Offsite clean up
Volume reduction and decontamination by heat-treatment of relatively highly contaminated soil and incineration ashes

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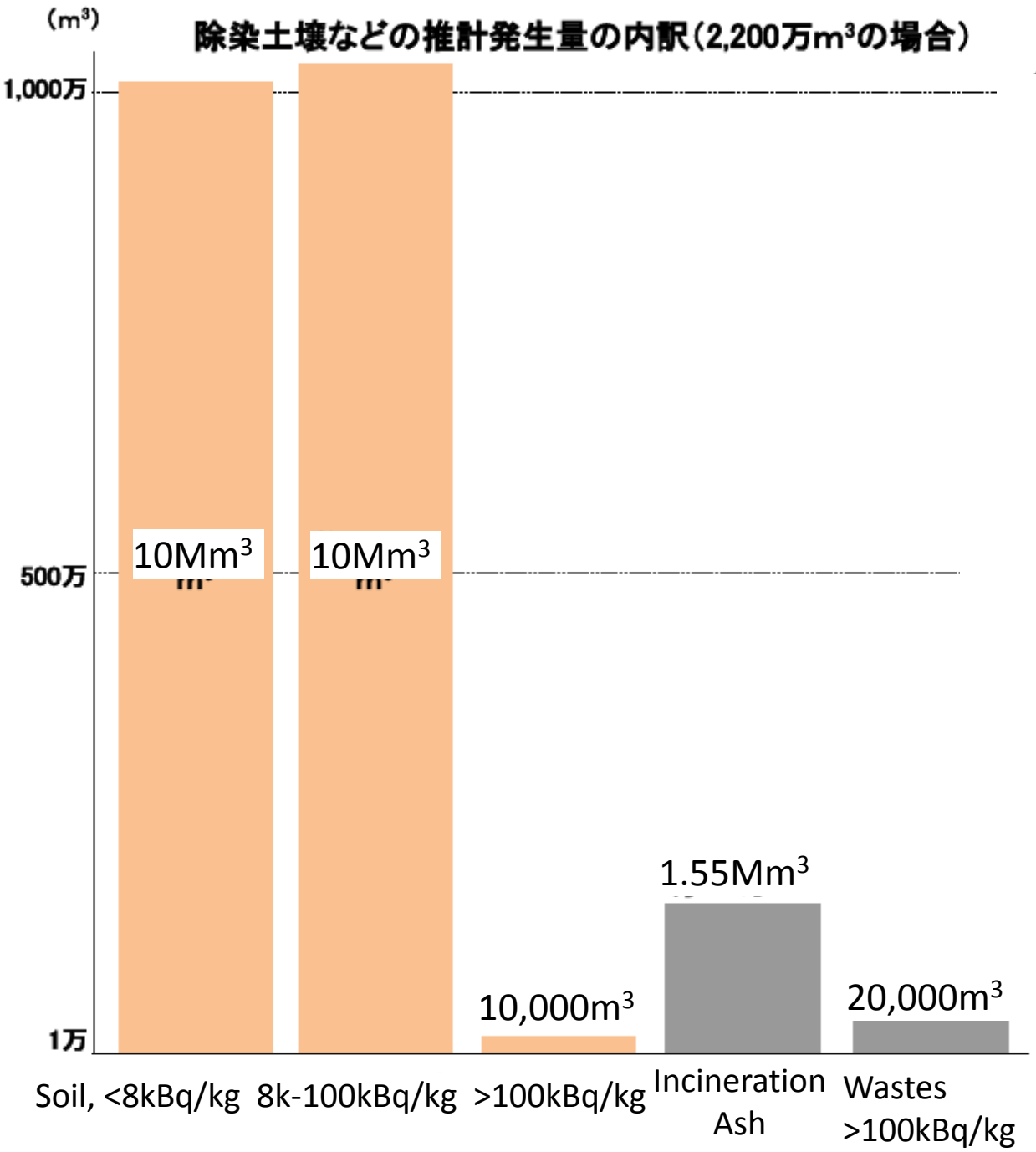
Background

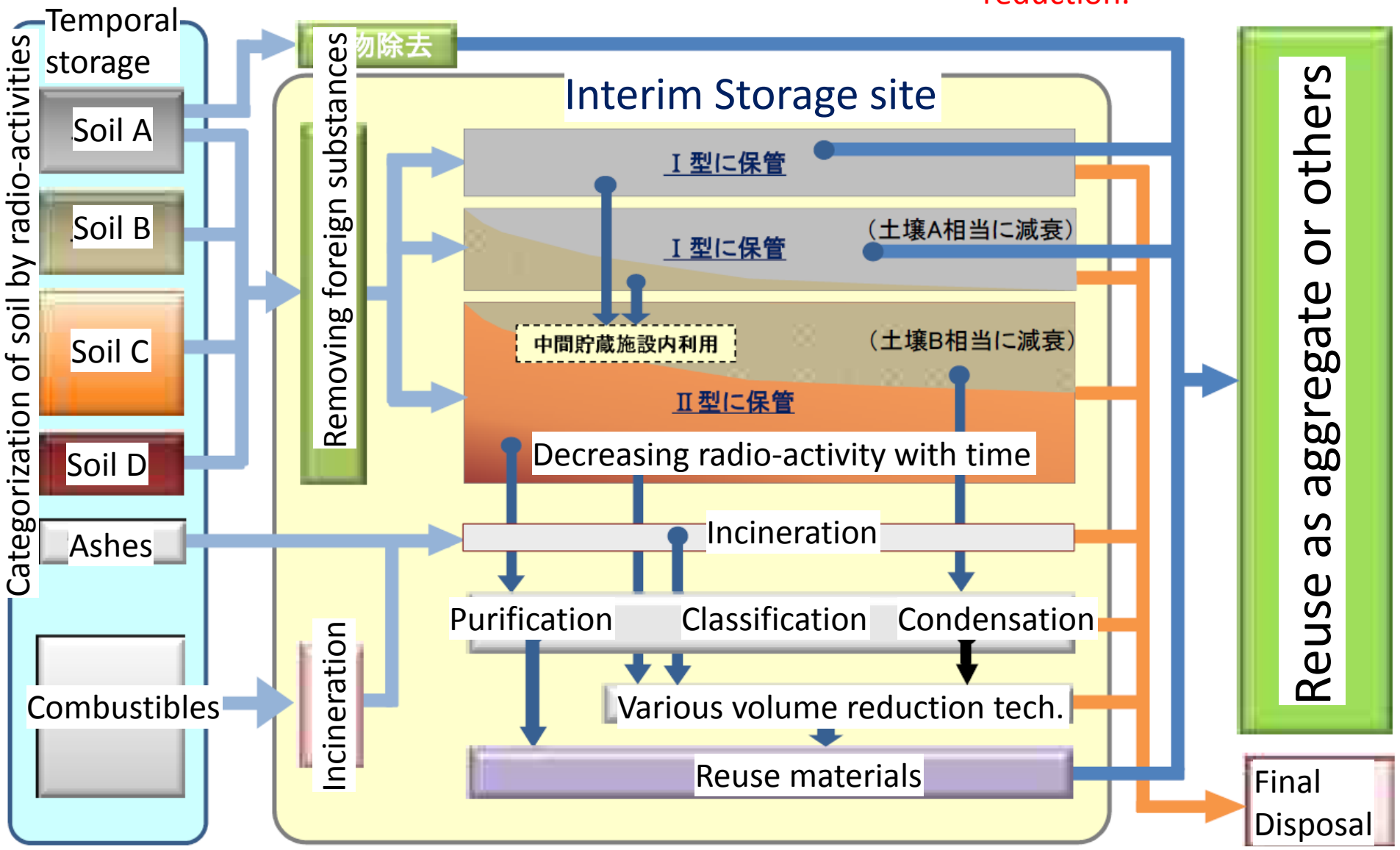
Trial to reduce 22 Mm^3 -contaminated wastes to the volume possible to dispose.



