

# Radioactive Nuclides in the Incinerator Ashes of Municipal Solid Wastes before and after the Accident at the Fukushima Nuclear Power Plant

Yuki IWAHANA,<sup>†</sup> Atsushi OHBUCHI, Yuya KOIKE, Masaru KITANO, and Toshihiro NAKAMURA

*Department of Applied Chemistry, Meiji University, 1-1-1 Higashimita, Tama, Kawasaki 214-8571, Japan*

Radioactive nuclides in the incinerator ashes of municipal solid wastes were determined by  $\gamma$ -ray spectrometry before and after the accident at the Fukushima nuclear power plant (March 11, 2011). Incinerator ash samples were collected in northern Kyushu, Japan, which is located approximately 1200 km west-southwest (WSW) of the Fukushima nuclear power plant, from April 2006 to March 2007 and from March 2011 to October 2011.  $^{40}\text{K}$ ,  $^{137}\text{Cs}$ ,  $^{208}\text{Tl}$ ,  $^{212}\text{Pb}$ ,  $^{214}\text{Pb}$ ,  $^{212}\text{Bi}$ ,  $^{214}\text{Bi}$ , and  $^{228}\text{Ac}$  were identified in the ashes before the accident (~February 2011) and  $^{134}\text{Cs}$  was identified along with these eight nuclides in the ashes after the accident (March 2011~). A sequential extraction procedure based on a modified Tessier method with added water extraction was used for 1st fly ash sampled in August 2011 because the highest activity concentrations of  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  were observed for this sample. The speciation of radioactive nuclides in the fly ash was achieved by  $\gamma$ -ray spectrometry and powder X-ray diffractometry for the extraction residues. Little variation was observed in the distribution of the chemical forms of  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  in 1st fly ash of municipal solid waste; one half of  $^{134}\text{Cs}$  existed as water soluble salts and the other half as carbonate compounds, whereas 75% of  $^{137}\text{Cs}$  existed as water soluble salts with the remainder as carbonates (10%) and sulfides (15%). These results show that 88% of the total radioactive Cs existed in water soluble and ion extractive forms and might be at risk for elution and diffusion with rain and wind.

(Received August 31, 2012; Accepted October 31, 2012; Published January 10, 2013)

## Introduction

The amount of municipal solid wastes (MSW), which is generated from daily life and office activity and consists of paper, garbage, saw dust, and small metallic objects (*i.e.*, staples), still continues to increase. Most of these wastes are incinerated, resulting in the increased production of ashes (MSWI-ashes). Incinerator ashes are classified as cinder (also called bottom ash) and soot (also called fly ash), and both types of ashes are ultimately sent to landfills. A part of the fly ash is recycled into raw materials used for cement. However, fly ash contains large amounts of hazardous heavy metals<sup>1,2</sup> and dioxins,<sup>3</sup> because these materials are volatilized during the incineration process and enriched on the surface of the fly ash particles. Therefore, fly ash is categorized as a “specially controlled industrial waste” under Japanese law<sup>4</sup> and the concentration of hazardous materials in the ash and leachate from disposal sites are strictly controlled. In Japan, a certification is provided by the Environment Agency of Japan as Notification No. 13,<sup>5</sup> and in the U. S., acid digestion with  $\text{HNO}_3$ ,  $\text{HClO}_4$  and  $\text{HF}$  is often accepted for ash samples.<sup>6</sup> Consequently, these materials are analyzed using various methods, such as X-ray fluorescence analysis (XRF),<sup>1,2</sup> instrumental neutron activation analysis (INAA),<sup>7,8</sup> atomic absorption spectrometry (AAS),<sup>9</sup> inductively coupled plasma atomic emission

spectrometry (ICP-AES),<sup>10</sup> and inductively coupled plasma mass spectrometry (ICP-MS).<sup>11</sup> In addition, in recent years, radon emissions from ash disposal sites<sup>12</sup> and recycled materials<sup>13</sup> have become a problem. Radon is an inert gas produced by the decay of Ra isotopes and taken into the lungs by breathing. Because Rn emits an alpha particle when it decays, it is a risk factor for lung cancer due to internal exposure of alpha-rays.<sup>14</sup> Hence, it is important to measure the radioactive nuclides including Rn isotopes, their parents nuclides and decay products as well as to determine other hazardous materials. In addition,  $^{40}\text{K}$  was also determined together with other natural nuclides for the estimation of internal exposure from  $^{40}\text{K}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$ .<sup>15</sup> In fact, the chemical and physical characteristics of fly ash have been analyzed in a number of cases. Studies have been done, for example, on the leaching characteristics of thermal power plant fly ash in Turkey,<sup>16</sup> the activity concentrations in surface soil for the fly ash disposal site in Poland,<sup>12</sup> the specific activity of building materials incorporating fly ash in Greece,<sup>17</sup> and Rn concentrations at three different fly ash depots in Croatia.<sup>18</sup> In addition, the radioactive nuclides in natural materials, which could be a source of MSW, such as soy, sugar, mint, and mate tea;<sup>19</sup> wood and its incinerator ash;<sup>20</sup> paper;<sup>21</sup> and sugar cane and its straw<sup>22</sup> have also been measured.

