5th International Conference on Sustainable Solid Waste Management
～ *ATHENS 2017* ～

## Session XXⅢ : Characterization of Waste Residues

# *Individual and inter-particle heterogeneity analysis of the surface and inner matrices of chelate-treated MSWI fly ash particles employing water extraction*

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# Introduction

## Municipal solid waste (MSW) management in Japan

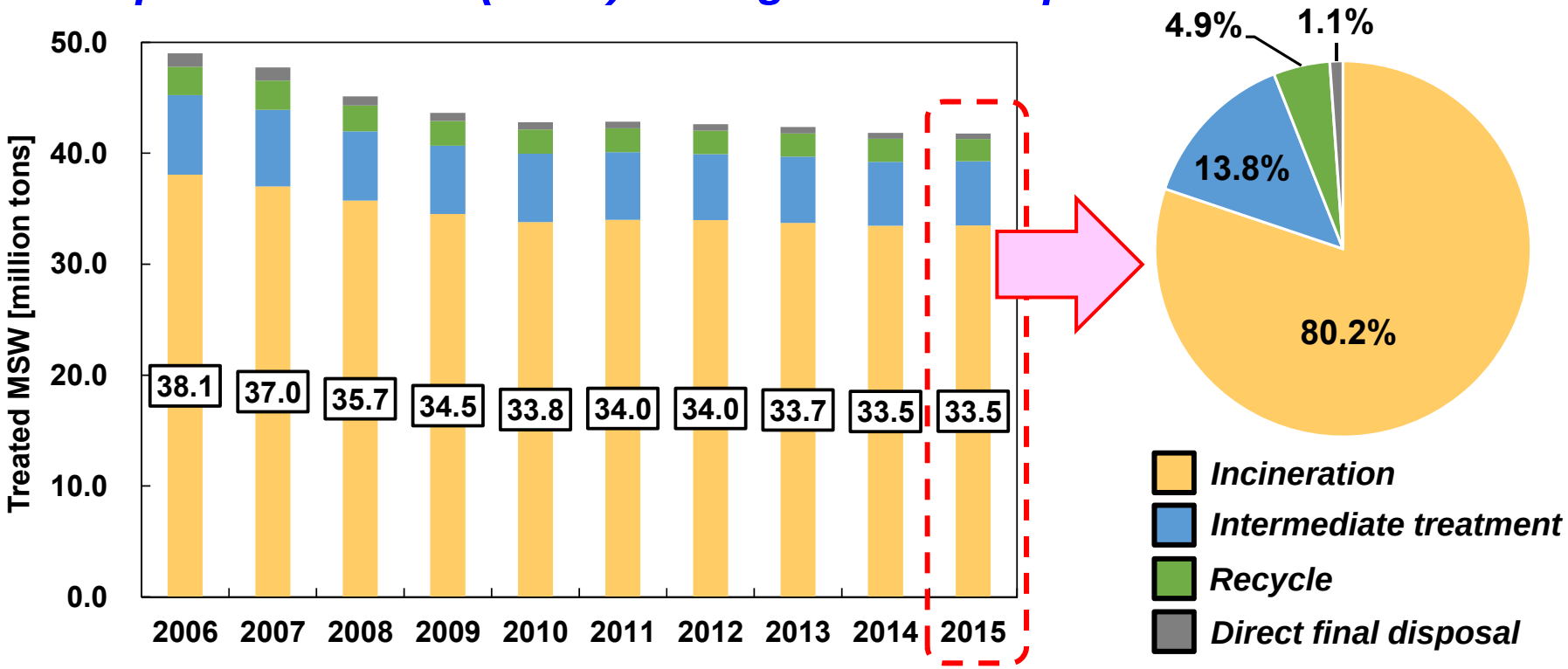



*Fig.1 MSW management method in Japan* [1)]

***Incineration is a main treatment method for MSW.***

1) *Ministry of the Environment, Japan, 2017. Annual report of waste management in Japan ("Nihon no Haikibutsu Shori")* (in Japanese)

