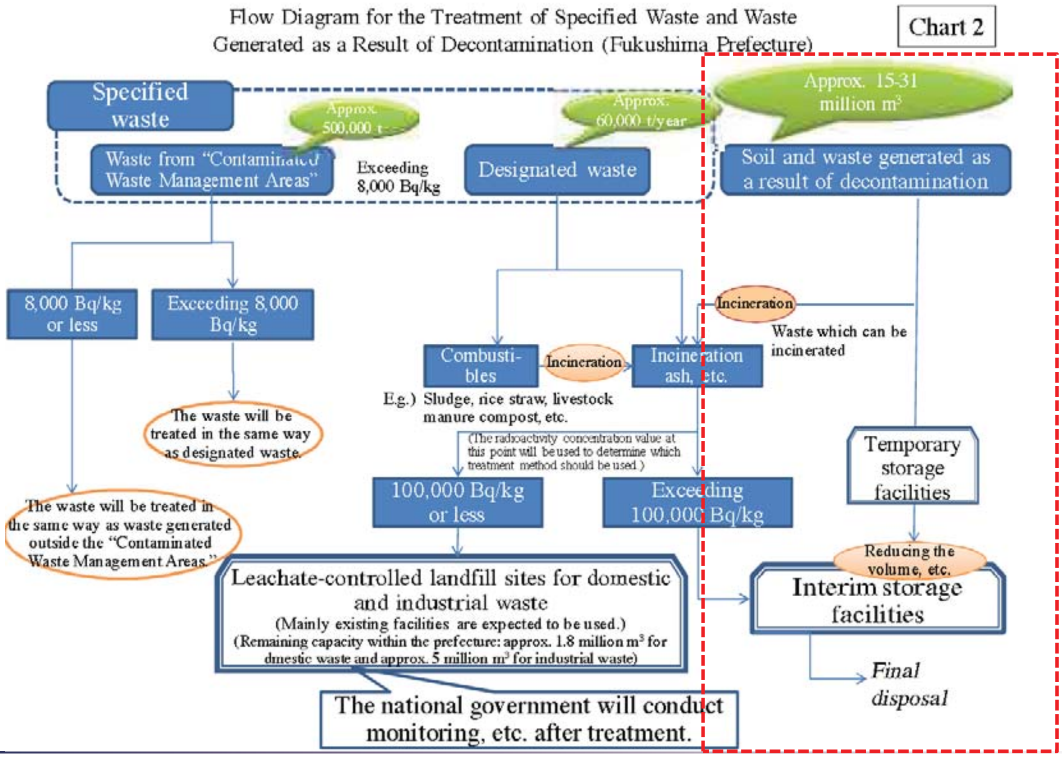
Outline

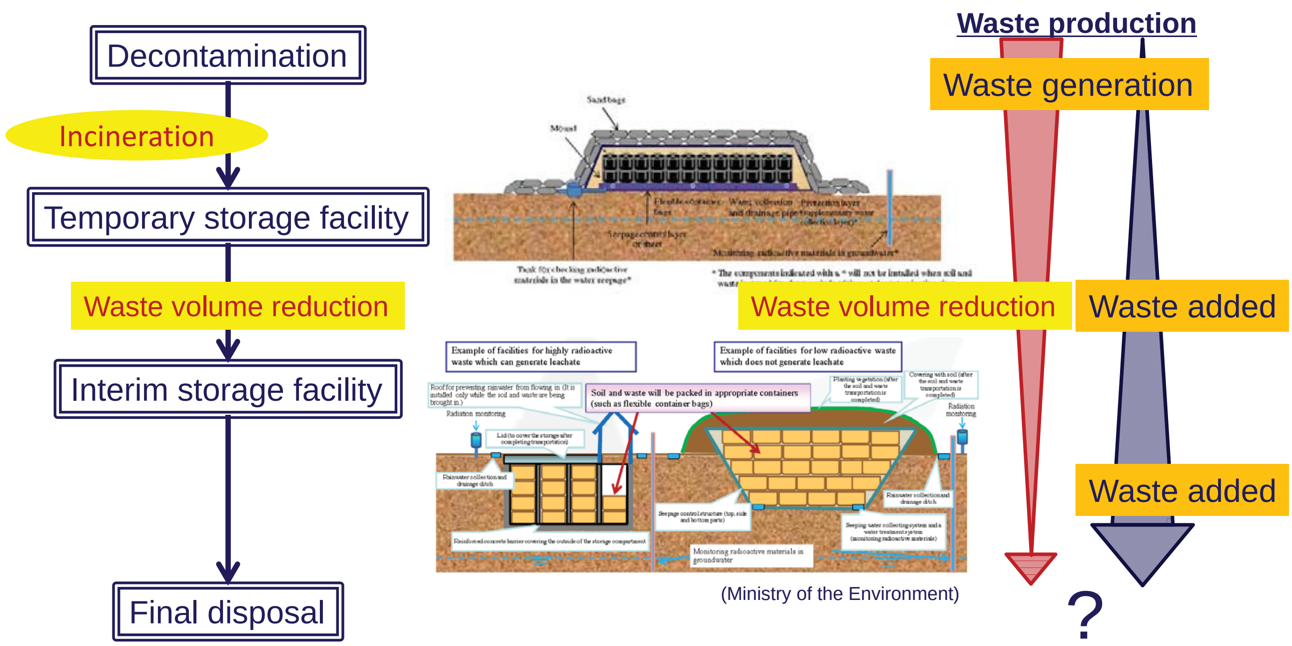
- Chemical treatment for waste volume reduction
- Cs fixation in clay minerals
- Stability of Cs in soil
- Future work of chemical treatment for waste volume reduction