On March 11, 2011, the Fukushima nuclear power plant was damaged by the Great East Japan Earthquake and Tsunami. Subsequently, a large amount of radioactive fission products of  $^{235}\text{U}$  in the fuel rods was released into the environment. This disaster was assigned as a “Level 7” incident on the International Nuclear Event Scale (INES), which is on the same level as the

<sup>†</sup> To whom correspondence should be addressed.  
E-mail: ukihana@meiji.ac.jp

“Chernobyl accident” that occurred in April 1986. The radionuclide contamination caused by the diffusion of radioactive nuclides attracted significant interest around the world directly after the accident and in particular, when it was reported that drinking water, marine water, food, and soils were contaminated by  $^{131}\text{I}$  and radioactive Cs. In addition, high concentrations of  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  were also detected in the incinerator ashes of the combusted MSW and sewage sludge. Following the accident, the Japanese Government established 100000 Bq/kg as the activity concentration limit for radioactive cesium in the incinerator ashes of MSW that were destined for landfill. In this study, the radioactive nuclides in the incinerator ash of the MSW were determined by  $\gamma$ -ray spectrometry and their concentrations were monitored. In particular, for 1st fly ash sampled after the accident, a speciation of the radioactive nuclides was performed *via* sequential extraction using an improved Tessier method<sup>23</sup> and powder X-ray diffractometry (XRD).

## Experimental

### Apparatus

The activity concentrations of the radioactive nuclides in the incinerator ashes were determined by direct  $\gamma$ -ray spectrometry using a well-shielded  $\gamma$ -ray spectrometer. The spectrometer contained a p-type high purity Ge/coaxial-type semiconductor detector (Princeton Gamma-Tech. IGP10200,  $\gamma$ -PGT Inc.) surrounded by a 100-mm thick lead shield, with an additional 5 mm of oxygen-free Cu and 5 mm of acrylic resin to reduce the exposure to cosmic radiation and X-rays. This detector was cooled with liquid  $\text{N}_2$  and coupled to an amplifier (FP-6300B, Aptec Engineer Ltd.) and multichannel analyzer (MCARD, Aptec Engineer Ltd.). The detector bias was operated with 2000 V. The efficiency curve was drawn with a  $^{152}\text{Eu}$  standard source (25 mm $\phi$  and 6.0 mm h), which was issued by the Japan Radioisotope Association, and correlation factor of the curve was 0.998. The standard source was set 5 cm away from the Ge-detector in consideration of the coincidence sum effect from  $^{152}\text{Eu}$  standard. The intercept corresponding to the detection efficiency of the efficiency curve was corrected using the intensity of the 1461 keV  $\gamma$ -ray emitted from  $^{40}\text{K}$  in KCl, and the efficiency curve was in validation with standard soil materials (JSAC 0471). As a result, the calculated activities of  $^{40}\text{K}$ ,  $^{134}\text{Cs}$ , and  $^{137}\text{Cs}$  with the curve corresponded closely with those of the reference activities.

$^{40}\text{K}$ ,  $^{134}\text{Cs}$ , and  $^{137}\text{Cs}$  were determined *via* their  $\gamma$ -rays (1460, 605, and 667 keV, respectively), whereas  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{228}\text{Th}$  were measured *via* the  $\gamma$ -rays of their daughter products  $^{214}\text{Pb}$  (351 keV),  $^{228}\text{Ac}$  (911 keV), and  $^{212}\text{Pb}$  (238 keV), respectively. Although,  $^{134}\text{Cs}$  also emits 765 keV  $\gamma$ -ray, this peak was not used for the determination because the efficiencies with two standards were identical and 796 keV  $\gamma$ -ray emitted from  $^{228}\text{Ac}$  overlapped on the peak of  $^{134}\text{Cs}$ . The counting uncertainties in the measurements are 2.6% ( $^{40}\text{K}$ ), 16% ( $^{134}\text{Cs}$ ), 12% ( $^{137}\text{Cs}$ ), 19% ( $^{226}\text{Ra}$ ), 15% ( $^{228}\text{Ra}$ ), and 7.5% ( $^{228}\text{Th}$ ), respectively.