MOE
出典：環境省　中間貯蔵除去土壌等の減容・再生利用技術開発戦略検討会(第1回)資料3

Volume reduction - Reuse

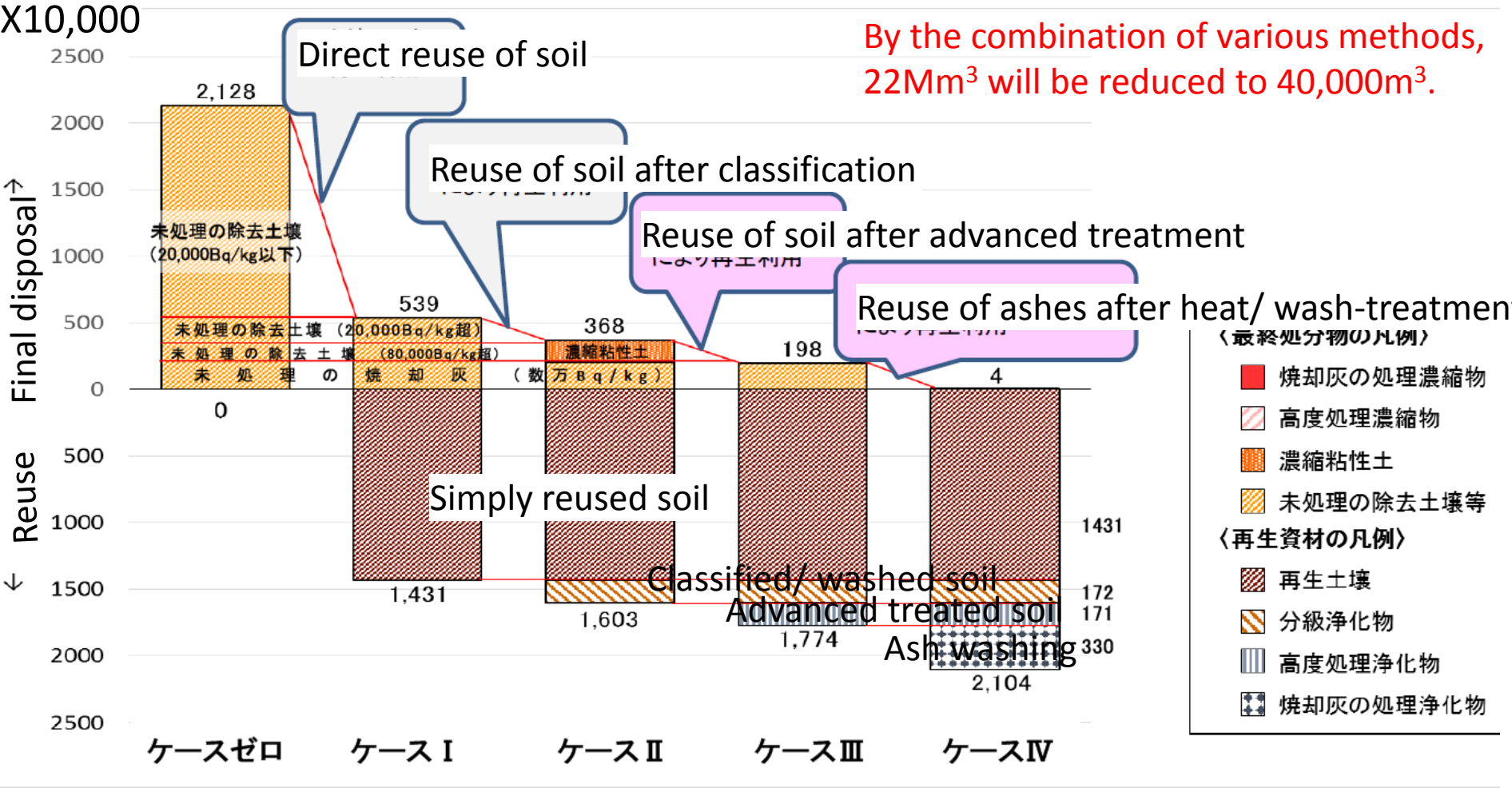
Reuse is the key of volume reduction.



MOE 出典：環境省平成27年12月21日中間貯蔵除去土壌等の減容・再生利用技術開発戦略検討会（第2回）
資料3　減容処理技術の開発課題及び目標について

Target of volume reduction-reuse technologies

■ Case study of reuse of materials less than 8kBq/kg



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Major volume reducing technologies

Various volume reducing technologies have been developed.
They have to meat the required processing capacity and cost.


Soil classificator

Three major technologies

1. Classification/ washing

Cs tends to be captured by fines in soil. Therefore, classification and washing to remove fine clays are effective way to reduce radio-Cs from soil.

2. Chemical treatment

By adding chemicals and heating, organic materials in the surface of soil are decomposed and Cs is segregated and recovered by sorbents.

3. Heat treatment: Sublimation, melting

By heating with the addition of appropriate volatilization accelerator of Cs, Cs is removed from soil or ashes and recovered by bag filter.