Flow Diagram for Treatment of Waste



(Ministry of the Environment)

Waste Production from Decontamination to Final Disposal



(Ministry of the Environment)

Waste volume reduction in the process to the final disposal

Possibility of Waste Volume Reduction in the Process to the Final Disposal

① Reduction of waste generation

e.g. *Plowing to replace surface soil with subsoil

② Volume reduction of generated waste

e.g. *Classification, *Incineration, *Chemical treatments

③ Suppression of added waste generation

e.g. *Rationalization of storage facility design and operation

④ Prevention of re-contamination

Decontamination → Temporary storage facility → Interim storage facility → Final disposal

① and ④ | **②, ③ and ④** | **②, ③ and ④**

Chemical Treatment for Waste volume Reduction

Direct waste volume reduction by chemical treatment

- **For volume reduction of generated waste**
- **For recovery of Cs from soil waste**

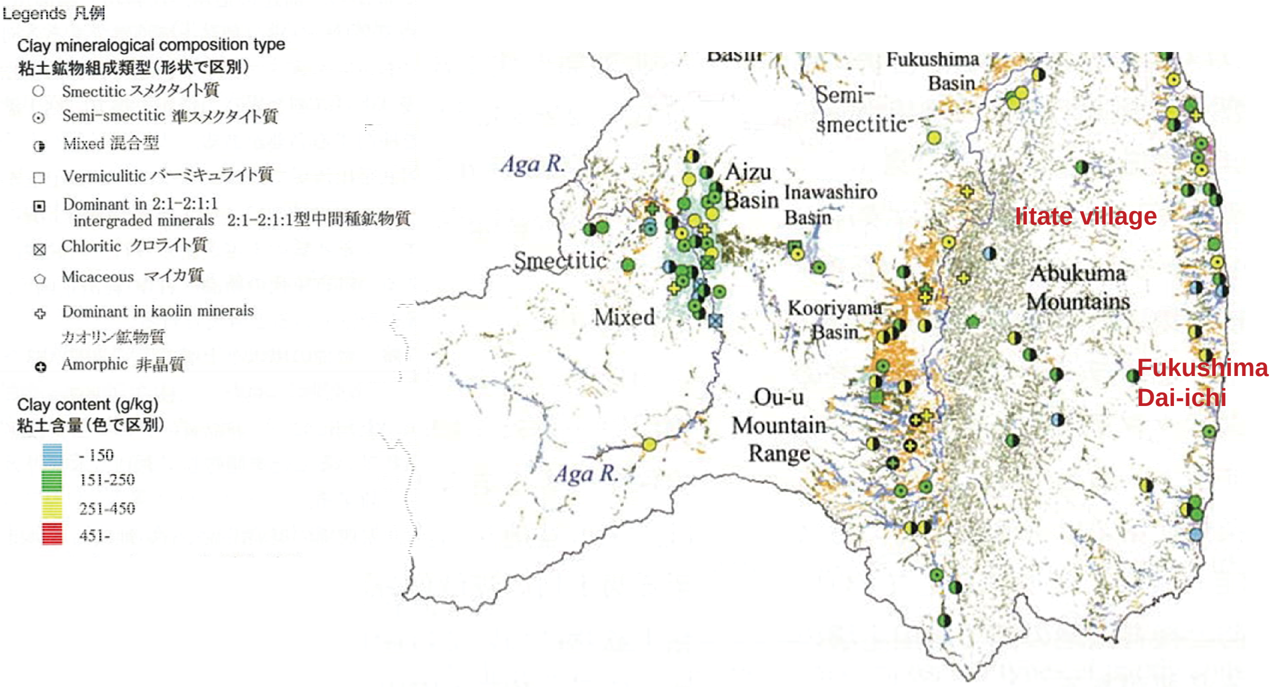
  - ☐ Extraction using inorganic and organic cations [ion exchange]
  - ☐ Acid and alkaline treatment [dissolution of soils]
  - ☐ Sequential extraction [ion exhagne, dissolution of soils]

