

## INFLUENCE OF WEATHERING OF BOTTOM ASH ON THE LEACHING BEHAVIOR OF CESIUM

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**ABSTRACT:** After nuclear accident in 2011, incineration residue contaminated by radioactive cesium had been produced. Government decided in 2011 that incineration residue with less than 8000 Bq/kg of radioactivity could be disposed of into conventional MSW landfill. Since radioactivity of bottom ash was reported to be low compared with fly ash, it had been disposed of MSW landfill based on the government regulation. However, long-term leaching behavior of cesium contained in bottom ash when being disposed of into landfill was not known. Thus, in this study, phase transformation and leaching of cesium from incineration bottom ash were investigated by conducting accelerating weathering experiment. Four kinds of weathering condition were set; namely, blank (under nitrogen gas condition), wetting and drying, freezing and thawing, and exposure to carbon dioxide gas. Leaching of cesium under blank condition didn't change. On the other hand, drastic decrease of leaching of cesium was identified under carbon dioxide exposure. From XRD analysis, formation of calcite was identified. It was deemed that newly formed calcite inhibited the leaching of Cs by covering reactive surface of bottom ash. In both wetting-drying and freezing-thawing condition, leaching of Cs increased initially. But it decreased after several weeks then it became lower than blank finally. This decrease of leaching also seems to be caused by formation of calcite. Besides, in order to confirm the assumption in which the restrain of cesium leaching occurred by calcite formation, SEM-EDS analysis was performed. By the analysis, calcite formation on the surface was clearly identified.

*Keywords: Incineration Bottom Ash, Cesium, Leaching, Carbonation, Weathering*

### 1. INTRODUCTION

After the accident of Fukushima-Daiichi nuclear power plant in 2011, municipal solid waste incinerators in east Japan generated ashes containing radioactive cesium (Cs) in high concentration. Government decided that the waste of 8000 Bq/kg or less could be disposed of into MSW landfill as before [1]. Radioactivity of fly ash was very high and special measure is necessary for its disposal. On the other hand, radioactivity of bottom ashes was low and many of them satisfied the government's criteria so that its disposal to MSW landfill has been carried out. National Institute for Environmental Studies was conducted sequential extraction test for various kinds of waste that were contaminated by radioactive cesium. And they reported that water-soluble form of cesium in bottom ash is only about 3% and approximately 80% of cesium existed as residual form (i.e. the last fraction of extraction tests) [2]. Their results indicated that possibility of cesium leaching was low even if the bottom ash was disposed of into ordinary MSW landfill sites. However, it is well known that the incineration residue is unstable substance and its mineral phases are changed by various environmental factors. Especially, leaching behavior of inorganic elements changes by weathering along with

elapsed time. Therefore, it is not certain that Cs keeps being stably captured in the ash for long-term after disposal into MSW landfill. Thus, in this study, the effect of weathering of the bottom ash on the leaching behavior of Cs was investigated in order to confirm their long-term stability in landfill.

### 2. MATERIALS AND METHODS

#### 2.1 Materials

In general, the total cesium content (stable cesium and radioactive cesium) in the incineration bottom ashes discharged from a real incinerator is very small, and moreover the content of radioactive cesium is also very small. For instance, total cesium content, which is comprised of mainly stable-cesium, is reported to be less than several mg/kg [3]. As for the content of radioactive cesium, it is estimated to be several ng/kg based on the specific activity, if radioactivity of the incineration ash is assumed to be thousands Bq/kg. These values imply that chemical analysis of cesium contained in the incineration residue is quite difficult, especially radioactive cesium. So, in this study, artificially created ash, of which stable cesium content was made quite high, was used. The ash was created by adding cesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) to RDF (Refuse-Derived Fuel) and by

incinerating it by pilot-scale stoker-type incinerator of which capacity was 3 tons/day [4]. After combustion, the bottom ash was cooled under ambient temperature. Since, the furnace allows collecting fly ash and bottom ash separately, the bottom ash doesn't contain fly ash.

After creation, 20 kg of the bottom ash was taken to the laboratory. Immediately, the ash was pulverized to less than 0.5 mm by jaw crusher (Retsch, BB-50) to obtain uniform sample. At first, the metal content was measured by aqua-regia digestion and the atomic absorption spectrometry in order to elucidate characteristics of this artificially created bottom ash. Moreover, to determine the amount of soluble cesium, the serial batch leaching test was executed [5]. In the serial batch test, leaching test in L/S (liquid to solid ratio) =10 was repeated five times. Fig. 1 shows the content of Cs, K, Na, and Ca.