# Introduction

## Municipal solid waste incineration (MSWI) residues

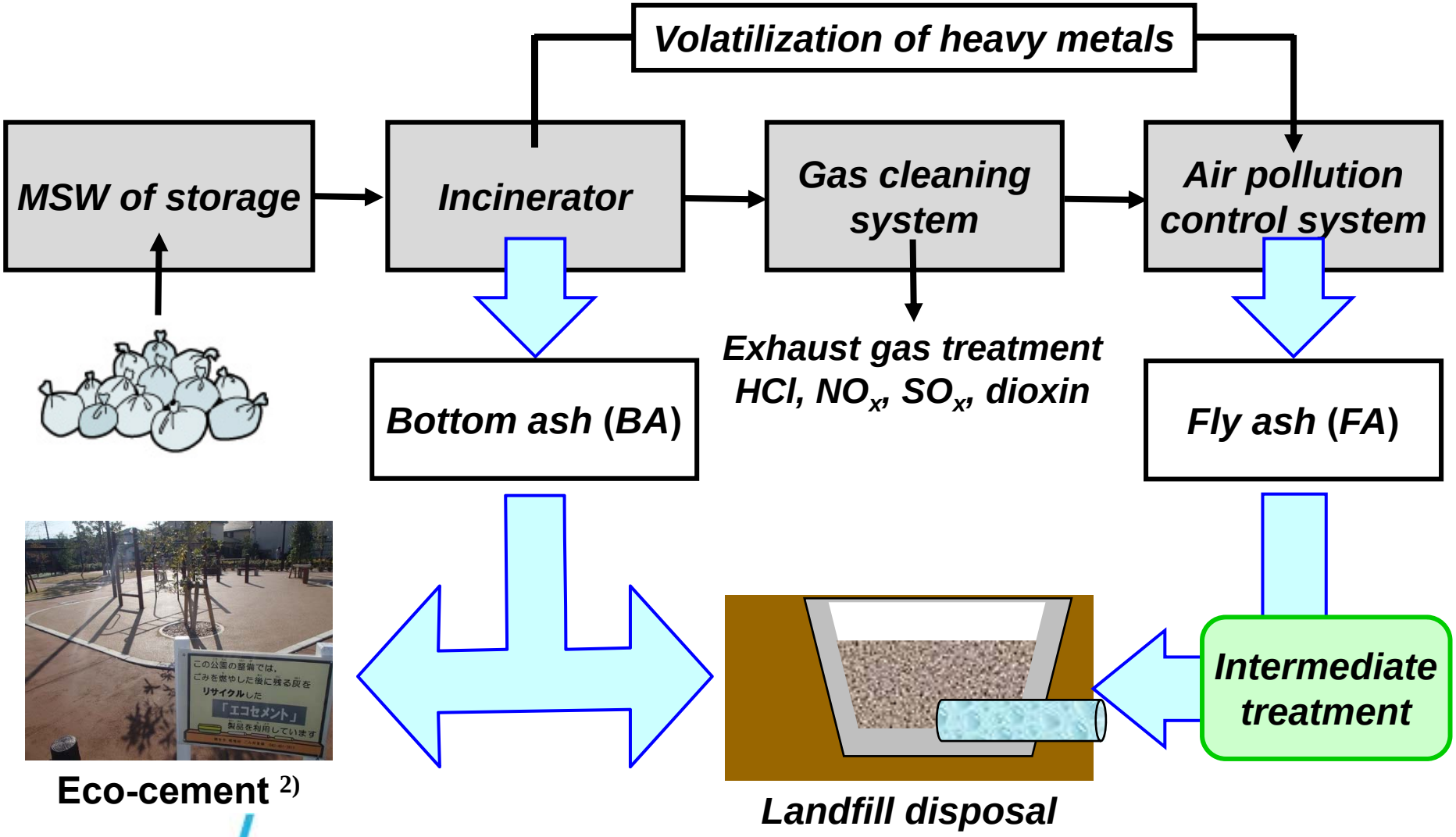



*Fig.2 Flowchart of MSWI process*

2) Chofu city, Eco-cement project (accessed April 1st, 2017, in Japanese)
http://www.city.chofu.tokyo.jp/www/contents/1391998933307/index.html

# Introduction

3) Sakanakura *et al.*, 2007. *Environ. Sci. Technol.* 41, 1717-1722.
4) Kitamura *et al.*, 2016. *Environ. Sci. Pollut. Res.* 23, 734-743.

## Regulatory treatments of MSWI FA before landfill disposal

- **Cement solidification**
- **Melting solidification**
- **Chemical treatment**
- **Acid extraction**

・*Chelate treatment for metal immobilization*

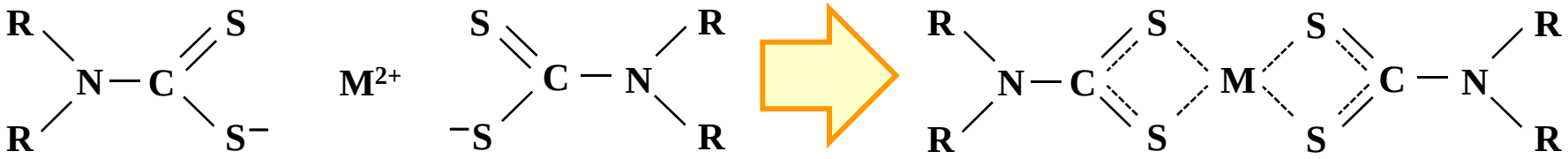



*Fig.3 Main immobilization mechanism of chelate treatment* [3)]