An X-ray diffractometer equipped with a Cu X-ray tube (Rint TTR-III, Rigaku) was operated at 15 kW, with a tube voltage of 50 kV and tube current of 300 mA. A Bragg-Brentano focusing optical system was used for the qualitative analysis and the data was recorded over the  $2\theta$  range  $5^\circ - 90^\circ$ , in steps of  $0.01^\circ$  with a counting time of 0.05 s for each step.

All samples were dried in a hot air rapid drying oven (DSE-113, Isuzu Seisakusho Co. Ltd., Japan) and weighed using a micro balance (AB204-S, Mettler Toledo).

### Incinerator ashes of municipal solid wastes

The incinerator bottom ashes and fly ashes of MSW were collected in northern Kyushu, Japan, which is located approximately 1200 km WSW of the Fukushima nuclear power plant ( $129^\circ 06' \text{ E}$ ,  $32^\circ 56' \text{ N}$ , 87 m of elevation, and a distance of 280 m from the nearest shore of the Pacific Ocean), from April 2006 to March 2007 and from March 2011 to October 2011. In the plant, the soot was collected on the first filter, and then the acidic gases including  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{NO}_x$ , and  $\text{SO}_x$  neutralized with a spray of slaked lime suspension collected on a bag filter. The soot in the first step was called 1st fly ash, and the material collected in the second step was 2nd fly ash. The bottom ash consisted of the generated cinder, which was cooled by water.

### Sample preparation

Approximately 15 g of incinerator ashes were placed in 24.3 cm<sup>3</sup> tin containers (inner diameter, 5.3 cm; height, 1.1 cm). The containers were made gas tight by sealing with an epoxy resin glue and stored for at least three weeks in order to allow radioactive equilibrium among  $^{226}\text{Ra}$  and its daughters.<sup>24</sup> These measurement samples were set away from the Ge-detector to prevent considering the coincidence sum effect. The  $\gamma$ -rays were measured for 48 h.

The solid samples used for XRD were ground with porcelain mortar and pestle for 10 min. The ground samples were then placed in an aluminum sample holder that had an 18 mm  $\times$  20 mm  $\times$  1.5 mm cuboid window on a glass plate. Powder paper was then placed over the powder and the powder was finger-pressed for 1 min.

### Speciation of radioactive nuclides

All solid samples were dried at  $110^\circ\text{C}$  for a period of 24 h in the drying oven.

The Tessier method<sup>23</sup> was applied for the speciation of the radioactive nuclides in the MSWI 1st fly ash. This method is often used for the speciation of heavy metals in soil and sediment samples, and the fractions are classified into six phases; namely, ion exchangeable fraction, carbonate bound fraction, Fe-Mn oxide fraction, bound to organic matter fraction, residual fraction, and extraction residue using appropriate extraction reagents. The Tessier method and related techniques, including additive water soluble extraction, have also been used for the speciation of trace metals in fly ash.<sup>25,26</sup> The extraction method used in this study included the following steps.

(i) *Water soluble step.* One-hundred milliliters of deionized water were added to 10 g of the 1st fly ash sample, and the mixture was agitated for 6 h at room temperature. The sample was then separated from the residue and extracts by filtration, and the extraction residue was dried at  $110^\circ\text{C}$  for at least 24 h and then weighed. Six specimens were prepared and used one at a time for the subsequent extraction/ $\gamma$ -ray measurements.

(ii) *Ion exchangeable step.* Five residues from step (i) were leached for 1 h at room temperature with continuous agitation using 80 mL of 1 M magnesium chloride.

(iii) *Carbonate bound step.* One mol per liter of sodium acetate and acetic acid solution with an adjusted pH of 5.0 was added to four residues from step (ii) for 5 h at room temperature in order to leach the carbonate bound materials.

(iv) *Free oxide step.* The free oxide phases were extracted with 200 mL of 25% (v/v) acetic acid containing 0.83 g of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  at  $96^\circ\text{C}$  for 5 h.

(v) *Sulfide bound step.* The solid phase remaining after step (iv) was agitated in 80 mL of 30%  $\text{H}_2\text{O}_2$  containing 1 mL of nitric acid at room temperature for 5 h.