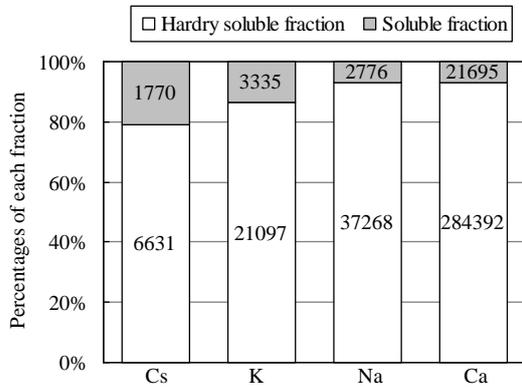


Fig.1 Content of hardly soluble and soluble fraction on Cs, K, Na, and Ca in artificially created bottom ash. Number in the bar shows each content (unit: mg/kg-ash).

In the figure, content of each element is indicated by distinguishing the soluble fraction and hardly soluble fraction. Although these metal contents and the amount of soluble fraction were almost the same with that of general incineration ashes [6], soluble fraction of Cs was 20% and it was higher than the one that had been detected in actual incinerators. Because hardly soluble Cs accounts for the majority of its content in the ash actually generated from the incinerator in East Japan, existence of soluble Cs is undesirable in the examination of a long-term leaching behavior of Cs. Therefore, the ash used for the weathering acceleration experiment was washed in L/S=10 beforehand. Amount of soluble Cs becomes to about 1% in total content after the pretreatment. And it was not below the detection limit. Thus, it was regarded as suitable to pursue the change in the leaching amount.

## 2.2 Methods of Weathering Acceleration

Four different conditions (Blank, Drying and wetting, Freezing-thawing, and CO<sub>2</sub> gas exposure) were established for the weathering experiment.

**Blank:** 10g of pretreated ash samples was put into the 50mL screw bottle. To prevent any reaction and so as not to cause weathering, nitrogen gas was purged into the head space. After capping, it was left sitting at the room temperature. To prevent any reaction as much as possible, nitrogen purge was done once a week. This system was created for the comparison with another three series.

**Drying and wetting:** 10g of the pretreated sample was filled in the small crucible and then the crucible was fixed in a steel tray in which the glass bead was spread. In order to make the sample to the saturated water content, distilled water was added. Then, it was left sitting for 30 minutes. After that, it was heated in the dryer for 1.5 hours at 100°C. This process was repeated three times a day and it was continued for eight weeks. This series was made in order to accelerate physical weathering (i.e. physical collapse of the particle structure of the ash) by repetition of drying and wetting.

**Freezing and thawing:** 10g of the pretreated sample was filled in the small crucible. After adding distilled water to the sample to make its saturated water content, the crucible was capped and it was put in the freezer for 1.5 hours. After that, the frozen sample was heated with the crucible for one hour at 40°C in the dryer, and the sample was thawed. This process was repeated three times a day and it was continued for eight weeks. This series was made in order to accelerate physical weathering (i.e. physical collapse of the particle structure of the ash) according to the expansion and shrinkage of pore water by the freezing and thawing.

**The CO<sub>2</sub> exposure:** 10g of pretreated sample was spread in the steel tray and then distilled water was added to make its water content at the field capacity. The tray with sample was put into the airtight desiccator and CO<sub>2</sub> gas was filled in it. To keep the humidity in the desiccator, steel tray filled with distilled water was placed inside. The moisture content was monitored everyday and readjusted to the field capacity. Besides, CO<sub>2</sub> gas was always kept injected into the inside. This series was made in order to accelerate chemical weathering (i.e. chemical transformation by contacting with CO<sub>2</sub>). This is because the major weathering reaction occurring in the incineration ash is reported to be the carbonation [7].

Eight pieces of sample were made for one weathering series. The weathering acceleration was done at the same time by above-mentioned

each four methods. One piece was collected every week, and the sample was subjected to the analysis.