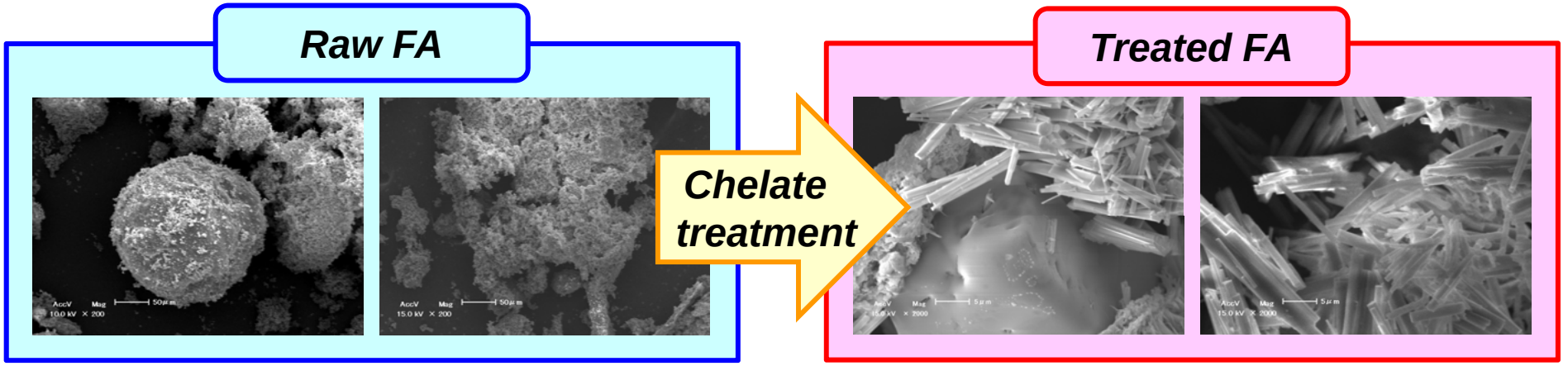
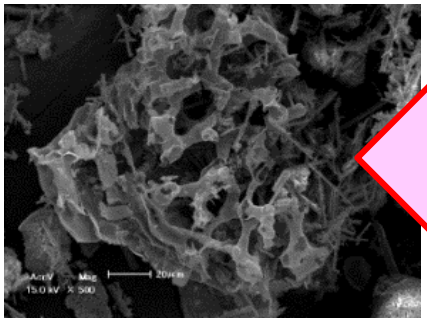



*Fig.4 Mineralogical characteristics of MSWI fly ash before and after chelate treatment* [4)]

# Introduction

## Inner structures of MSWI FA particle

***MSWI FA is considered as homogeneous owing to fine particles.***



*Si-based*
*Complicated structure*

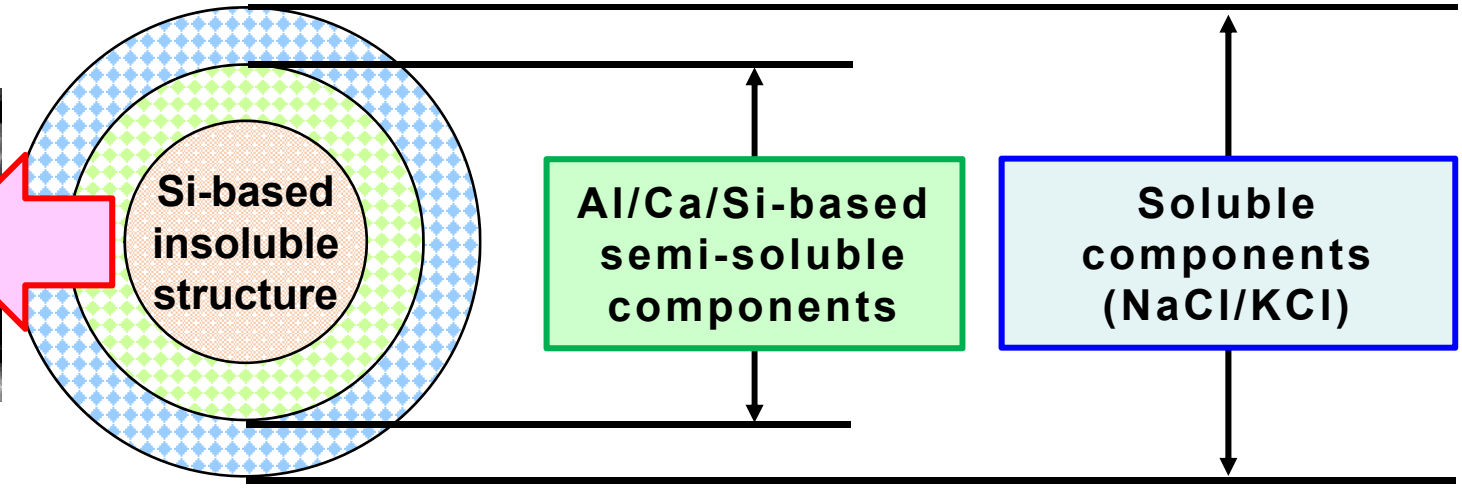



*Fig.5 Component model of a MSWI fly ash particle* [4)]

***"Homogeneous" or "Heterogeneous" ?***

***How much the impact on leaching behaviors of heavy metals?***

**Study objective**

***To investigate intra/inter-particle heterogeneity of the surface / inner matrices for chelate-treated MSWI fly ash.***

4) Kitamura *et al.*, 2016. *Environ. Sci. Pollut. Res.* 23, 734-743.