The solid material remaining step (v) was referred to as the

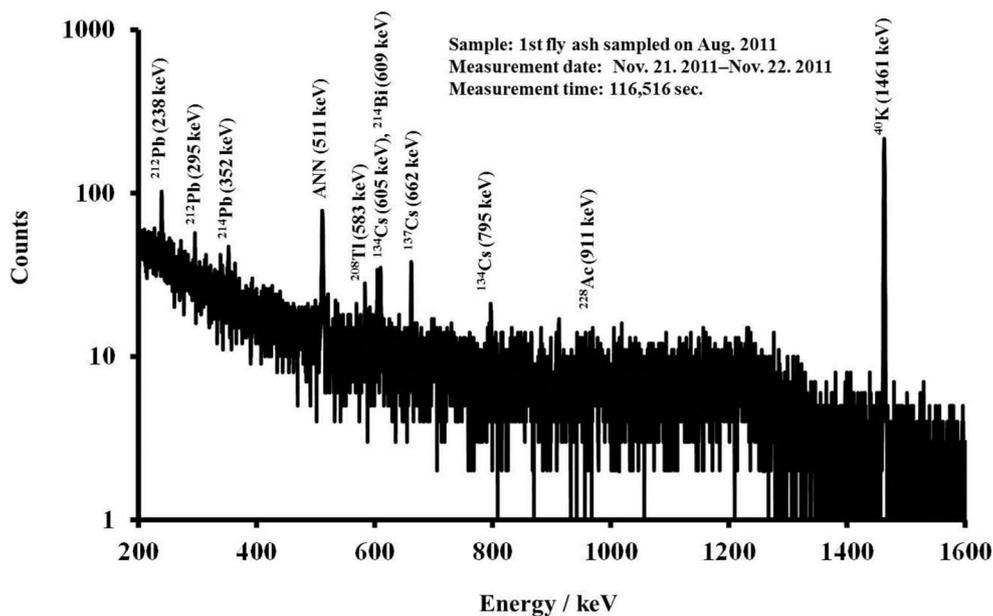


Fig. 1 Gamma-ray spectrum of 1st fly ash of MSW sampled in northern Kyushu, Japan, approximately 1200 km WSW from the Fukushima nuclear power plant in August 2011.