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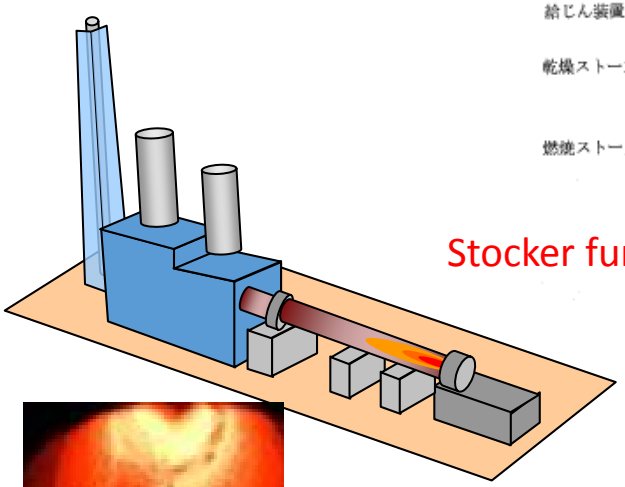
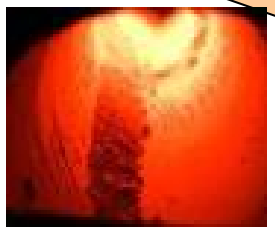
※After MOE

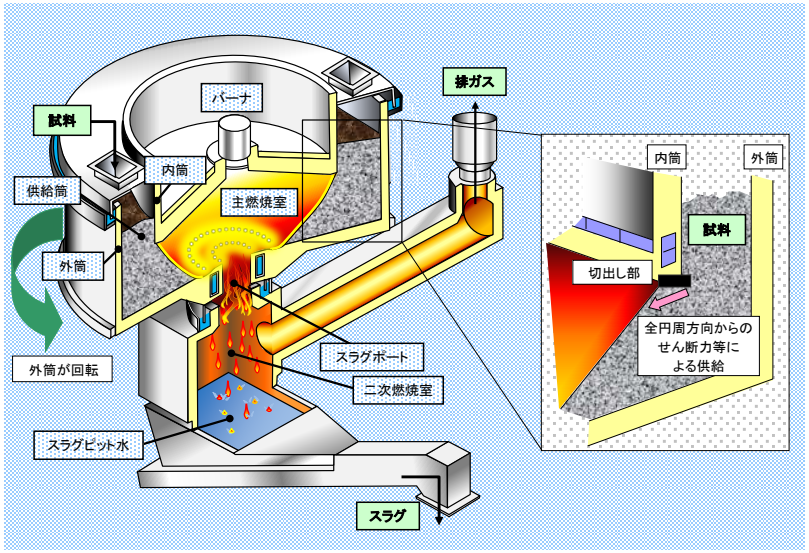
3 ways of heat treatments applied by existing systems for large capacities

- Incineration of combustible wastes. Cs evaporation depends on the origins.
- Clinkering to produce burned aggregate or cement after adjusting chemical composition. Cs evaporates perfectly.
- Melting of soil and incineration ashes to produce slag. Cs evaporates efficiently.

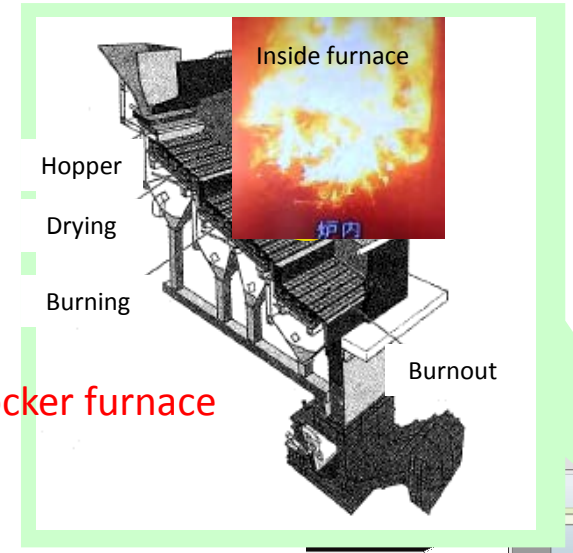




Stocker furnace



Stoker Incinerator



MSW

Bag filters (BF)