# Experimental methods

## Experimental samples

- **Chelate-treated MSWI FA (from a stoker combustor in Japan)**

→ Water extraction (Japan leaching test 46th : JLT46)

→ Shaking mixture of pure water / FA (L/S=10) at 200 rpm for 6 hours

- **Residual materials after JLT46**

## Mineralogical analysis

- **Mineralogical characteristics : XRD (MultiFlex, Rigaku)**

## Microscopic observation

- **Morphological characteristics : SEM (JSM-6610LA, JEOL Ltd.)**
- **Elemental compositions and distributions : EDX (EX-94300S4L1Q, JEOL Ltd.)**

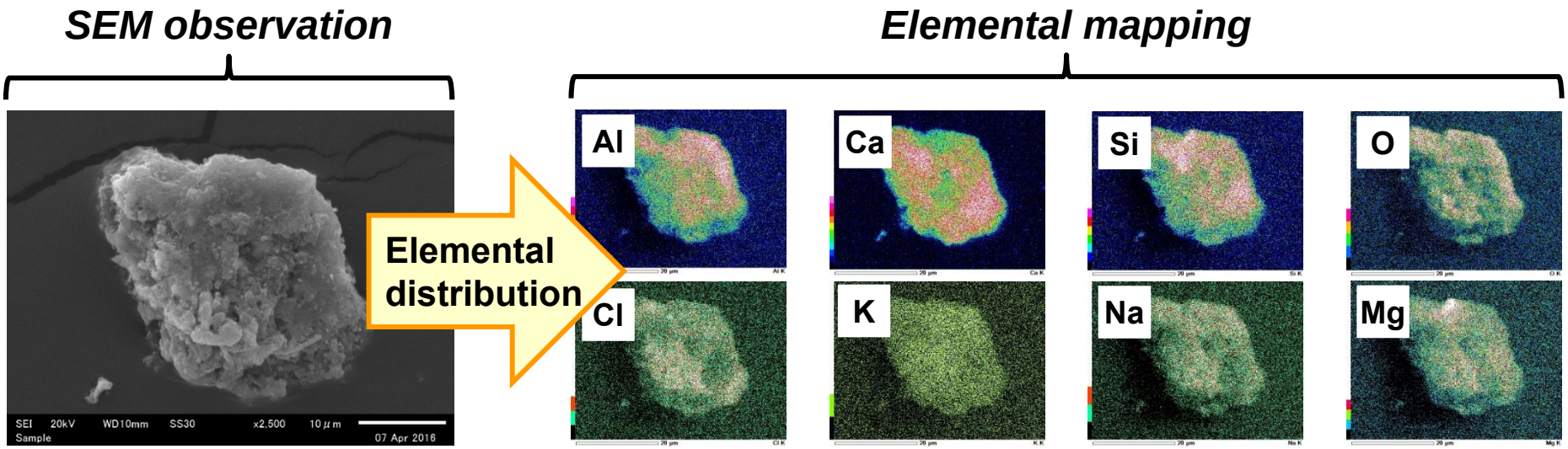



*Fig.6 SME images and elemental mapping by SEM-EDX*

# Experimental methods

## "Intra-particle heterogeneity" analysis conducted by line profile

*Heterogeneity inside each FA particles*

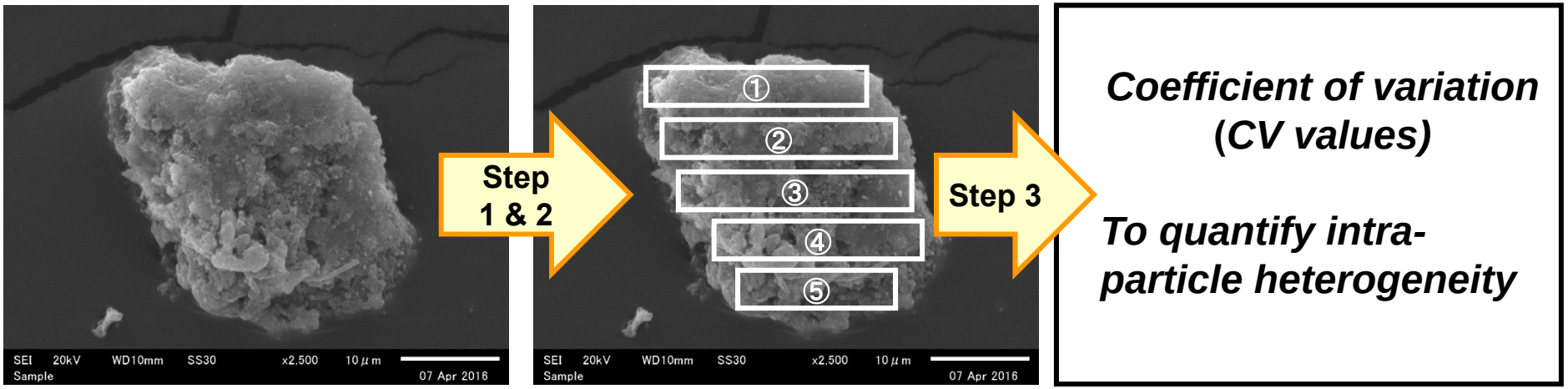



*Fig.7 The dividing method of one fly ash particle for line profile analysis*

1. *One FA particle is divided to 5 sections horizontally.*

2. *Relative intensity of major elements are measured by "line profile analysis".*