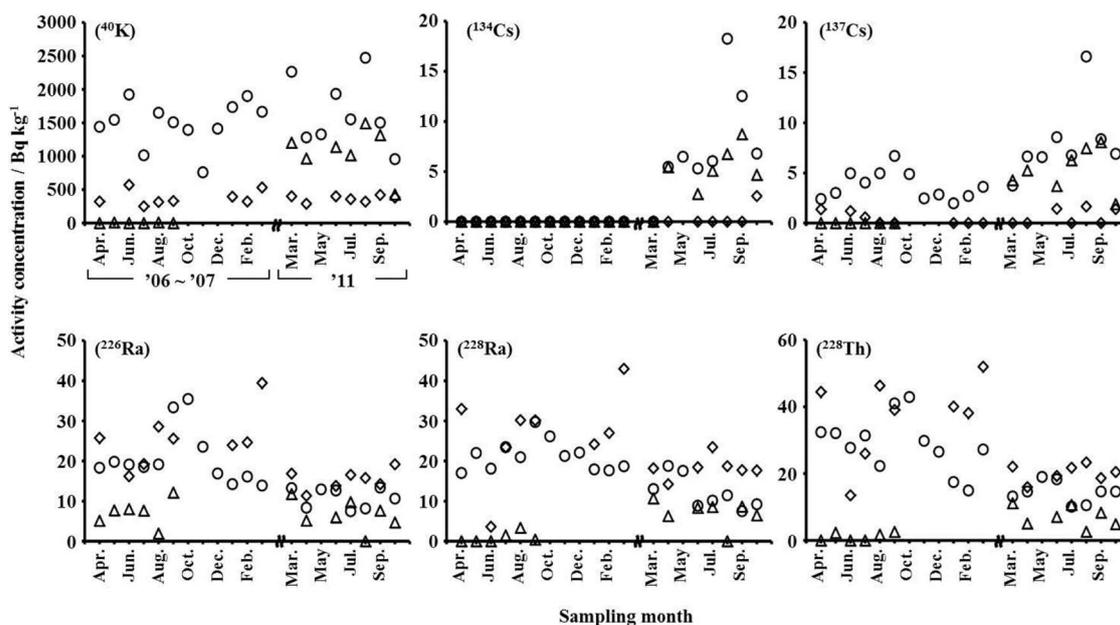


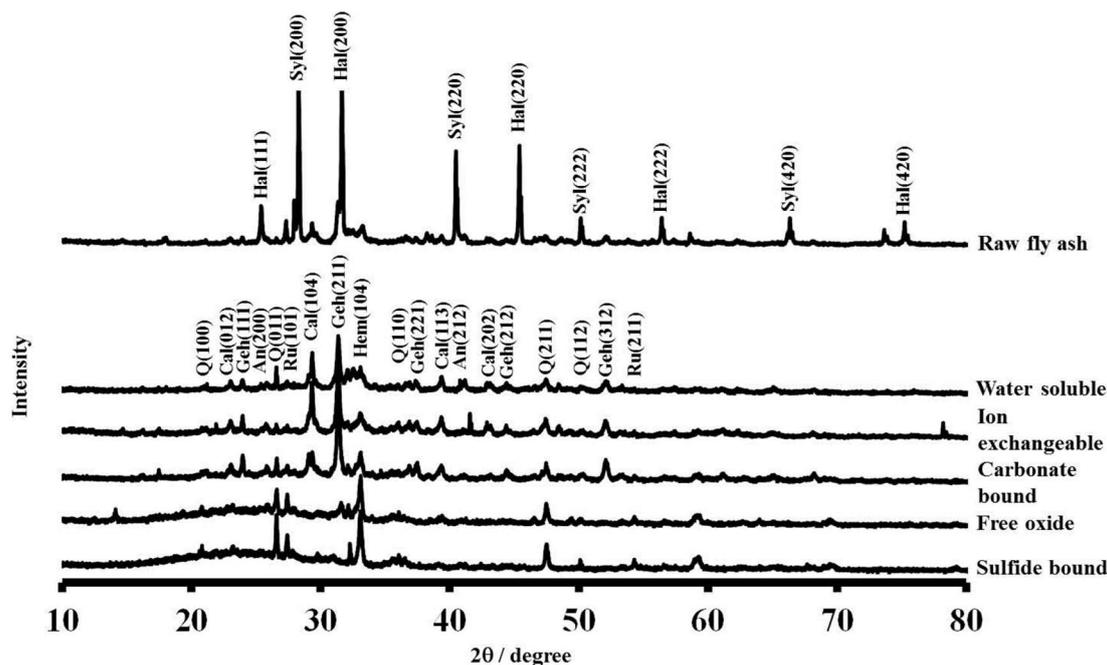
Fig. 2 Variations into activity concentrations of  $^{40}\text{K}$ ,  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  in the incinerator ashes of MSW before and after the accident at the Fukushima nuclear power plant: ○, 1st fly ashes; △, 2nd fly ashes; ◇, bottom ashes.

“residual materials.” 1st fly ash and the five residues from extraction steps (i) – (v) were analyzed *via* powder XRD for speciation of crystalline phases and using  $\gamma$ -ray spectrometry. Approximately 4 g of the 1st fly ash and the five residues from extraction steps (i) – (v) were placed in 12.5 cm<sup>3</sup> tin containers (inner diameter, 3.8 cm; height, 1.1 cm).

## Results and Discussion

### Radioactive nuclides in the incinerator ashes of MSW

Figure 1 shows the  $\gamma$ -ray spectrum of the 1st fly ash after the accident, and activity concentration variations are shown in Fig. 2.  $^{40}\text{K}$ ,  $^{137}\text{Cs}$ ,  $^{208}\text{Tl}$ ,  $^{212}\text{Pb}$ ,  $^{214}\text{Pb}$ ,  $^{212}\text{Bi}$ ,  $^{214}\text{Bi}$ , and  $^{228}\text{Ac}$  were identified in the spectrum of the sample collected before the accident (~February 2011), and  $^{208}\text{Tl}$ ,  $^{212}\text{Pb}$ ,  $^{214}\text{Pb}$ ,  $^{212}\text{Bi}$ ,  $^{214}\text{Bi}$  and  $^{228}\text{Ac}$ , with short half-lives, were also determined as  $^{226}\text{Ra}$  ( $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$ ),  $^{228}\text{Ra}$  ( $^{208}\text{Tl}$ ,  $^{212}\text{Pb}$ ,  $^{212}\text{Bi}$ ).  $^{134}\text{Cs}$



An: anhydrite ( $\text{CaSO}_4$ ), Cal: calcite ( $\text{CaCO}_3$ ), Geh: gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ), Hal: halite ( $\text{NaCl}$ ), Hem: hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), Q: quartz ( $\alpha\text{-SiO}_2$ ), Ru: rutile ( $\text{TiO}_2$ ) and Syl: sylvite ( $\text{KCl}$ )

Fig. 3 X-ray diffraction patterns of raw fly ash and residues obtained at each extraction step of the Tessier method for fly ash MSW sampled in northern Kyushu, Japan, in August 2011.

was identified from the samples after the accident (March 2011~).