Air

Fly ash

Bottom ash

Image :
Hitachinaka-Tokai Clean Center

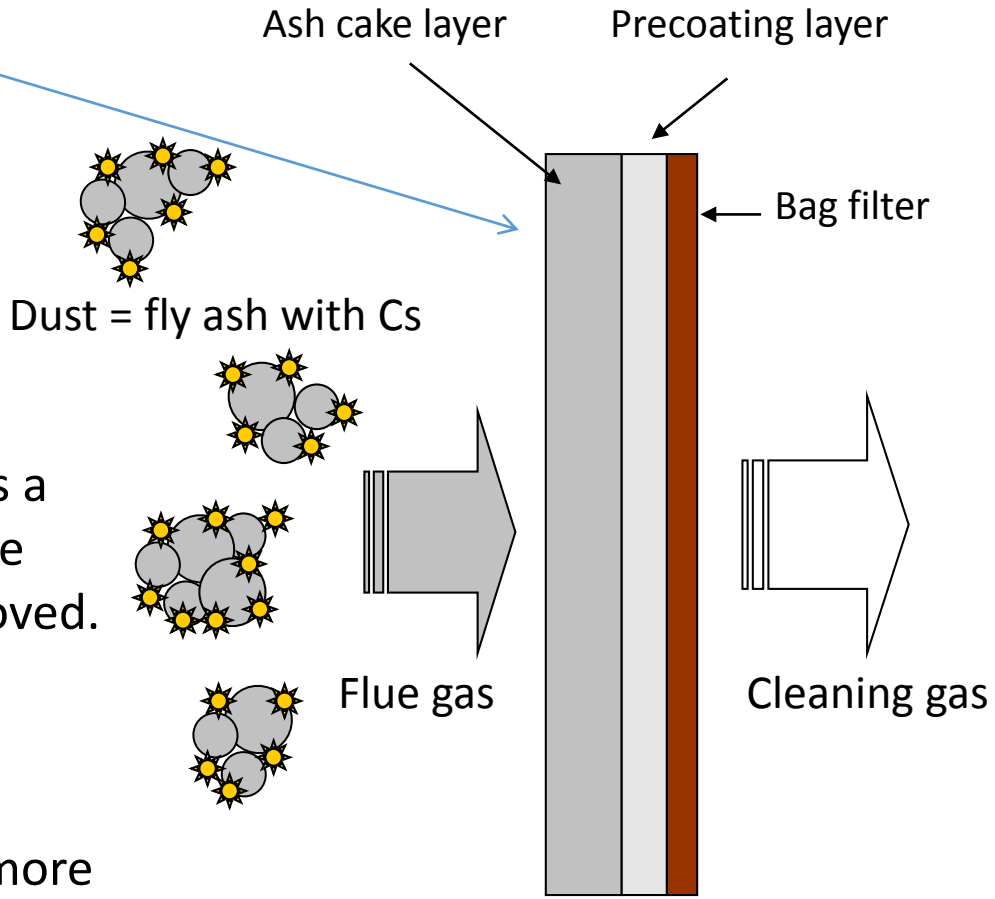
Flow of solid residues

Flow of flue gas

Flow of dust

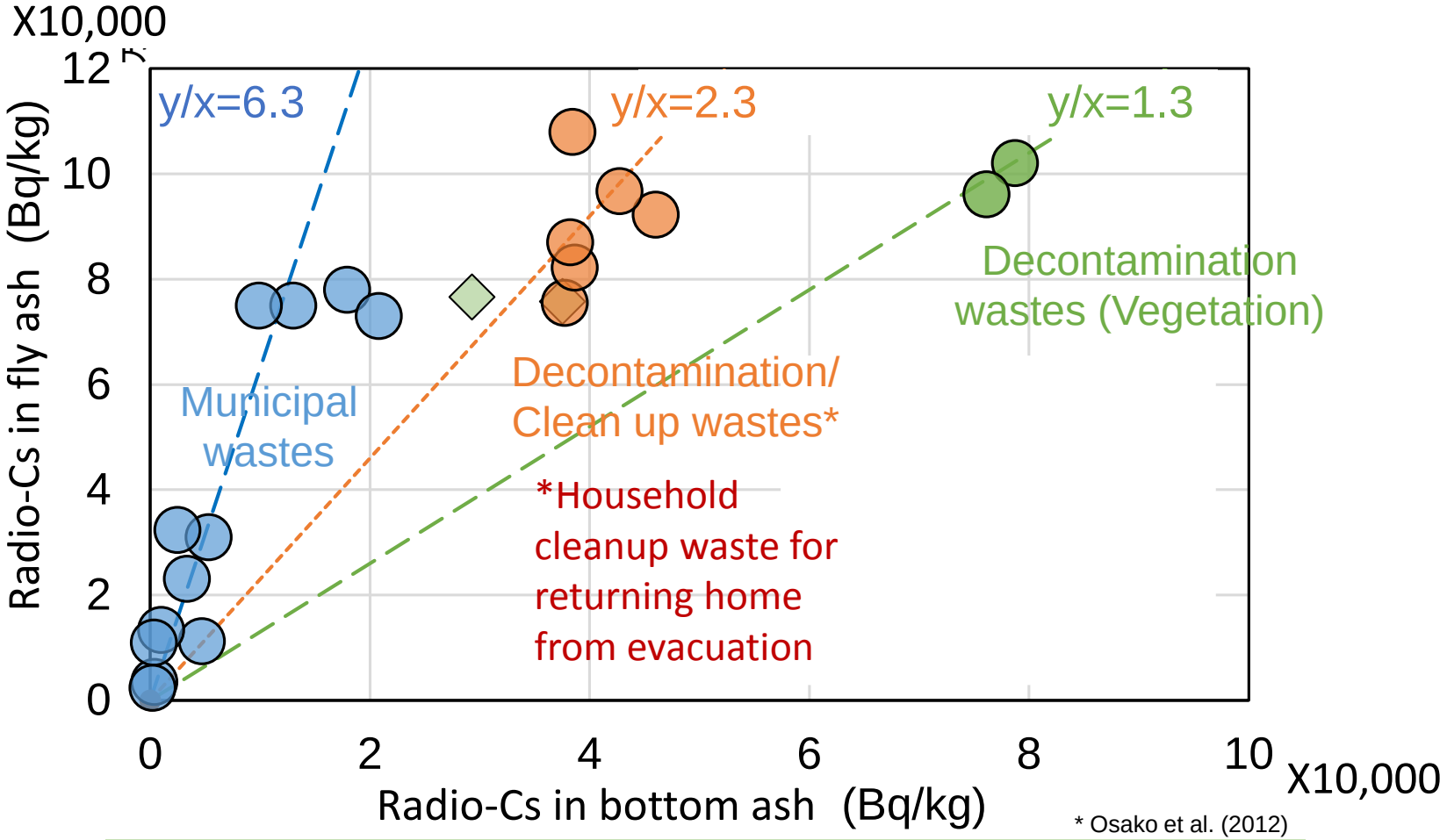
Radio-Cs is removed from flue gas by conventional bag filter

In a baghouse



- ✓ In a baghouse, dusts are removed. As a result, r-Cs chemicals solidified on the dust during gas cooling are also removed.
- ✓ The presence of ash cake layer and precoating layer enables bag filter to remove finer dusts in the efficiency more than 99.9%.

Distribution of radio-Cs between bottom and fly ashes

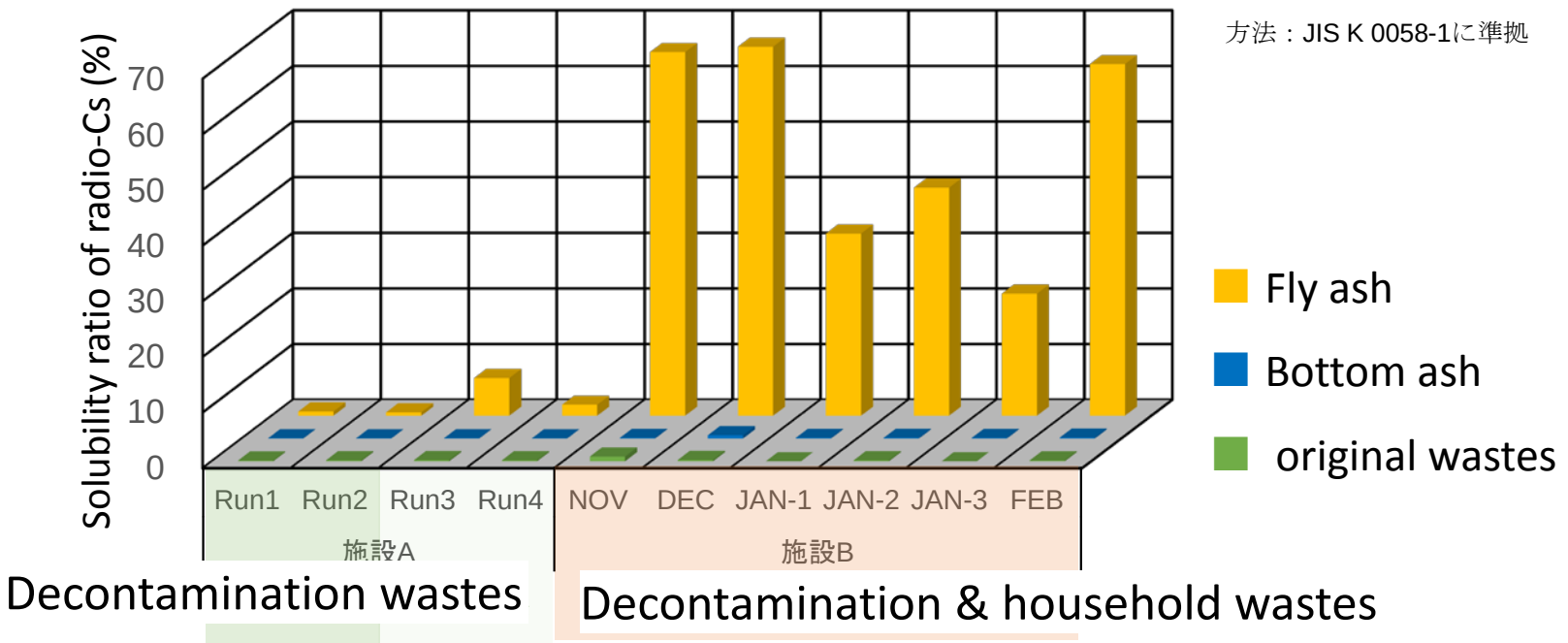


* Osako et al. (2012)