Indirect waste volume reduction by chemical treatment

- **For reduction of waste generation**
- **For suppression of added waste generation**

  - ☐ **Estimation of stability of Cs in soil waste**
  - ☐ Estimation of mobility of Cs in soil waste

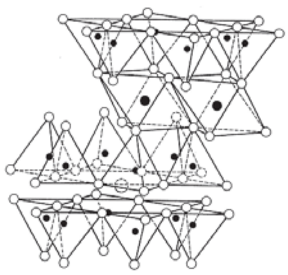
Clay mineralogical composition of paddy soil



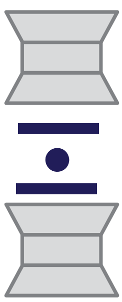
Sano et al. 2010

Key Clay Minerals for Cs Sorption

● Interlayer Cation
▬ Water layer

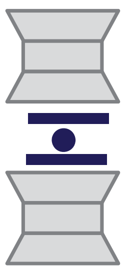


Smectite



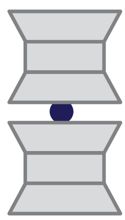
- Layer chareg：0.2～0.6
- Expandability
- Exchangeable cation

Vermiculite



- Layer chareg：0.6～0.9
- Expandability
- Exchangeable cation

Mica



- Layer chareg：0.6～1.0
- Non-expandability
- Non-exchangeable cation

Cs Fixation in Clay Minerals

Cesium fixed by clay minerals against five extractions with
0.1 *N* chloride solutions of extracting cation.

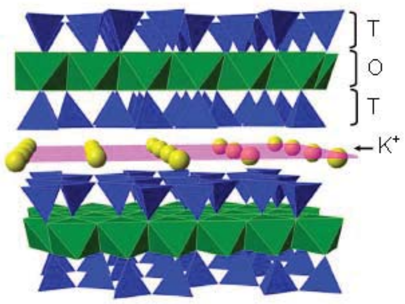
Saturating cation	Extracting cation	Cs fixed, µg/g					
		Bt	Ill	Kl	Mt	Musc	Vr
K^+	K^+	20	18	1	0	21	17
K^+	Ca^{2+}	69	66	6	7	60	54
Ca^{2+}	K^+	73	72	1	5	65	64
Ca^{2+}	Ca^{2+}	116	105	8	8	119	67

Sawhney 1964

Bt: Biotite (Mica), **Ill**: Illite (Mica), **Kl**: Kaolinite, **Mt**: Montmorillonite,
Musc: Muscovite (Mica), **Vr**: Vermiculite

