

**Part II**  
**Decontamination and Radioactive Waste**

# Chapter 7

## Safety Decontamination System for Combustion of Forestry Wastes

Hirohisa Yoshida, Hideki Ogawa, Kahori Yokota, Shio Arai, Shigemitsu Igei, and Ritsuko Nakamura

**Abstract** The safety decontamination system of the contaminated forestry wastes by combustion was developed. Under the laboratory scale test with 10 g of cedar bark, about 35 % of radiocesium in the contaminated bark flowed out as a gaseous state by the combustion above 500 °C. The developed system consisted of three modules, the smoke extraction apparatus by water, the combustion ash coagulate apparatus and the radiocesium filtration unit from the sewage water. The demonstration combustion tests were carried out in March 2012. Forestry wastes (6.3 kg), pine needles, Japanese cedar bark and sapwood chips including radiocesium were combusted at 550–700 °C. The exhaust smoke was washed by the jet stream of water, the sewage water included small amount of soot and the radiocesium concentration of sewage water without soot was 50 Bq/kg. After the filtration of 550 L of sewage water by the radiocesium absorption filter consisting of wool dyed by Prussian blue, the radiocesium concentration decreased less than 0.2 Bq/kg. The filtrated water was recyclable in this system. No gaseous radiocesium was detected in the exhausted air from this system during the decontamination of forestry wastes. The combustion ash (140 g), consisting of cesium oxide alloy including various metal ions, was collected and packed under the reduced pressure automatically.

**Keywords** Forestry wastes • Combustion • Smoke extraction • Radiocesium • Decontamination • Sewage water • Cedar • Bark • Pine needles • Ash

---

H. Yoshida (✉) • K. Yokota • S. Arai • S. Igei • R. Nakamura  
Graduate School of Urban Environmental Science, Tokyo Metropolitan University,  
Hachioji, Tokyo, Japan  
e-mail: [yoshida-hirohisa@tmu.ac.jp](mailto:yoshida-hirohisa@tmu.ac.jp)

H. Ogawa  
Graduate School of Urban Environmental Science, Tokyo Metropolitan University,  
Hachioji, Tokyo, Japan

Fukushima Forestry Research Center, Fukushima-shi, Fukushima, Japan

## 7.1 Introduction

Although 4 years have passed after the accident of Tokyo Electric Power Co. (TEPCO) Fukushima Daiichi Nuclear Power Station (FDPS), a huge amount of radionuclide remains in the forest at Fukushima [1]. The main components of radionuclide from FDPS disaster, cesium134 ( $^{134}\text{Cs}$ ) and cesium137 ( $^{137}\text{Cs}$ ), became the environmental contamination problem and disturbed both agricultural and forestry works in Fukushima [2, 3]. Most radiocesium fallout on the ground tightly bound with soil and formed the complex with clay minerals [4], the ionic  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  were a few in the environment [5, 6].

Fukushima Daiichi Nuclear Power Station accident induced the serious situation to revive the forestry works in Fukushima, especially in Abukuma forest area located at west from FDPS with heavy radioactive contamination. The regular maintenance of forest became difficult due to the high air dose environment, the low demand of woods and the forestry wastes including radionuclide. The fallout radiocesium ( $^{134}\text{Cs}$  and  $^{137}\text{Cs}$ ) existed on bark and leaves of trees [7–9], and the Japanese cedar woods absorbed radiocesium through bark and leaves in 2011 and 2012 [10, 11].

In Fukushima prefecture, about 970,000 ha of forest is the subject area for the periodic thinning from 2013 to 2030 in the current plan. For 1000 ha of the thinning area in forest, about 10 % of woods corresponding to 150,000 m<sup>3</sup> of Japanese cedar will be cut down. The thinning of 1000 ha of forest will produce about 30,000 m<sup>3</sup> of twigs including leaves and about 15,000 m<sup>3</sup> of barks. The total forestry wastes produced by the periodic thinning is estimated at 3,445,000,000 m<sup>3</sup> for each year. Before FDPS accident, the forestry wastes were used as composts for forestry and agriculture uses. The forestry wastes including radiocesium or other radionuclide have no way for utilization. These forestry wastes are disposable by the combustion or the fermentation as the energy resource.

One of the possible ways of forestry waste disposal is the biomass power generation. Ministry of the Environment planned the construction of two biomass power generations with 12 MW at Samekawa village and Hanawa town in 2013. The benefit of biomass power generation is the effective utilization of forestry waste and the power generation; on the other hand, the release of gaseous radionuclide and the mass transportation of biomass contaminated with radionuclide from the forest to the power plant are the risk of biomass power generation in Fukushima at present. The construction of biomass power generation (10 MW scale) in Hanawa town was canceled in October 2013 by the local residents' campaign based on the unclearness of these risks [12]. However, Fukushima prefecture decided to construct again the biomass power generation in Hanawa town in May 2015 [13]. The insecurities of large-scale biomass power station are the leak of radionuclide from the discharge gas during the burning of forestry wastes, the fly out risk of the concentrated ash and the radiation exposure of workers in the biomass power plant.