- In municipal wastes incineration, concentration in fly ash is 6 times more than bottom ash.
- In decontamination wastes, 1.3 times.
- In mixing with clean-up wastes, 2.3 times.

Fujiwara, Kuramochi, et al., 第27回廃棄物資源循環学会研究発表会2016

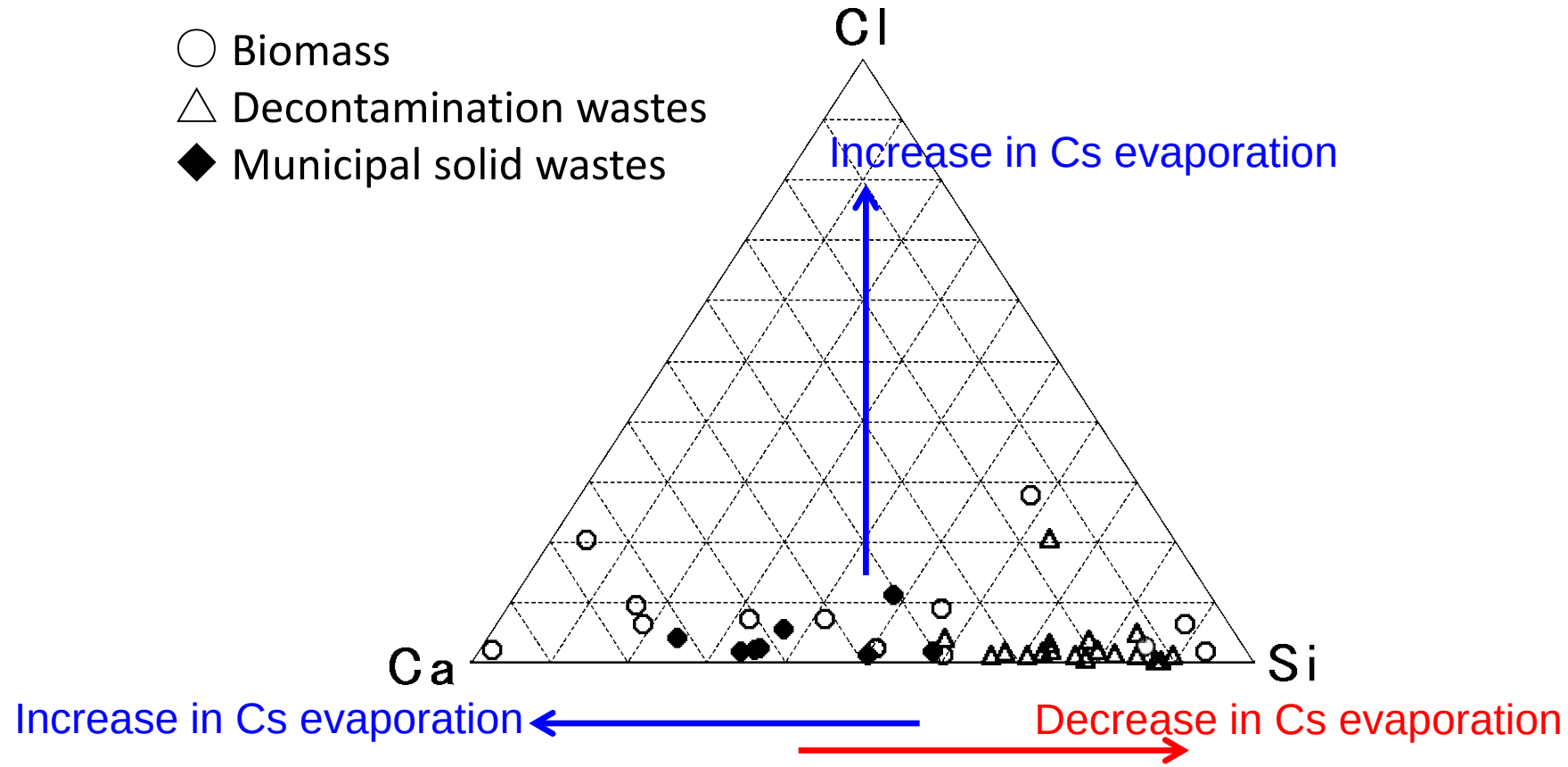
Dissolution ratio of radio-Cs



- Almost no leaching from original wastes and bottom ash.
- Solubility from fly ash is very low less than 1% when decontamination wastes are incinerated.
- Solubility is intermediate and varied (22 – 66%) when household wastes are mixed and incinerated.
- Solubility of municipal solid wastes fly ash is high (40 - 100%).

Fujiwara, Kuramochi, et al., 第27回廃棄物資源循環学会研究発表会2016

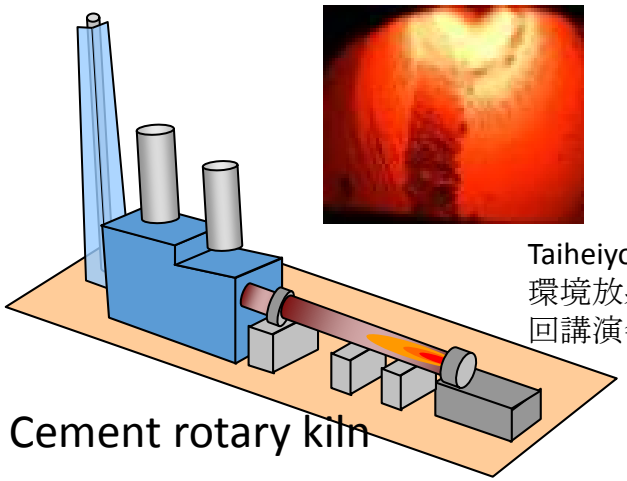
Effects of major elements for Cs evaporation



- Based on experiments, high concentration in Cl and Ca results in high evaporation, high concentration in Si results in low evaporation.
- Decontamination wastes (containing soil) is rich in Si and radio-Cs is expected not to evaporate and remained in bottom ash.