Natural Example of Cation Fixation in Clay Minerals

Mica minerals



Tamura et al. 2008

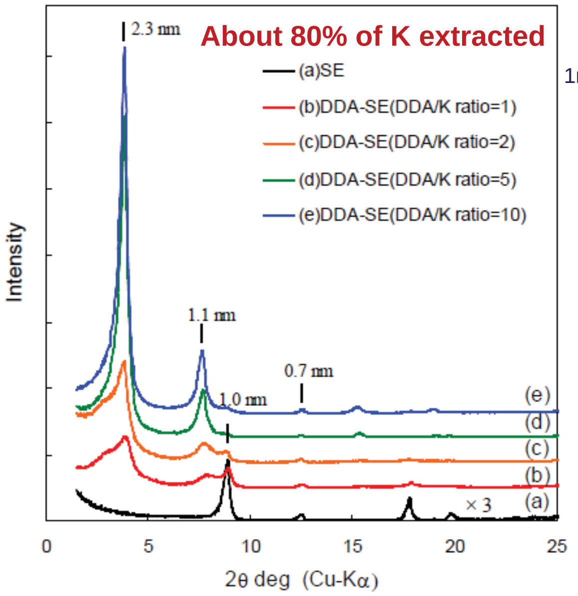
- Layer chareg : 0.6～1.0
- Non-expandability
- Non-exchangeable cation

Mica minerals exist stably on a geological time scale.

Potassium in mica minerals is also stable for long term

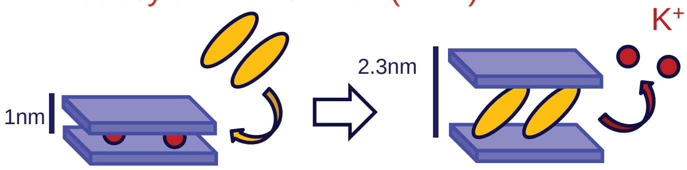
Radiocesium adsorb strongly by the clay minerals as the potassium in mica ?

Alkylammonium Treatment for K Extraction



Tamura et al. 2008

Dodecylammonium ion (DDA)



Stability of radiocesium in the soils

Extraction by inorganic cation

Yes → Exchangeable cation in smectite

No ↓

Extraction by DDA

Yes → Potassium in mica

No ↓

More stable

Sample and Methods

Sample:

Rice paddy, Farm land and Play ground
(Iitate village, Fukushima prefecture)

Extraction experiment using inorganic cations:

Soil : Solution ratio:	20g (wet) : 200mL
Concentration of solution :	1mol/L
Reaction time :	over 90min
Agitation :	Handshake (15min intervals)
Measurement:	Cs-134 + Cs-137

Extraction experiment using DDA :

Soil : Solution ratio:	2.5g (wet) : 100mL
Concentration of solution :	0.1 and 0.5 mol/L
Temperature:	65, 85 and 110 ˚C
Reaction time :	2 days + 1 day
Measurement:	Cs-137

Leaching Ratio in Each Extraction Experiment using Inorganic Cations

Rice paddy

Reagent	Reaction time (min)	Leaching ratio (%)
Ammonium nitrate	101	3.6
Ammonium acetate	107	3.6
Ammonium dihydrogen phosphate	111	3.4
Ammonium hydrogen carbonate	100	3.4
Ammonium chloride	84	2.7
Potassium dihydrogen phosphate	95	-
Potassium chloride	97	-
Sodium dihydrogen phosphate	232	-
Sodium chloride	107	3.7
Aluminum chloride hexahydrate	83	-

Farm land

Reagent	Reaction time (min)	Leaching ratio (%)
Ammonium nitrate	99	7.2
Ammonium acetate	96	6.8
Ammonium dihydrogen phosphate	89	4.7
Ammonium hydrogen carbonate	95	5.8
Ammonium chloride	97	6.3
Potassium dihydrogen phosphate	100	3.4
Potassium chloride	100	7.4
Sodium dihydrogen phosphate	120	-
Sodium chloride	89	-
Aluminum chloride hexahydrate	91	-