In this study, the risk of radiocesium released in the environment during the combustion of forestry waste was estimated by the laboratory-scale combustion experiment. The demonstration combustion test of forestry wastes was carried to

evaluate the possibility of safety combustion method. The safety combustion system designed based on the results of laboratory-scale experiments was developed for the decontamination of forestry wastes.

## 7.2 Experimental

### 7.2.1 Samples

Samples used in this study were Japanese cedar bark (from 5000 to 21,000 Bq/kg), cedar leaves (from 5000 to 20,000 Bq/kg), cedar sapwood (less than 20 Bq/kg), cedar heartwood (less than 10 Bq/kg) and pine needles (from 10,000 to 25,000 Bq/kg) collected at Fukushima Forestry Research Center in autumn 2011. After drying at 60 °C for 3 days, samples were used for the experiments. The water content of samples evaluated from the mass loss after drying was 28.6 % for cedar bark, 56.8 % for cedar leaves, 61.8 % for sapwood, 54.3 % for heartwood and 10 % for pine needle based on the wet mass.

### 7.2.2 Combustion Test

Laboratory-scale combustion tests of radiocesium-contaminated Japanese cedar bark (20,000 Bq/kg) were carried out using the combustion instrument made of glass shown in Fig. 7.1. About 10 g of cedar bark in alumina crucible (A) was put in the quartz sample tube (B) and combusted at 300–900 °C under air flow condition. The combustion gas was cooled at the glass tube (C) by ice/water bath and was collected

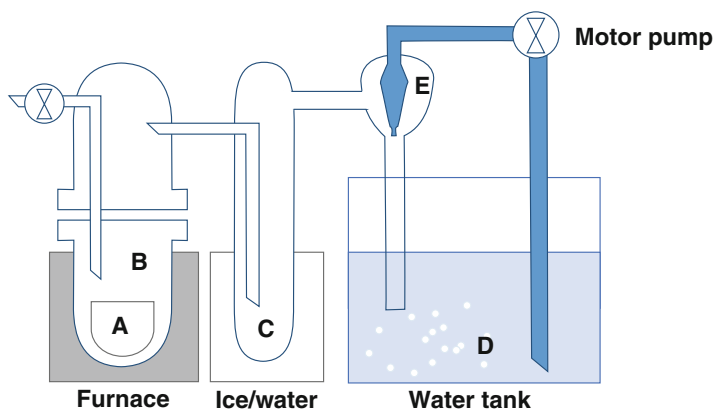


Fig. 7.1 Schematic drawing of combustion instrument for laboratory scale test

in 2 L of water sink (D) using an aspirator (E). Before and after the combustion, the radioactivity of sample and water in sink D were determined. The mass loss by the combustion was also determined.

Demonstration tests of forest waste were carried out at Fukushima Forestry Research Center in March 2012. Two times demonstration tests using 2.3 kg of pine needles, 3.6 kg of Japanese cedar bark and 0.4 kg of cedar sapwood were carried out by the combustion system described later.

### **7.2.3 Measurements**

Radioactivity of samples was measured by the Germanium semiconductor detector (SEG-EMS: SEIKO EG&G Inc., Japan) with 100 mL of U8 container at 10,000–40,000 s of accumulation time to obtain 1–2 Bq/kg of the lower limit. The radiation decay was compensated at March 1, 2012.

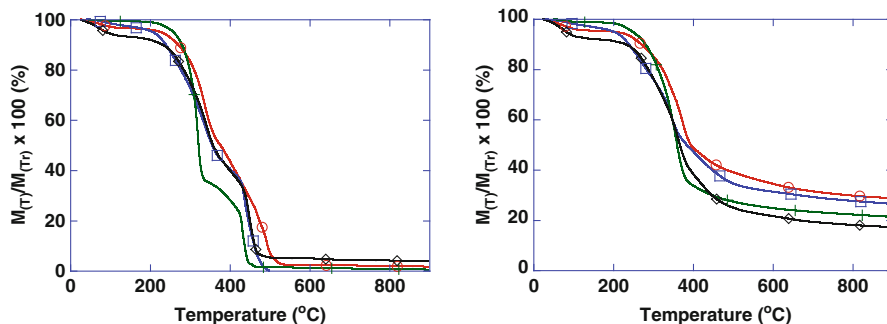
Thermogravimetry measurements of forest wastes, Japanese cedar sapwood chip, cedar bark, cedar leaves and pine needles were carried out by TG/DTA 7200 (Hitachi High-Tech Science Co., Japan) under air and nitrogen gas flow atmospheres. About 3 mg of samples were heated at 20 K/min from room temperature to 900 °C. The evolved gas during combustion was analyzed by the online Fourier Transfer Infrared Spectroscopy FTIR 650 (JASCO, Japan) connected with TG/DTA [14].