Calcination and melting

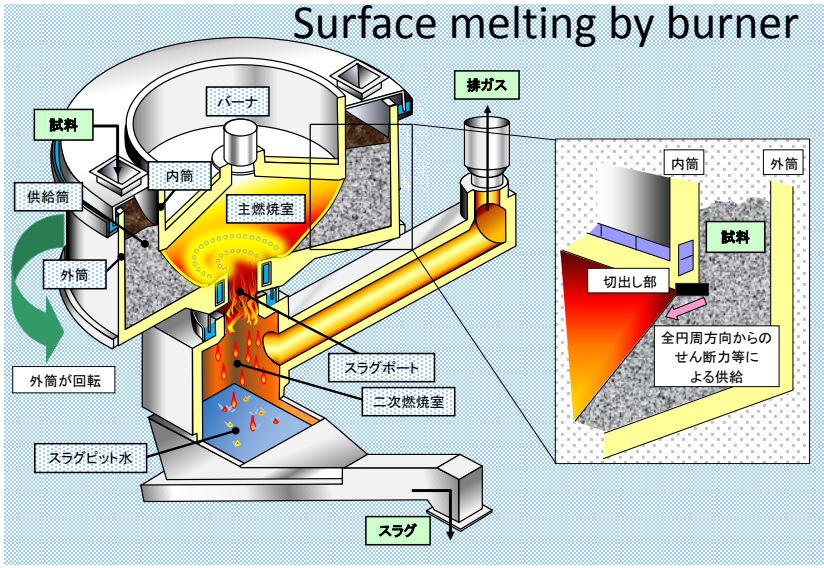
- Higher temperature around 1300-1500 ºC than incineration around 800-900ºC.
- Target chemical composition
  - ✓ Calcination: Clinkering by liquid phase generation to form calcination aggregate or cement.
  - ✓ Melting: Total melting (Upper limit for CaO)
- In both methods, multi-valence cation and chloride are added to accelerate sublimation of Cs as water soluble CsCl.
- Already used in markets and plenty of know-how for operation.
- Material and energy costs are limited except radiation exposure control.



Cement rotary kiln

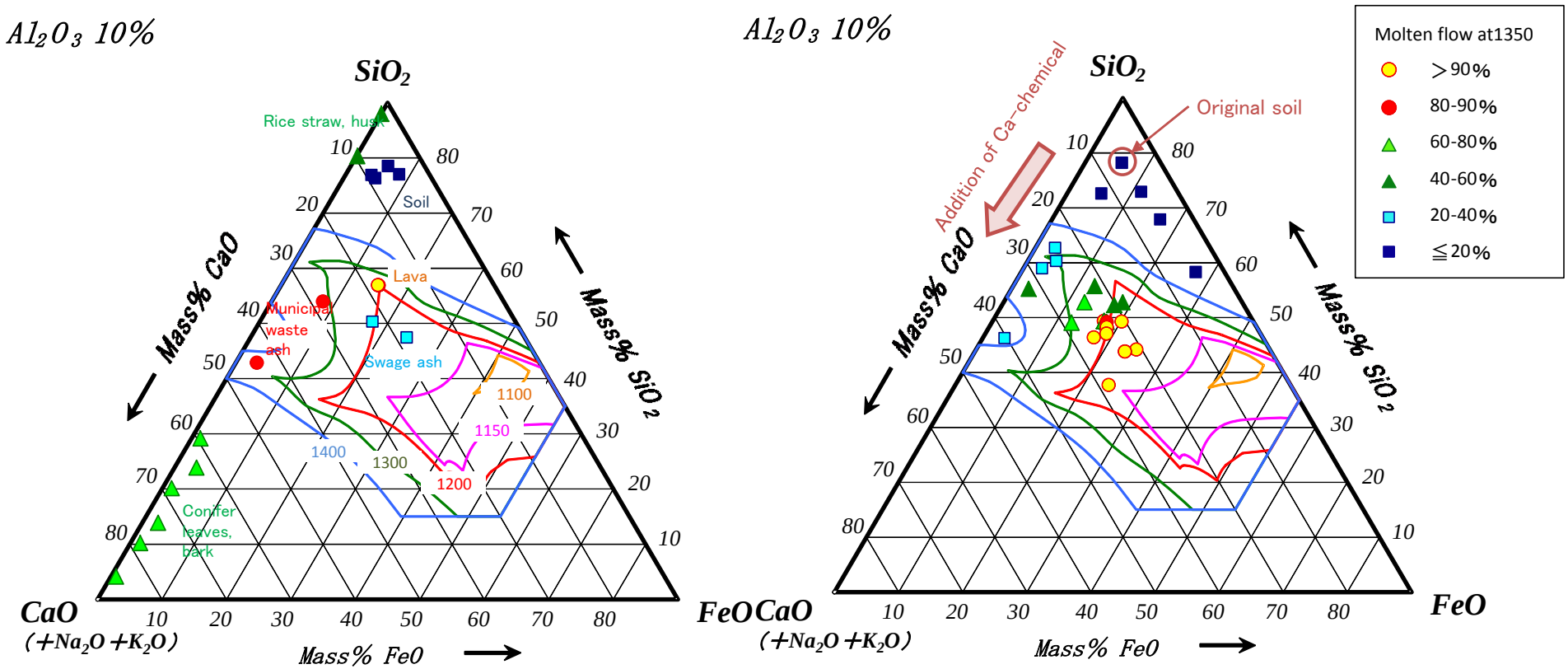
Taiheiyo Cement et al., 2016
環境放射能除染学会第11回講演会