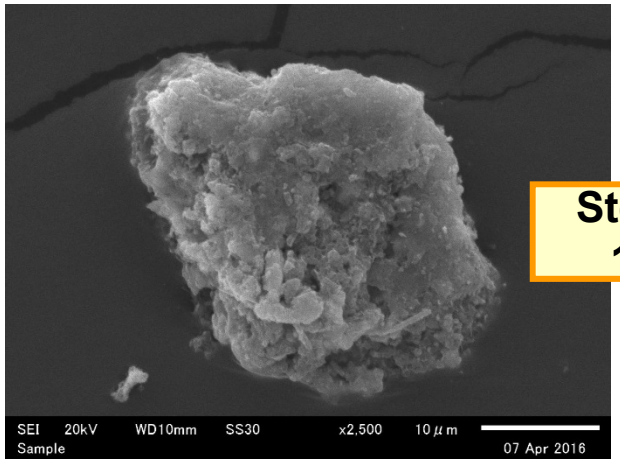
3. *CV values are calculated based on relative intensity data.*
   *They are defined as indicator to quantify intra-particle heterogeneity.*

$$CV = \frac{\sigma(Standard\ deviation)}{\mu(Mean\ value)}$$

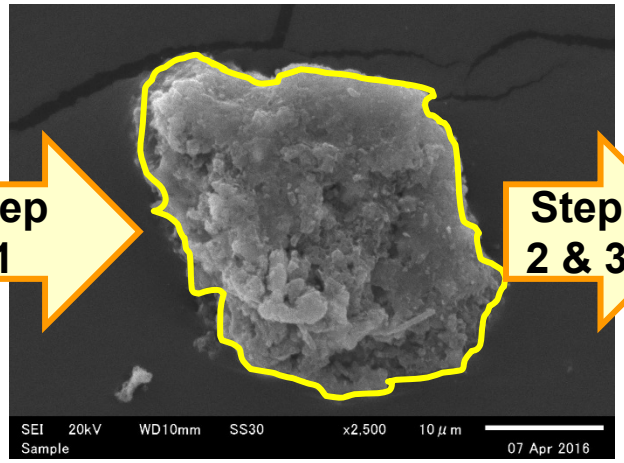
# Experimental methods

## *"Inter-particle heterogeneity" analysis conducted by area analysis*

*Heterogeneity among FA particles*




Step 1




Step 2 & 3

| Al | Ca | Si | O |
|---|---|---|---|
| 9.57 | 31.59 | 9.98 | 38.19 |
| **Cl** | **K** | **Na** | **Mg** |
| 3.22 | 1.51 | 2.40 | 3.54 |