### 2.3 Leaching Test Procedure

2g of weathered sample was put into Erlenmeyer flask and 20mL of distilled water was added (L/S=10). The flask was shaken for six hours by using the desk-top shaker. It was reported that there are two types of Cs leaching from soil (i.e. Cs absorbed with soil colloid and free ion state) [8]. Thus, in this study, the leaching liquids were filtered through two stages. At first, it was filtered by 1 $\mu$ m glass-fiber filter and then a part of the filtrate was used for the analysis. After that, remainder filtrate was filtered by 0.1 $\mu$ m membrane filter. Both liquids were analyzed by frame atomic absorption spectrometry (AAS: Hitachi Z-8200). Analyzed elements were Cs, K, Na, and Ca.

### 2.4 Identification of Minerals

The Samples after two weeks of weathering were subjected to the Powder X-ray Diffraction (XRD) analysis in order to investigate changes of major minerals contained in the ash. Before analysis, samples were dried at 80°C and then they were milled. X-ray diffractometer (Rint-2000, Rigaku) with Cu-K $\alpha$  radiation was used. Scan range was 5-80° with scan speed 4° per minute.

### 2.5 Microscopic Analysis of Weathered Ash

In the weathering experiment, obvious inhibition of Cs leaching was confirmed in the sample of CO<sub>2</sub> exposure condition. Thus, by using weathered sample of the CO<sub>2</sub> exposure and blank, thin sections were prepared. Thin sections were observed by Scanning Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDS: JEOL JSM-6360LA) and elemental distribution was investigated. Besides, to analyze formation of newly formed minerals in weathered ash samples, Polarizing microscopes (OLYMPUS CX31-P) was used.

## 3. RESULTS AND DISCUSSION

### 3.1 Change of Leaching Behavior of Cs by Weathering

The leaching amount of Cs from the ash exposed to each weathering condition is shown in Fig. 2. Though the direct result obtained by AAS is the concentration of Cs in the leaching liquid, the leaching amount, which is converted from the concentration by using L/S ratio, is indicated. Each panel shows the result of the sample that was exposed to each weathering condition. In addition, the results of two filtration stages are shown by separate line. As indicated in the figure, the leaching amount obtained by both filtration stages

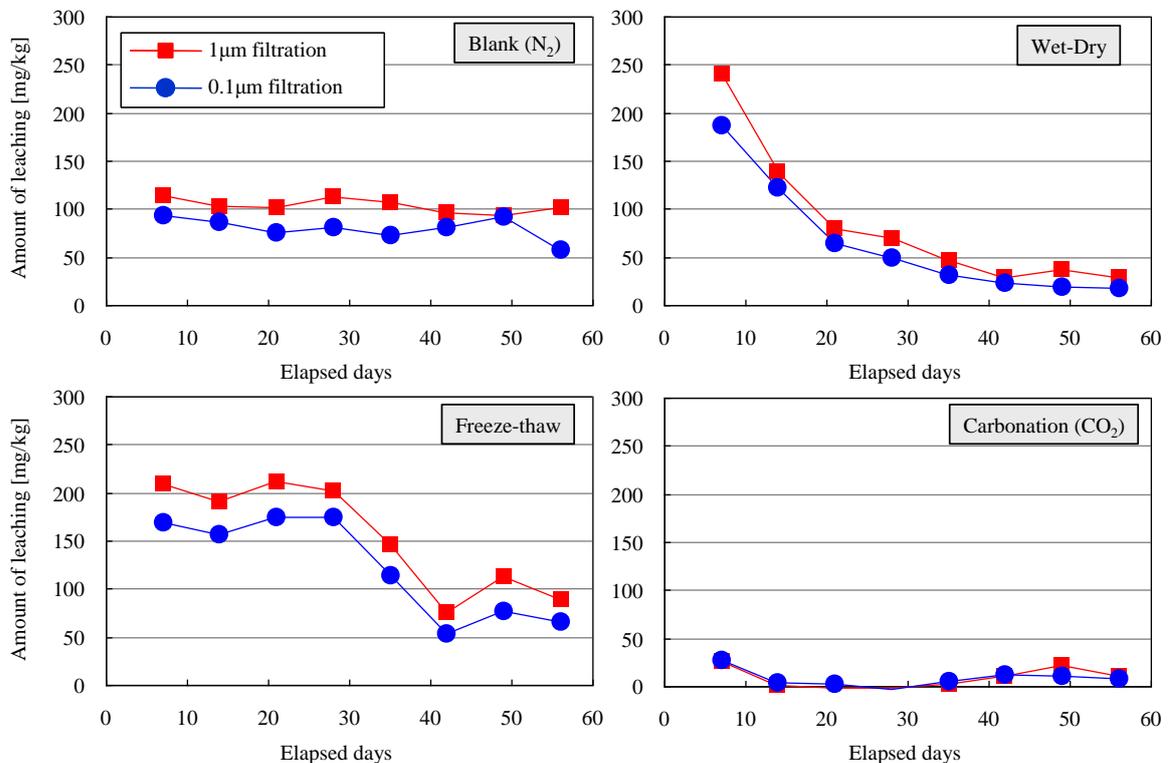


Fig. 2 The amount of Cs that leached out from the weathered bottom ash at each elapsed day

didn't differ much. Concentration of the filtrate obtained by 1µm filter is slightly high. This implies that Cs leached out in this study was mainly ionic form.