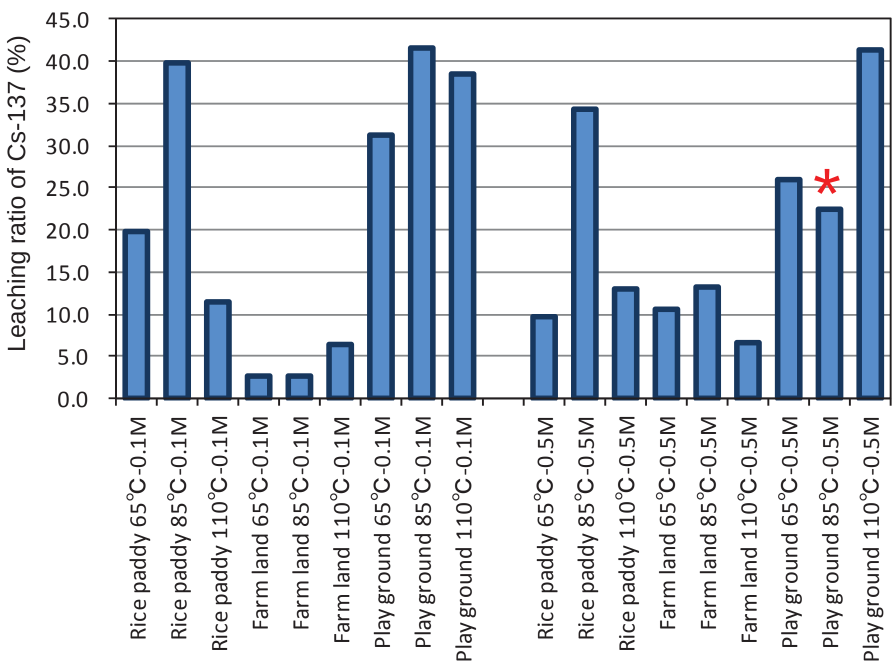
Play ground

Reagent	Reaction time (min)	Leaching ratio (%)
Ammonium nitrate	92	4.2
Ammonium acetate	97	4.5
Ammonium dihydrogen phosphate	108	4.4
Ammonium hydrogen carbonate	131	5.2
Ammonium chloride	95	3.8
Potassium dihydrogen phosphate	104	5.2
Potassium chloride	91	4.5
Sodium dihydrogen phosphate	94	5.1
Sodium chloride	91	2.2
Aluminum chloride hexahydrate	97	1.2

The leaching ratio of the radiocesium (Cs-134 + Cs-137) from the soil was less than 7 %

Radiocesium is fixed in the soils as the potassium in mica minerals

Leaching Ratio in DDA Treatment



Soil:

Play ground > Rice Paddy ≫ Farm land

Concentration:

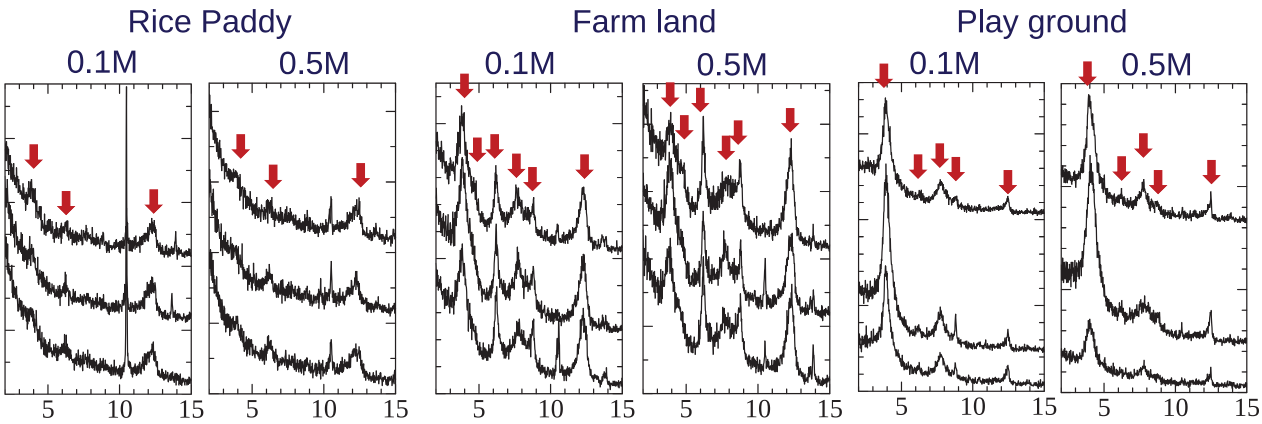
0.1 M ≒ 0.5 M

Temperature:

85˚C > 110˚C ≧ 65˚C

*: Only 1st measurement

XRD Patterns and d-values of Clay Minerals



Sample	d-value (Å)
0.1M-65℃	22.4, 14.3, 7.2
0.1M-85℃	22.6, 14.2, 7.2
0.1M-110℃	22.6, 14.0, 7.2
0.5M-65℃	22.3, 14.2, 7.2
0.5M-85℃	22.3, 14.2, 7.2
0.5M-110℃	22.4, 14.3, 7.2