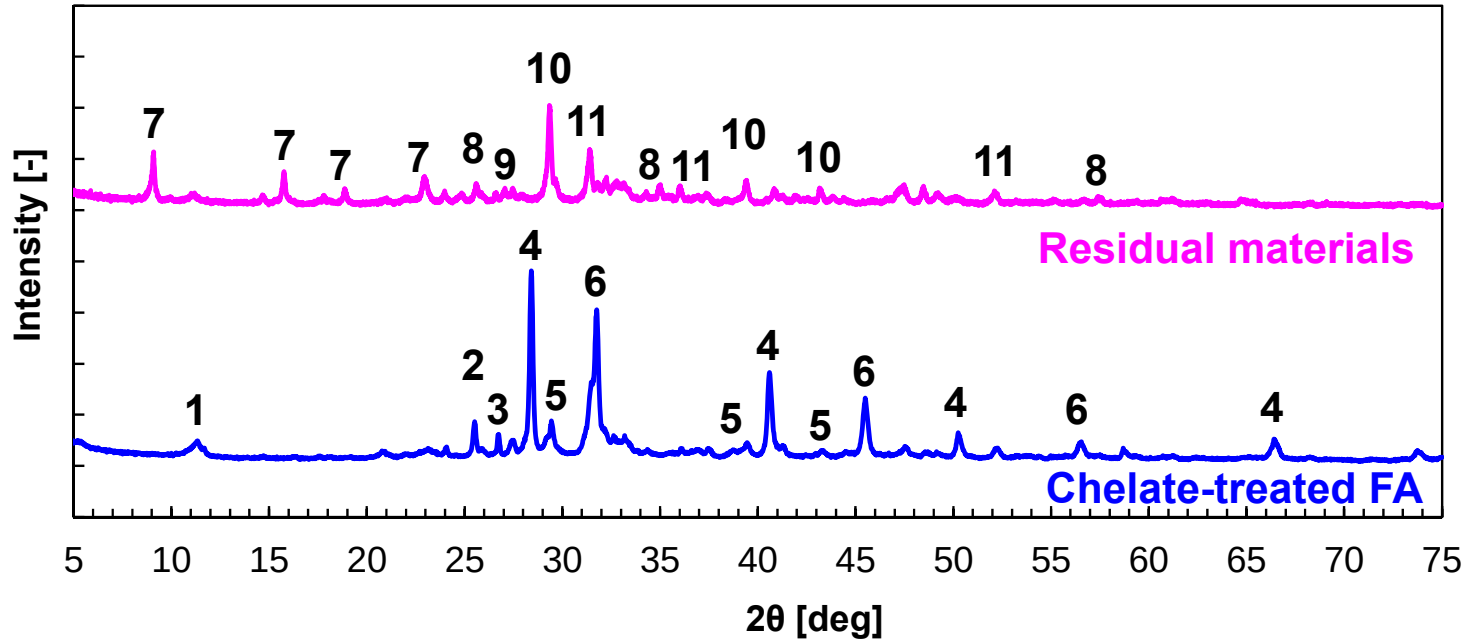
**[ weigh percent (wt%)]**

*Fig.8 Area analysis for measurement of weigh percent [wt%]*

1. ***Weight percent [wt%] of particle surfaces are measured by "area analysis".***
2. ***The weight percent data are plotted in histogram.***
3. ***Spread of histogram distribution is defined as indicator to quantify inter-particle heterogeneity.***

# Results and discussion

## Mineral compositions of chelate-treated MSWI FA and residual materials




**Chelate-treated MSWI FA**

1 : Gypsum ($CaSO_4 \cdot 2H_2O$)
2 : Anhydrite ($CaSO_4$)
3 : Quartz ($SiO_2$)
4 : Sylvite (KCl)
5 : Calcite ($CaCO_3$)
6 : Halite (NaCl)

**Residual materials after JLT46**

7 : Ettringite
$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$
8 : Corundum ($Al_2O_3$)
9 : Quartz ($SiO_2$)
10 : Calcite ($CaCO_3$)
11 : Gehlenite ($Ca_2Al_2SiO_7$)

*Fig.9 Mineral compositions of chelate-treated MSWI fly ash and residual materials after JLT46*

# Results and discussion

## Intra-particle heterogeneity of chelate-treated FA / residual materials

### Heterogeneity inside each FA particles

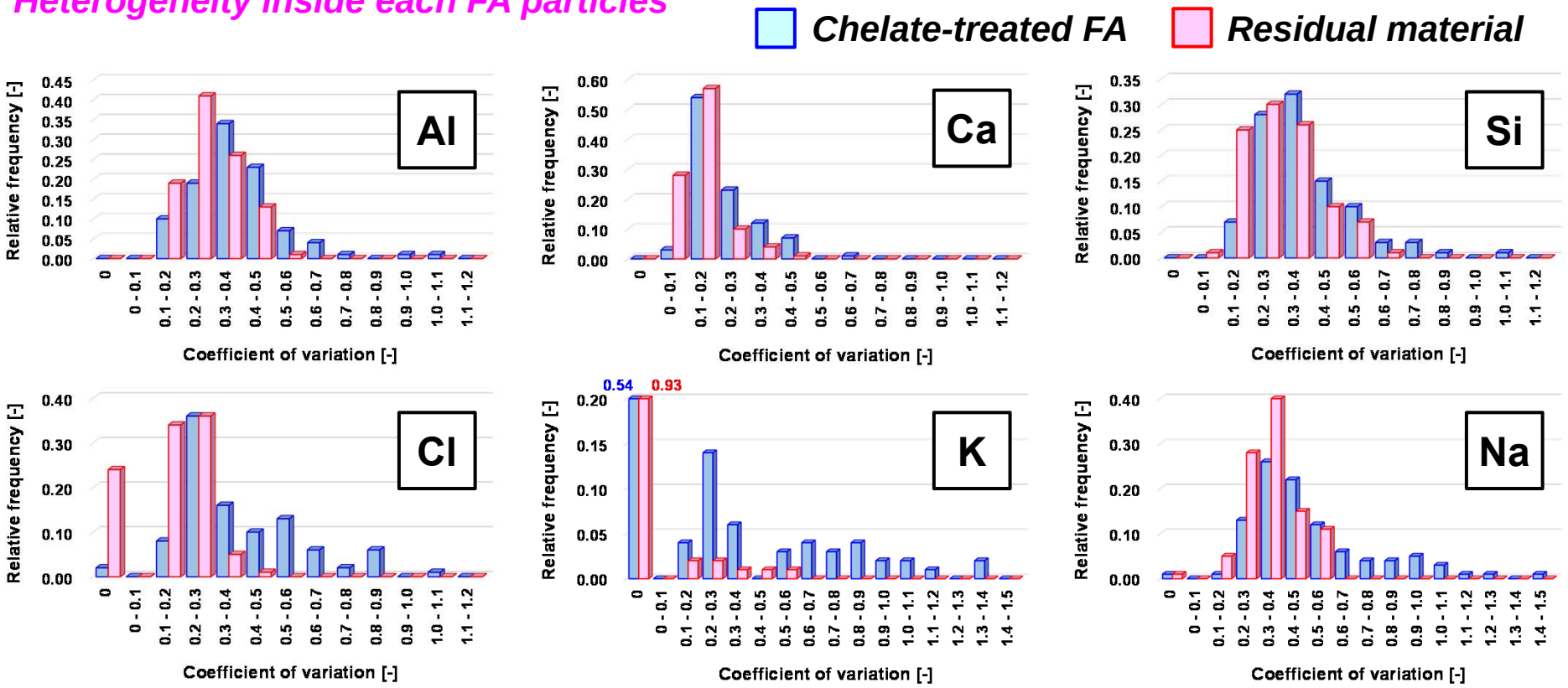



*Fig.10 CV values of major elements for chelate-treated MSWI fly ash and residual materials after JLT46*