Y. Kamata (Kubota Corp.), 2016、環境放射能除染学会　第11回講演会



Melting range

SiO_2－CaO－FeO phase diagram ［Al_2O_3 10%］

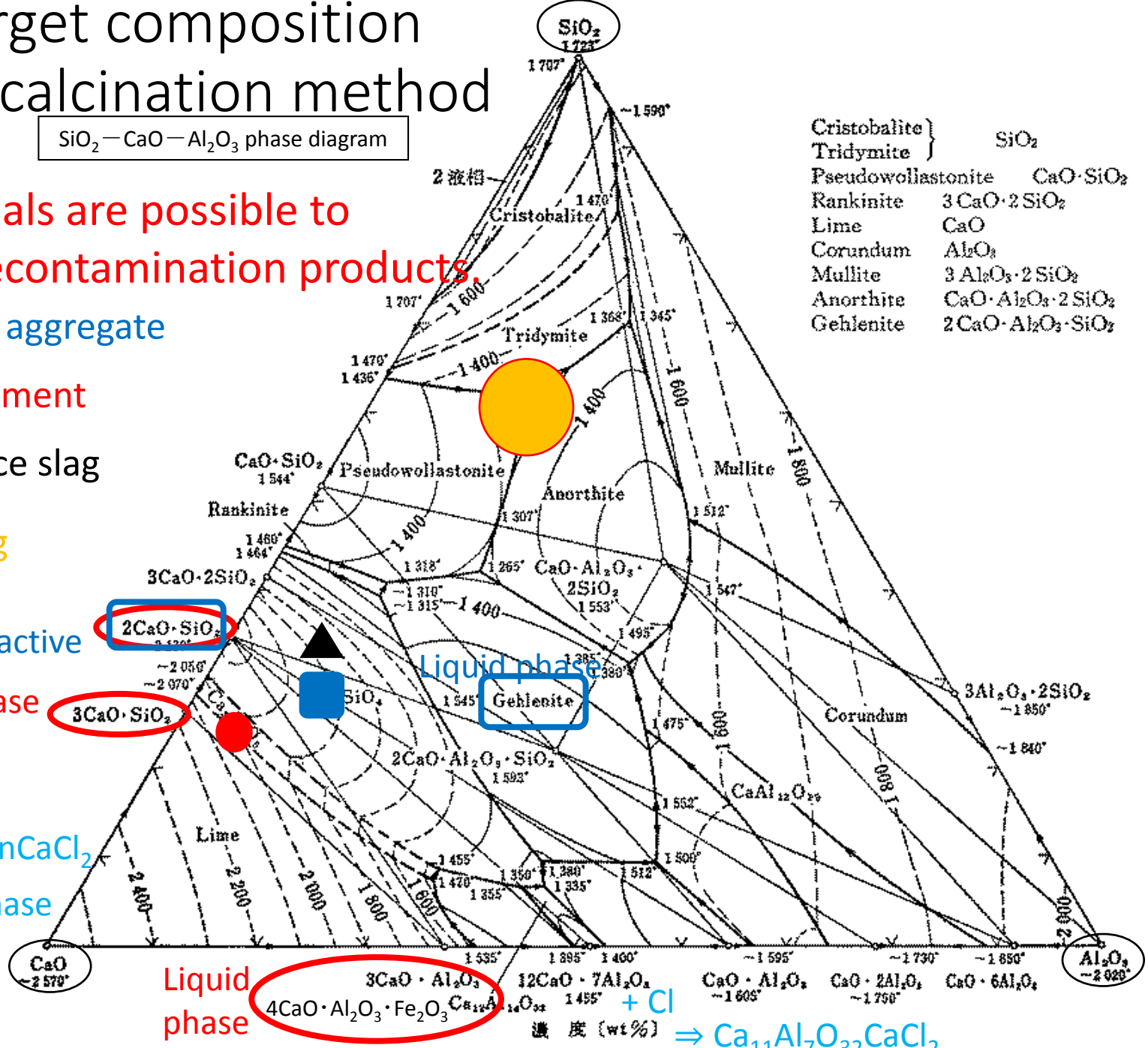


- By adjusting chemical composition of various waste, melting process becomes possible.

Y. Kamata (Kubota Corp.), 2016、環境放射能除染学会　第11回講演会

Target composition of calcination method

SiO_2—CaO—Al_2O_3 phase diagram



Various materials are possible to generate as decontamination products.

- Calcination aggregate
- Portland cement
- Blast furnace slag
- Ash melting

Less reactive

Main reaction phase

+ Cl

↓

$Ca_{3-x}SiO_5nCaCl_2$

Typical chloride phase in the system of SiO_2-Al_2O_3-CaO

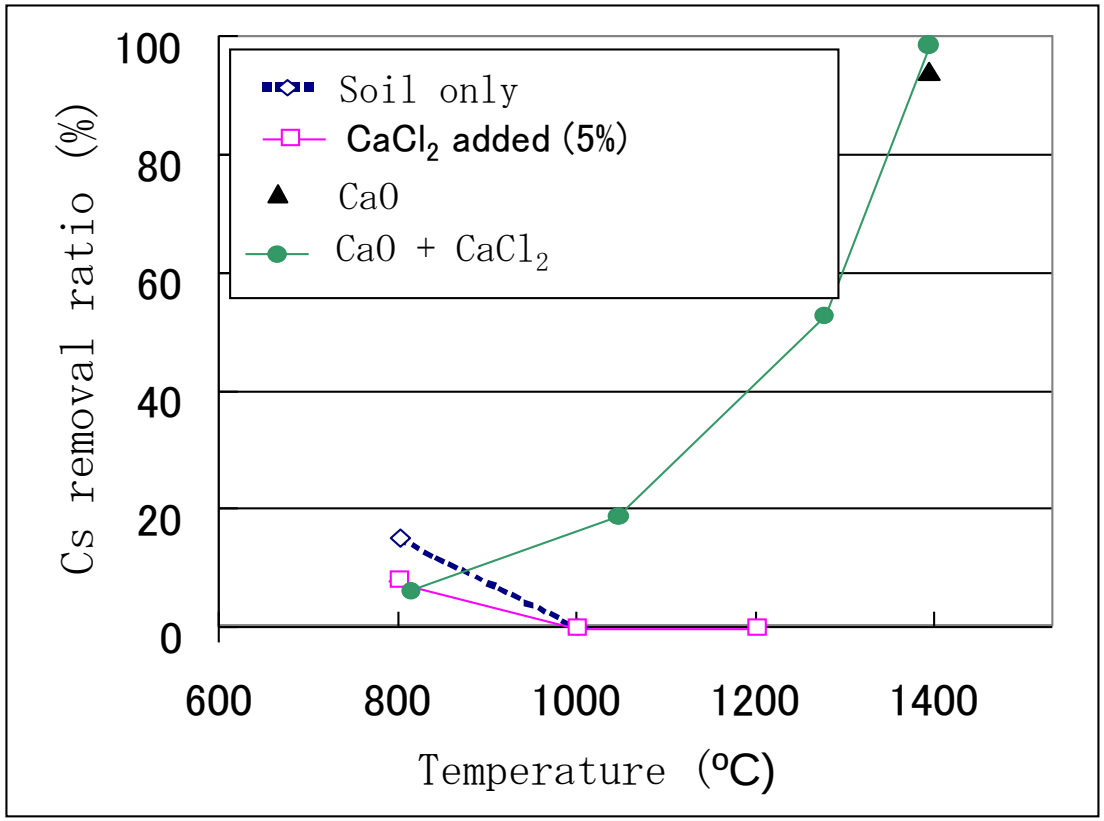
Liquid phase

Liquid phase

+ Cl

⇒ $Ca_{11}Al_7O_{32}CaCl_2$

Cs removing behaviors by lab tests (stable Cs)



- CaO is added to obtain the chemical composition forming aggregate results in easing Cs to evaporate from clay minerals or other alumino-silicate.
- $CaCl_2$ is added to evaporate Cs as chloride.