The concentrations of  $^{40}\text{K}$ ,  $^{134}\text{Cs}$ , and  $^{137}\text{Cs}$  increased in the order 1st fly ash > 2nd fly ash > bottom ash. The vaporization points of most alkali metal compounds are lower than the combustion temperature (over  $850^\circ\text{C}$ ). These compounds were condensed and attached to the surface of the fly ash particles, whereas in the bottom ash, the concentrations of radium isotopes and  $^{228}\text{Th}$ , which originates in silicate rocks, were higher than those in the 1st and 2nd fly ash.

#### Homogeneity of 1st fly ash

Four 1st fly ash samples collected in August 2011 were pretreated following the same procedure described in the Experimental section. The concentrations of  $^{40}\text{K}$ ,  $^{134}\text{Cs}$ , and  $^{137}\text{Cs}$  were measured in order to check the homogeneity of the radioactive nuclides in the 1st fly ash. The relative standard deviation ( $n = 4$ ) of the concentrations of these nuclides were 2.5 - 9.5%, which is smaller than the 10 - 15% counting uncertainty associated with the current  $\gamma$ -ray measurements. Therefore, the distributions of  $^{40}\text{K}$ ,  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  in the 1st fly ash were considered to be homogeneous.

#### Speciation of radioactive nuclides

The most dominant mass fraction (34.0 mass%) of the 1st fly ash was the water soluble fraction. The ion exchangeable phase was 3.7 mass%; carbonate bound fraction, 22.4 mass%; free oxide bound phase, 15.3 mass%; sulfide bound fraction, 8.2 mass%; and remaining residual material, 16.4 mass%; respectively.

Anhydrite ( $\text{CaSO}_4$ ), calcite ( $\text{CaCO}_3$ ), gehlenite ( $\text{Ca}_2\text{Al}_2\text{Si}_7$ ), halite ( $\text{NaCl}$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), quartz ( $\alpha\text{-SiO}_2$ ), rutile ( $\text{TiO}_2$ ) and sylvite ( $\text{KCl}$ ) were identified in the diffraction patterns of the incinerator fly ash, as shown in Fig. 3.

The crystalline phase in each extraction fraction was estimated on the basis of the disappearance of X-ray diffraction peaks. After the water extraction step, the halite and sylvite peaks completely disappeared, indicating that the eluted materials were probably halides. After the extraction step for ion exchangeable species, no remarkable disappearance was observed, but an unknown peak at  $78.2^\circ$  appeared in the diffraction pattern. This peak disappeared after the next extraction step for the carbonate bound species. While the calcite peaks significantly decreased with sodium acetate extraction, the calcite was not completely removed. This result is due to the higher concentration of carbonate compounds than those of the soil and sediment. After the free oxide extraction step, the remaining calcite and gehlenite disappeared and trace rutile was clearly identified in the diffraction pattern of residue. In addition, detailed observation showed gently sloping hills from  $18^\circ$  to  $35^\circ$  in the diffraction pattern of the residue after the free oxide extraction, indicating the existence of an amorphous component such as glass and/or gel in the incinerator fly ash. From the diffraction patterns of the residues for the oxide and sulfide extraction steps, aluminosilicate and amorphous phases were identified as the major phases after the completion of the entire Tessier method. In the last step, anhydrite was extracted into the sulfide bound fraction, whereas hematite, quartz, and rutile still remained in the residual fraction.

Figure 4 shows the distribution of the radioactive nuclides in the 1st fly ash of the MSW after the accident at Fukushima (sampled in August 2011).  $^{40}\text{K}$ ,  $^{134}\text{Cs}$ , and  $^{137}\text{Cs}$  existed as water soluble salts and carbonate compounds, whereas  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{228}\text{Th}$  were stable in their free oxide form and contained in aluminosilicate.

Little variation was observed in the chemical forms of  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  in the MSW. One half of  $^{134}\text{Cs}$  existed as water soluble salts and the other half as carbonate compounds, whereas 75%