- *MSWI FA seems to be heterogeneous inside each FA particles.*
- *Soluble components (Cl, K, Na) seem to be more heterogeneous.*
- *Ca is the most slightly heterogeneous inside each FA particles.*

# Results and discussion

## Intra-particle heterogeneity of chelate-treated FA / residual materials

5) Zhu *et al.*, 2008. *Environ. Sci. Technol.* 42, 3932-3937.

**Table 1 Correlation matrix of CV values for chelate-treated MSWI FA**

| Element | Correlation coefficient | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | O | Na | Mg | Al | Si | S | Cl | K | Ca |
| O | 1.00 | | | | | | | | |
| Na | 0.63 | 1.00 | | | | | | | |
| Mg | 0.23 | 0.12 | 1.00 | | | | | | |
| Al | 0.73 | 0.57 | 0.11 | 1.00 | | | | | |
| Si | 0.72 | 0.65 | 0.24 | 0.74 | 1.00 | | | | |
| S | 0.23 | 0.38 | 0.14 | 0.32 | 0.42 | 1.00 | | | |
| Cl | 0.39 | **0.74** | 0.06 | 0.50 | 0.55 | 0.36 | 1.00 | | |
| K | 0.29 | 0.54 | 0.11 | 0.32 | 0.45 | 0.28 | **0.61** | 1.00 | |
| Ca | 0.51 | 0.59 | 0.17 | 0.69 | 0.64 | 0.27 | **0.64** | 0.54 | 1.00 |

*Soluble components such as $CaCl_2$, KCl, NaCl* [5] *on the particle surface*

**Table 2 Correlation matrix of CV values for residual materials after JLT46**

| Element | Correlation coefficient | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | O | Na | Mg | Al | Si | S | Cl | K | Ca |
| O | 1.00 | | | | | | | | |
| Na | 0.81 | 1.00 | | | | | | | |
| Mg | 0.54 | 0.68 | 1.00 | | | | | | |
| Al | 0.56 | 0.66 | 0.51 | 1.00 | | | | | |
| Si | 0.54 | 0.65 | 0.63 | 0.60 | 1.00 | | | | |
| S | 0.32 | 0.41 | 0.36 | 0.40 | 0.43 | 1.00 | | | |
| Cl | 0.18 | **0.36** | 0.36 | 0.28 | 0.38 | 0.51 | 1.00 | | |
| K | -0.01 | 0.07 | 0.12 | 0.16 | 0.20 | 0.19 | **0.18** | 1.00 | |
| Ca | 0.29 | 0.37 | 0.38 | 0.33 | 0.38 | 0.26 | **0.29** | 0.42 | 1.00 |

*Semi-soluble components in inner matrices ?*

# Results and discussion

## Intra-particle heterogeneity of chelate-treated FA / residual materials

6) Eighmy *et al.*, 1995. *Environ. Sci. Technol.* 29, 629-646.

**Table 1 Correlation matrix of CV values for chelate-treated MSWI FA**

| Element | Correlation coefficient | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | O | Na | Mg | Al | Si | S | Cl | K | Ca |
| O | 1.00 | | | | | | | | |
| Na | **0.63** | 1.00 | | | | | | | |
| Mg | 0.23 | 0.12 | 1.00 | | | | | | |
| Al | **0.73** | **0.57** | 0.11 | 1.00 | | | | | |
| Si | **0.72** | **0.65** | 0.24 | **0.74** | 1.00 | | | | |
| S | 0.23 | 0.38 | 0.14 | 0.32 | 0.42 | 1.00 | | | |
| Cl | 0.39 | 0.74 | 0.06 | 0.50 | 0.55 | 0.36 | 1.00 | | |
| K | 0.29 | 0.54 | 0.11 | 0.32 | 0.45 | 0.28 | 0.61 | 1.00 | |
| Ca | **0.51** | 0.59 | 0.17 | **0.69** | **0.64** | 0.27 | 0.64 | 0.54 | 1.00 |

*Calcium aluminosilicate* [6)]
- *gehlenite* ($Ca_2Al_2SiO_7$)
- *corundum* ($Al_2O_3$)
- *quartz* ($SiO_2$)