Leaching amount of Cs from blank sample (i.e. N<sub>2</sub> exposure) didn't change and it kept almost constant value similar to the initial for through entire experimental period. On the other hand, leaching of Cs from sample exposed to CO<sub>2</sub> circumstance drastically decreased within a week as indicated in the lower right panel. It reached to below the detection limit at two weeks. This rapid decrease is thought to be caused by the formation of calcite at the surface and it may inhibit the Cs leaching by covering the ash particle. The result obtained from both drying-wetting and freezing-thawing conditions shows slight increase of Cs leaching in the first week. The increase of leaching amount was almost 2.5 times to the result of blank. This increase is thought to be caused by collapse of the ash particle structure, which captures Cs to the inside of it, by the physical action due to the thermic effect or the expansion/contraction of pore space. For example, Saffarzadeh [9] reported that Cs is captured in glassy-amorphous phase or some alminosilicates. Thus, if these structures are affected by weathering, leaching of Cs seems to be possible. However, subsequently, the leaching of Cs from both weathering conditions showed the decreasing trend. Especially, Cs leaching from the ash subjected to the drying-wetting condition became lower than it of the blank. This means that the soluble Cs contained in the ash was transformed to the hardly soluble Cs. The conceivable reason of this trend is the carbonation similar to the CO<sub>2</sub> exposure condition. In both weathering conditions, the ash is exposed to the atmosphere. As for the wetting-drying condition, the ash is exposed to the atmosphere during drying. In the freezing-thawing, the situation is the same.

### 3.2 Change of Mineral Phases by Weathering

Minerals identified in XRD analyses which were conducted for each sample after two weeks are indicated in Table 1. The values in the table are the peak height of these minerals. Moreover, the X-ray diffraction charts of each sample are also shown in Fig. 3. In the figure, main peak of calcite is enclosed by the rectangle of dashed line. The peak height of calcite in weathered sample except for the blank increased in common. Especially, the height of the CO<sub>2</sub> exposed sample became five times higher than the blank. From these results, carbonation is deemed to be occurred in the weathered sample and calcite formed. This calcite formation might affect the leaching of Cs.

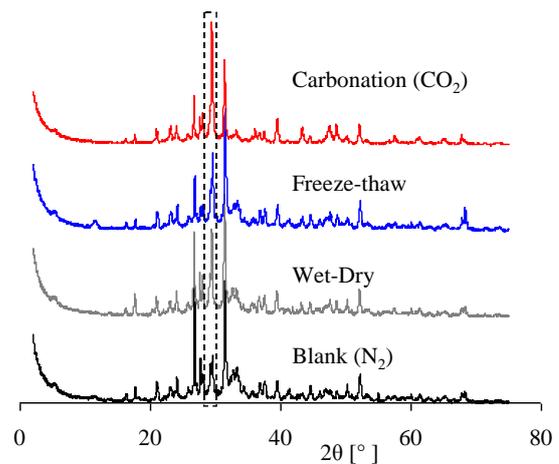


Fig.3 Powder XRD diffractogram on the each weathered bottom ash samples (after two weeks). Rectangle drawn by dashed line encloses main peak of calcite.