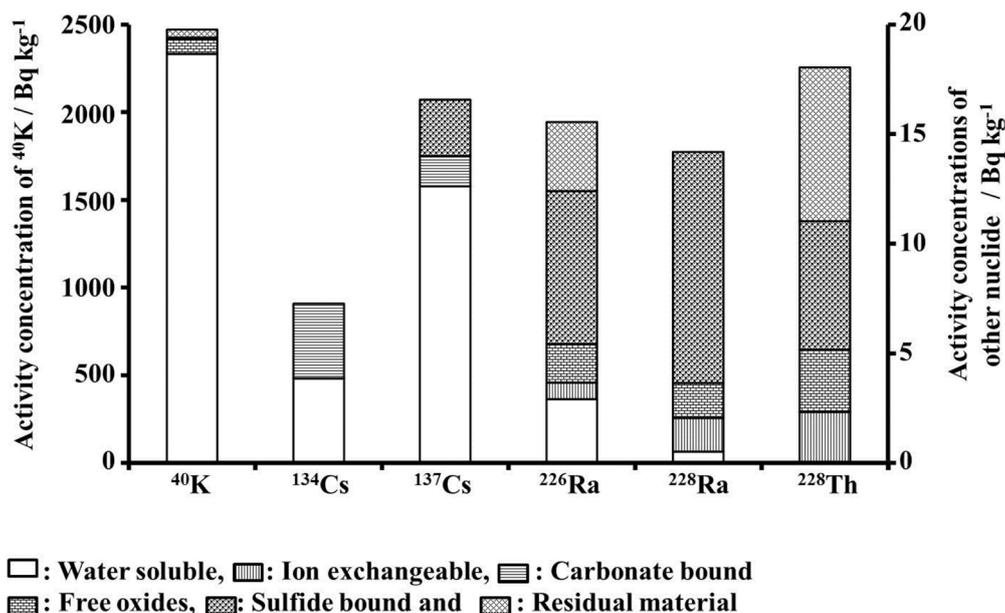


Fig. 4 Distributions of radioactive nuclides in 1st fly ash of MSW sampled in northern Kyushu, Japan, in August 2011.

of  $^{137}\text{Cs}$  existed as water soluble salts, 10% as carbonate bound material, and 15% as sulfides.

In Japan, most of the incinerator ash of MSW is sent to landfill and these ashes are thus exposed to wind and rain for long periods. Typically, the pH of rainwater is approximately 5.6, which is similar to the pH of the sodium acetate/acetic acid extraction medium used in this study. Therefore, these results suggest that 88% of the total radioactive cesium existed in water soluble and ion extractive forms and might be at risk for elution and diffusion due to exposure to rain and wind.

#### Mass balance of sequential extraction

In general, the eluted materials are determined with the Tessier method and other extraction techniques by using a liquid reagent; however, in this study, the residues were measured in order to determine the distribution of the nuclides. Therefore, mass balance verification of the water soluble fraction was attempted because there was no contamination from any reagents. The material mass of both extract and residue were obtained. However, only the concentrations of  $^{40}\text{K}$ ,  $^{134}\text{Cs}$ , and  $^{137}\text{Cs}$  were determined because the peaks for these nuclides were detected in both materials.

Water extraction was achieved using 15 g of the 1st fly ash. After separation, 2 mL of conc.  $\text{HNO}_3$  was added to the extraction in order to prevent adsorption to the glass beaker, and the solution was recrystallized on an evaporating dish. The precipitate was dried for 24 h in an oven ( $110^\circ\text{C}$ ) and then the dried sample was stored in a tin container.

The calculated results for the weight and activity concentrations of the raw fly ash, extraction residue, and precipitate are shown in Table 1. As observed from the table, there is little difference between the activity of the raw ash and sum of the activities of the materials for each nuclide after extraction. In addition, the weight of the raw ash was nearly equal to the sum of the extraction materials; therefore, no contamination or loss of fly ash occurred during the extraction.

Table 1 Mass balances between residue and extract in water soluble fraction

	Weight/g	$^{134}\text{Cs}/\text{Bq}$	$^{137}\text{Cs}/\text{Bq}$	$^{40}\text{K}/\text{Bq}$
Residue ( <i>R</i> )	10.0869	33	52	1600
Extract ( <i>E</i> )	5.4903	54	140	31100
<i>R + E</i>	15.5772 (102)	87 (124)	190 (86)	32700 (94)
Raw ash	15.2994	70	220	34700

( ): Ratio to Raw ash/%

#### Conclusion

$^{40}\text{K}$ ,  $^{137}\text{Cs}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{228}\text{Th}$  existed in the incinerator ashes of the municipal solid wastes both before and after the accident at the Fukushima nuclear power plant, whereas  $^{134}\text{Cs}$  was only detected in samples collected after the accident. In four 1st fly ash samples collected in August 2011, the distributions of  $^{40}\text{K}$ ,  $^{134}\text{Cs}$ , and  $^{137}\text{Cs}$  were considered to be homogeneous, because the relative standard deviation ( $n = 4$ ) of these nuclides was 2.5 - 9.5%, which is smaller than the 10 - 15% counting uncertainty associated with current  $\gamma$ -ray measurements. Anhydrite, calcite, gehlenite, halite, hematite, quartz, rutile, and sylvite were identified in the diffraction patterns of the incinerator fly ash. The crystalline phase in each extraction fraction was estimated, and the eluted materials after water extraction were determined to probably be halides. Calcite was not completely extracted in the carbonate phase because of the higher concentration of carbonate compounds than those of the soil and sediments. In the free oxide step, the remaining calcite and gehlenite were eluted and trace rutile and an amorphous phase were clearly identified. In the last step, anhydrite was extracted, whereas hematite, quartz, and rutile still remained in the residual fraction.