**Table 2 Correlation matrix of CV values for residual materials after JLT46**

| Element | Correlation coefficient | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | O | Na | Mg | Al | Si | S | Cl | K | Ca |
| O | 1.00 | | | | | | | | |
| Na | **0.81** | 1.00 | | | | | | | |
| Mg | 0.54 | 0.68 | 1.00 | | | | | | |
| Al | **0.56** | **0.66** | 0.51 | 1.00 | | | | | |
| Si | **0.54** | **0.65** | 0.63 | **0.60** | 1.00 | | | | |
| S | 0.32 | 0.41 | 0.36 | 0.40 | 0.43 | 1.00 | | | |
| Cl | 0.18 | 0.36 | 0.36 | 0.28 | 0.38 | 0.51 | 1.00 | | |
| K | -0.01 | 0.07 | 0.12 | 0.16 | 0.20 | 0.19 | 0.18 | 1.00 | |
| Ca | 0.29 | 0.37 | 0.38 | 0.33 | 0.38 | 0.26 | 0.29 | 0.42 | 1.00 |

*Sodium aluminosilicate* [6)] ($NaAlSi_3O_8$)

# Results and discussion

## Inter-particle heterogeneity of chelate-treated FA / residual materials

### Heterogeneity among FA particles

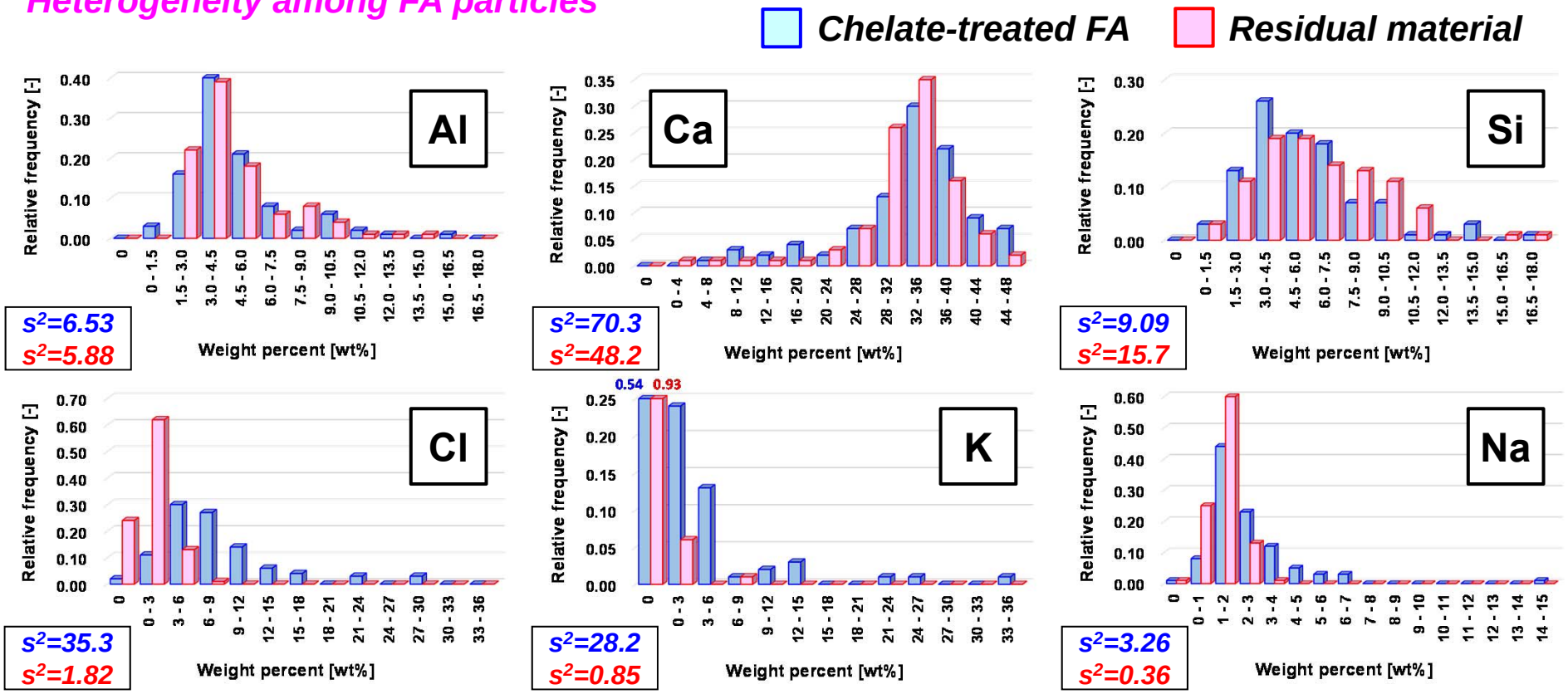



*Fig.11 Weight percent of major elements for chelate-treated MSWI FA and residual materials*

- *MSWI FA seems to be heterogeneous among FA particles.*
- *Ca is the most heterogeneous among FA particles.*

# Conclusion

## 1. Intra-particle heterogeneity

***MSWI FA seems to be heterogeneous at even micro-scale level.***
***Soluble components seem to be more heterogeneous.***
***Ca is the most slightly heterogeneous inside each FA particles.***

## 2. Inter-particle heterogeneity

***MSWI FA seems to be heterogeneous among FA particles.***
***Ca is the most heterogeneous characteristics among FA particles.***

## Future Work

***To investigate the impacts of heterogeneity on leaching behaviors of heavy metals using by geochemical modelling, etc.***

# Thank you for your kind attention!