Table 1 Change of main peak height of minerals identified each bottom ash samples.

| Mineral   | Blank | Wet-Dry | Freeze-thaw | CO <sub>2</sub> exposure |
|-----------|-------|---------|-------------|--------------------------|
| Gehlenite | 1327  | 1575    | 1290        | 1503                     |
| Quartz    | 1381  | 1198    | 579         | 965                      |
| Lime      | 193   | 206     | 181         | 196                      |
| Calcite   | 438   | 851     | 784         | 1903                     |
| Hematite  | 235   | 201     | 185         | 121                      |

### 3.3 Microscopic Analysis on the mechanism of the leaching inhibition of Cs

Since calcite formation in weathered ash could be confirmed from the result of XRD, microscopic analyses were performed to verify the existence of calcite and its location. At first, some ash particles were observed at a low magnification by using polarizing microscope. Images observed by the transmissive light mode on the blank and the CO<sub>2</sub> exposed sample are shown in Fig. 4. Some ash particles exposed to CO<sub>2</sub> can be seen in panel (b). It seems that the perimeter of the particles shines in yellow. When the observed object emits various colors depending on the rotation angle in the polarizing microscope analysis, the object is considered to be some crystal. This is because mineral in general is composed of some crystal structure and it has polarization property. Therefore, the image of these particles shows that some sort of mineral formed in the sample exposed to CO<sub>2</sub>.

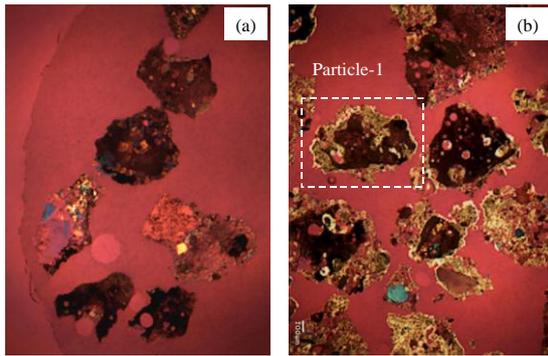


Fig.4 Observed image of weathered ash particles by polarizing microscope; (a) blank, (b) CO<sub>2</sub> exposure.

Next, a particle (Particle-1) shown in Fig. 4 (b) (enclosed by rectangle) was focused and observed with much higher magnification. As indicated in Fig. 5, obvious luminescence at the perimeter of the particle can be confirmed.

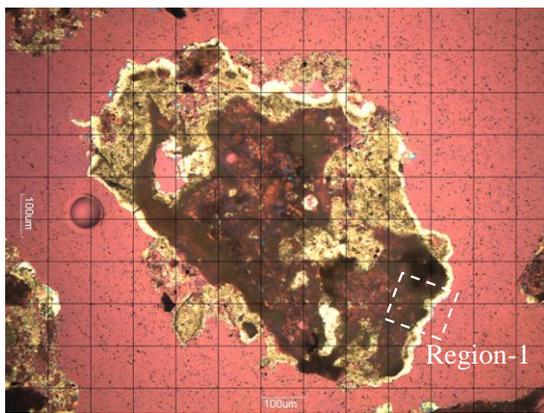


Fig.5 Magnified image of a particle-1 in Fig. 4.

In order to identify the kind of the substance formed at the perimeter of the particle, a region (Region-1) which is enclosed by rectangle in Fig. 5 was observed by SEM. Figure 6 shows the backscattered electron image (BEI) of the Region-1. The edge of the particle is located at slightly right side of the center. In this image, existence of some sort of substance at the edge of the particle is obvious and it is seen as pale gray color. This substance seems to be formed as if it surrounds the particle.

Moreover, EDS analysis was performed in this region in order to know the element distribution. Element mapping image of calcium and silicon is indicated in Fig. 7. Much Ca is distributed at the peripheral region of the particle. The location where Ca is abundant coincides with the gray color part in Fig. 6. Furthermore, this region corresponds to the perimeter which shines in yellow in the image of polarizing microscope. On the other hand, as for the distribution of Si, its intensity is high at

the inside of the particle. And Si is not much distributed at the peripheral region. This implies that some sort of calcium mineral surrounded the particle comprised of silicon.

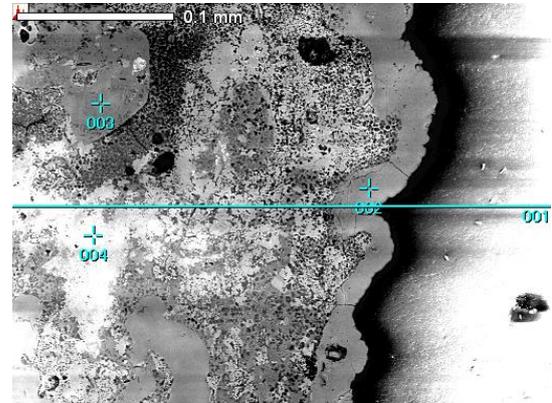


Fig.6 Backscattered electron image of a region-1 in Fig. 4 and EDS analyzing line and points.