$^{40}\text{K}$ ,  $^{134}\text{Cs}$ , and  $^{137}\text{Cs}$  existed as water soluble salts and carbonate compounds, whereas  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{228}\text{Th}$  were stable in their free oxide forms and were contained in the aluminosilicate. In addition, little variation in the chemical

forms of  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  in the 1st fly ash of the MSW were observed.

In Japan, most of the incinerator ash of MSW is sent to landfill and these ashes are thus exposed to wind and pH 5.6 rainwater for long periods. As a result, 88% of the total radioactive cesium might be at risk for elution and diffusion due to exposure to rain and wind.

### Acknowledgements

The authors are grateful to Dr. Hiroyuki Toda for the helpful discussions and advice.

### References

1. A. Ohbuchi, M. Kitano, and T. Nakamura, *X-Ray Spectrom.*, **2008**, *37*, 237.
2. A. Ohbuchi, J. Sakamoto, M. Kitano, and T. Nakamura, *X-Ray Spectrom.*, **2008**, *37*, 544.
3. H. Huang and A. Buekens, *Chemosphere*, **1995**, *31*, 4099.
4. Japan, Ministry of the Environment Government, **1970**, Waste Management and Public Cleansing Law.
5. Notification No.13 of Environment Agency of Japan, **1973**, February 17.
6. Method 3050B, "Acid digestion of sediments, sludges, and soils", **1996**, U. S. Environmental Protection Agency (USEPA).
7. J. J. Rowe and E. Steinnes, *Talanta*, **1977**, *24*, 433.
8. S. Suzuki and S. Hirai, *Bunseki Kagaku*, **1982**, *31*, 443.
9. Z. Mester, M. Angelone, C. Brunori, C. Crenisini, H. Muntau, and R. Morabito, *Anal. Chim. Acta*, **1999**, *395*, 157.
10. S. J. Huang, C. Y. Chang, D. T. Mui, F. C. Chang, M. Y. Lee, and C. F. Wang, *J. Hazard. Mater.*, **2007**, *149*, 180.
11. A. K. Das, R. Chakraborty, M. de la Guardia, M. C. Cervera, and D. Goswami, *Talanta*, **2001**, *54*, 975.
12. E. M. Bem, H. Bem, and P. Wiczorkowski, *Sci. Total Environ.*, **1998**, *220*, 215.
13. K. Kovler, *Constr. Build. Mater.*, **2009**, *23*, 246.
14. D. M. Bonotto and L. Caprioglio, *Appl. Radiat. Isot.*, **2002**, *57*, 931.
15. O. B. Flores, A. M. Estrada, R. R. Suárez, J. T. Zerquera, and A. H. Pérez, *J. Environ. Radioact.*, **2008**, *99*, 1834.
16. A. Baba and A. Kaya, *J. Environ. Manag.*, **2004**, *73*, 199.
17. H. Papaefthymiou and O. Gouseti, *Radiat. Meas.*, **2008**, *43*, 1453.
18. I. Lovrencic, D. Barisic, V. Orescanin, and S. Lulic, *Nucl. Instrum. Meth. B*, **2007**, *263*, 186.
19. V. Scheibel and C. R. Appoloni, *J. Food Compos. Anal.*, **2007**, *20*, 650.
20. L. Högbom and H. Ö. Nohrstedt, *Sci. Total Environ.*, **2001**, *280*, 133.
21. A. Kobashi, *Appl. Radiat. Isot.*, **2001**, *55*, 327.
22. F. T. da Conceição, D. M. Bonotto, J. R. Jiménez-Rueda, and J. A. F. Roveda, *Appl. Radiat. Isot.*, **2009**, *67*, 1114.
23. A. Tessier, P. G. C. Campbell, and M. Bisson, *Anal. Chem.*, **1979**, *51*, 844.
24. K. Nagai, E. Hashimoto, and J. Sato, *Radioisotopes*, **2006**, *55*, 567.
25. A. Funatsuki, M. Takaoka, D. Kokubu, K. Oshita, and N. Takeda, *Bunseki Kagaku*, **2010**, *59*, 801.
26. M. Takaoka, K. Kuramoto, N. Takeda, and K. Fujiwara, *Doboku Gakkai Ronbunshuu*, **2001**, *685*, 79.