Sample	d-value (Å)
0.1M-65℃	23.0, 18.5, 14.2, 11.4, 10.0, 7.2
0.1M-85℃	22.9, 18.8, 14.2, 11.4, 10.0, 7.2
0.1M-110℃	23.1, 18.8, 14.3, 11.5, 10.0, 7.2
0.5M-65℃	23.1, 19.1, 14.2, 11.3, 10.1, 7.2
0.5M-85℃	22.8, 18.4, 14.3, 11.5, 10.0, 7.2
0.5M-110℃	22.6, 18.2, 14.2, 11.4, 10.0, 7.2

Sample	d-value (Å)
0.1M-65℃	22.5, 14.2, 11.4, 10.1, 7.1
0.1M-85℃	22.2, 14.3, 11.4, 10.0, 7.1
0.1M-110℃	22.5, 14.1, 11.4, 10.0, 7.1
0.5M-65℃	22.0, 11.4, 10.1, 7.1
0.5M-85℃	21.7, 14.3, 11.3, 10.0, 7.1
0.5M-110℃	21.6, 14.3, 11.4, 10.0, 7.1

Layer Charge of Clay Minerals in Soil

Soil－Conc.	Temp.	d-value			Layer Charge		
		Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
Rice paddy－0.1M	65	22.4		14.3	0.68		0.27
	85	22.6		14.2	0.69		0.26
	110	22.6		14	0.69		0.26
Farm land－0.1M	65	23	18.5	14.2	0.71	0.39	0.26
	85	22.9	18.8	14.2	0.70	0.40	0.26
	110	23.1	18.8	14.3	0.71	0.40	0.27
Play ground－0.1M	65	22.5		14.2	0.68		0.26
	85	22.2		14.3	0.67		0.27
	110	22.5		14.1	0.68		0.26
Rice paddy－0.5M	65	22.3		14.2	0.67		0.26
	85	22.3		14.2	0.67		0.26
	110	22.4		14.3	0.68		0.27
Farm land－0.5M	65	23.1	19.1	14.2	0.71	0.41	0.26
	85	22.8	18.4	14.3	0.70	0.39	0.27
	110	22.6	18.2	14.2	0.69	0.38	0.26
Play ground－0.5M	65	22			0.66		
	85	21.7		14.3	0.64		0.27
	110	21.6		14.3	0.64		0.27

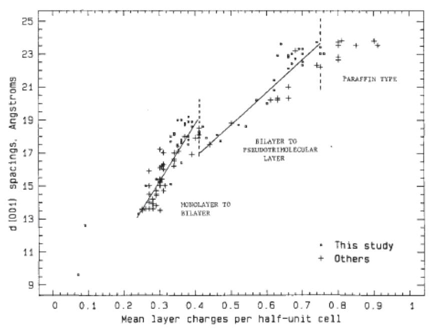


FIG. 5. Mean layer charges *vs.* *d*(001) spacings of dodecylammonium ion (n_C = 12)-exchanged 2:1 clay minerals.

High-Charge:
Mean Layer Charge ＝(d-value - 8.71)／20.25
Low-Charge:
Mean Layer Charge ＝(d-value - 5.52)／32.98

Olis et al., 1990

Clay minerals with high layer charge (i.e. Vermiculite and Mica minerals) are contained in each soil.

Conclusion

Rice paddy, Play ground

- Cs in the soil is hardly extracted by chemical treatment using inorganic cation.
- Most extracted Cs-137 by DDA treatment exist in the clay minerals with high layer charge (i.e. vermiculite and mica minerals).
- 60% of Cs-137 contained in the soil is not still extracted by DDA treatment.

Farm land

- Cs in the soil is hardly extracted by chemical treatment using both inorganic cation and DDA.
- Cs-137 contained in the soil is probably fixed in mica mineral because unreacted mica mineral is observed after DDA treatment.

In natural environment,
Cs in the soil is stable as the potassium in mica.

Future Work for Waste volume Reduction

Direct waste volume reduction by chemical treatment

◆Environmentally-friendly systems
- Low waste solution (e.g. recycle of reagent solution)
- Development of adsorbent to recover Cs from solution
- Effective utilization of the soil waste after chemical treatment

Indirect waste volume reduction by chemical treatment

◆Quantitative estimation of each affecting factor to stability of Cs
- Concentration of Cs in the soil
- Clay mineralogical composition of the soil
- Time-dependent effect
- wet-dry cycle