Soil only
Chloride addition
→ Unable to remove Cs

With the addition of CaO ($CaCO_3$)
→ Able to remove Cs

→ CaO is indispensable to remove Cs

Taiheiyo Cement et al., 2016　環境放射能除染学会第11回講演会

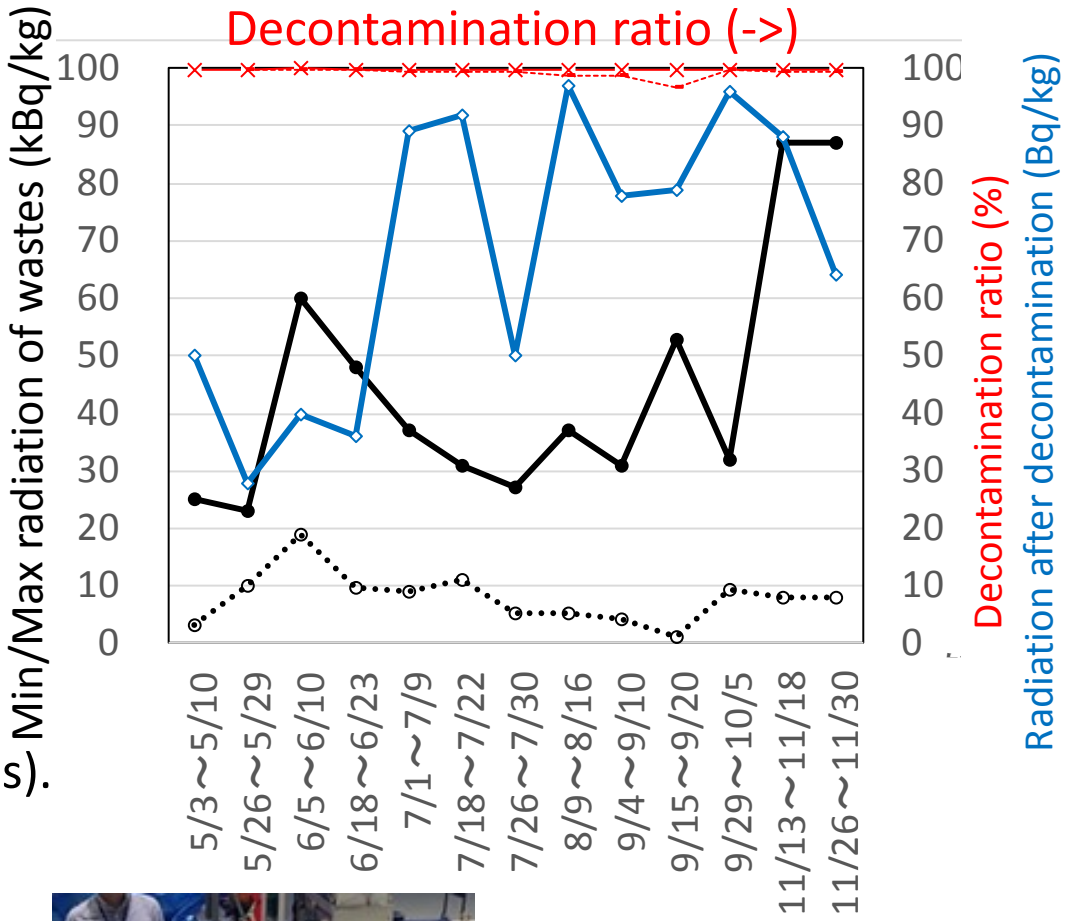
Verification

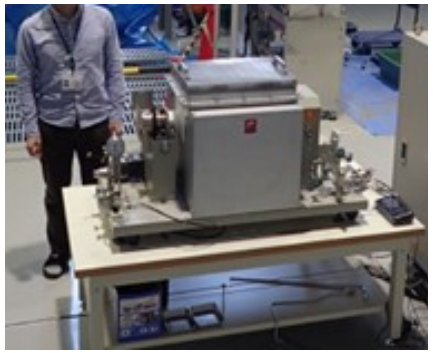
- For burned aggregate producing, in a pilot plant in Warabidaira, stable clearance level has been achieved (real contaminated wastes).

  https://shiteihaiki.env.go.jp/initiatives_fukushima/waste_disposal/iitate/materials_warabidaira.html

- Volume of wastes reduce in 1/20.

- For cement producing, small rotating furnace in Fukushima branch and pilot rotary kiln have been used and decontamination in clearance level were confirmed.





Fukushima branch, NIES

Collaboration among NIES-JIRCA-Taiheiyo Cement

Basic mechanism of Cs evaporation by heating

- Radio-Cs is trapped firmly in clay minerals and insoluble.
- During heating or incineration, some Cs moves into alumino-silicate mineral or glass.
- Ca makes Cs movable from clay or alumino-silicates.
- Cl assists Cs to sublimate or evaporate.
- Only addition of Ca cannot be a solution of Cs evaporation because Cs oxide is stable.
- Only addition of Cl is insufficient because alkali chloride can be dissolved in alumino-silicate phases.
- Simultaneous addition of Ca and Cl is indispensable.
- There are many Ca silicate having different cation contents and more amount of Ca is beneficial for higher efficiency of Cs evaporation. Cement system is ideal for Cs removal.
- Evaporation of Cs is competing reaction making chloride with K and Na. Therefore, sufficient amount Cl is required for higher evaporation ratio even tendency of evaporation is in the order of Cs>K>Na.
- Almost every Cl moves to fly ash.

Discussion & Summary

- Importance of volume reduction-reuse is introduced.
- Among various technologies, 3 ways of heat treatment are introduced.
- By the experiences in incineration of combustible wastes, it has been understood that the distribution between bottom and fly ashes and the solubility of Cs depends on the type of wastes.
- Higher decontamination efficiency is achieved by calcination and melting having similar removing mechanism, chloride evaporation.
- Further problems:
  - There are no established way of final disposal of Cs in the form of soluble salt with high concentration of KCl that reduces absorbing ability of Cs by clay or zeolite.
  - Heat treatment changes Cs to water-soluble form and reduces the volume but makes radiation doze rate significantly higher.
  - 40,000m^3 seems not enough for final disposal.
  - As Cs is water-soluble, it is possible to propose a highly efficient volume-reducing method using ferro-cyanide and the final volume will be 100m^3.