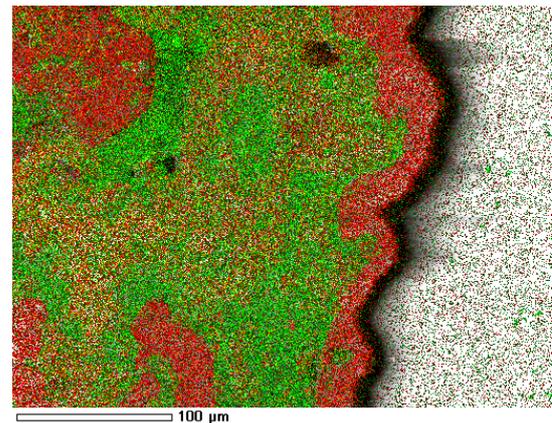


Fig.7 EDS mapping image (red: calcium, green silicon)

The result of EDS line analysis on line001 in Fig. 6 is shown in Fig. 8. Peak intensities of calcium and silicon along with the distance are indicated. Peak intensity of Si is higher than Ca until 2mm of distance from left side. However, when the distance exceeds 2mm, their intensities become reverse. The point of reversal corresponds to the gray color part in the BEI (Fig. 6). And also it corresponds to the area where the Ca is abundant in the element mapping image (Fig. 7). Results of EDS point analysis are shown in Table. 2. When focusing on Ca, it was 9.5% at the point 004 that is the inside of the particle. However, at the point 002 that locates at the perimeter, percentage of Ca increased to 26.5%. From all of the results mentioned above, it can be concluded that some sort of calcium mineral formed at the perimeter of the ash particle which is exposed to the CO<sub>2</sub> as the weathering acceleration.

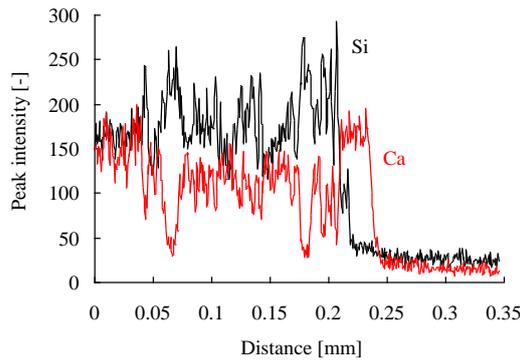


Fig.7 Result of EDS line analysis on line001 in Fig. 6.

Table 2 Result of elemental analysis by Energy Dispersive X-ray Spectroscopy (EDS) on points indicated in Fig. 6.

| Point | 002  | 003  | 004  |
|-------|------|------|------|
| C     | 23.7 | 19.9 | 19.4 |
| O     | 42.5 | 48.9 | 36.1 |
| Al    | 1.1  | 1.1  | 8.2  |
| Si    | 2.3  | 2.7  | 15.8 |
| Ca    | 26.5 | 25.2 | 9.5  |
| Other | 3.9  | 2.3  | 11.0 |
| Total | 100  | 100  | 100  |

Numbers in the table indicate percentage of each element (%).

It is difficult to determine concretely that the formed mineral is calcite from the element ratio identified by EDS. However, as mentioned earlier, the peak of calcite was increased in XRD analysis. Besides, the trend of Cs leaching inhibition is most remarkable in the ash subjected to CO<sub>2</sub> exposure. Based on these facts, the possibility of calcite formation at the surface of the ash particle is quite high. And it will work to restrict Cs leaching from the incineration ash disposed of into MSW landfill.

#### 4. CONCLUSION

In this study, to confirm long-term stability of Cs contained in incineration ash disposed of into MSW landfill, leaching of Cs from ash and phase transformation were investigated by conducting accelerating weathering experiment. Drastic decrease of the Cs leaching was identified under carbon dioxide exposure. From XRD analysis, formation of calcite was identified. By microscopic analysis by using SEM-EDS and polarizing microscope, newly formed mineral that is comprised of Ca mainly was identified at the perimeter (i.e. surface) of the ash particle. Thus, it deemed that newly formed mineral is calcite and it

inhibited the leaching of Cs by covering surface of bottom ash. Incineration bottom ash is highly alkaline material and carbonation promptly occurs after disposal. Since the pH of the ash landfill is reported to be kept high for long-term, Cs in bottom ash will be kept stably by calcite for a long term.

#### 5. ACKNOWLEDGEMENTS

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