Transmission electron microscopic observation of ash was performed by JEM 3200FS (JEOL, Japan) operated at 300 kV. The ash sample was dispersed on the copper glide and coated with carbon. The energy-dispersive X-ray spectroscopic analysis (EDX) was carried out for ash sample. Powder X-ray diffraction of ash was observed by Rint TTR III (Rigaku Co., Japan) operated at 50 kV and 300 mA with  $2\theta/\theta$  scanning at 2°/min.

## **7.3 Results and Discussion**

### **7.3.1 Laboratory-Scale Tests**

Mass loss curves of Japanese cedar sapwood chip, bark, leaves and pine needles obtained by TG/DTA were shown in Fig. 7.2 in air flow (left) and nitrogen gas flow (right) atmospheres. The mass loss occurred in three steps below 200 °C, 200–400 °C and above 400 °C in both conditions; however, the third mass loss in air atmosphere occurred in the narrow temperature range; in contrast, the third step in nitrogen atmosphere occurred in the wide temperature range. The first mass loss below 200 °C was caused by the evaporation of water and volatile components without the combustion of main components of forestry waste, such as cellulose,



**Fig. 7.2** Mass change of Japanese cedar sapwood chip (*cross*), cedar bark (*circle*), cedar leaves (*square*) and pine needles (*rhombus*) under air (*left*) and nitrogen gas (*right*) gas atmosphere

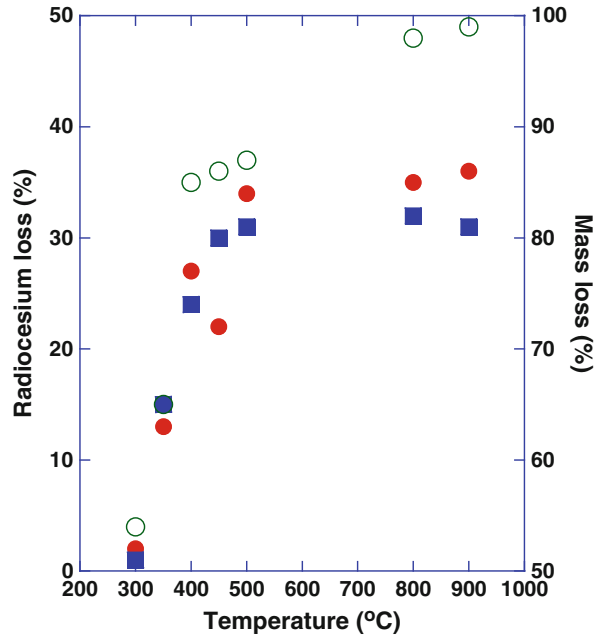
lignin and hemicellulose. The main component of mass loss below 150 °C was water from the evolved gas analysis. The second mass loss occurred above 250 °C and levelled off below 400 °C for both conditions; these mass losses were caused by thermal decomposition of cellulose and hemicellulose. The major components evolved in this stage were CO<sub>2</sub> and CH<sub>4</sub> in air atmosphere and CO and CH<sub>3</sub>OH in nitrogen atmosphere. The third mass loss stage was caused by the dehydration of samples; the major components in this stage were CO<sub>2</sub>, CH<sub>4</sub> and phenolic derivatives for air atmosphere and CO and H<sub>2</sub> for nitrogen atmosphere which were almost similar to the compounds obtained by the pyrolysis of wood [15].

The residues of each sample at 800 °C and 890 °C were 0.8 % and 0.6 % for Japanese cedar sapwood chip, 1.9 % and 1.7 % for bark, 0.5 % and 0.4 % for leaves, 4.2 % and 4.0 % for pine needles in air atmosphere and 22.4 % and 21.4 % for sapwood chip, 29.8 % and 28.9 % for bark, 27.7 % and 26.6 % for leaves and 18.2 % and 17.3 % for pine needles in nitrogen atmosphere, respectively. The residues obtained in air and nitrogen atmospheres were inorganic materials and char, respectively, by XRD analysis of residues.

The mass loss and the radiocesium loss, normalized by the initial mass and the initial concentration of <sup>134</sup>Cs and <sup>137</sup>Cs, during the combustion of cedar bark at various temperatures were shown in Fig. 7.3. Under the laboratory scale combustion test, the mass loss at the combustion temperature below 500 °C was less than 90 %, which was lower than the mass loss evaluated by TG measurement under air flow condition. However, the mass loss behavior occurred in three steps, which was consistent with TG behavior shown in Fig. 7.2.

For the combustion at 300 °C, most radiocesium (98 %) remained in the residues, which was 46 % of the initial mass; however, radiocesium in the residues decreased with the increase of combustion temperature. About 15–25 % of radiocesium evaporated by the combustion at temperature from 350 to 450 °C and about 30–35 % of radiocesium released by the combustion at temperature above 500 °C. After seven combustion tests at temperatures from 300 to 900 °C, the radiocesium concentration (<sup>134</sup>Cs + <sup>137</sup>Cs) of trapped water was 153 Bq/L, which corresponded

**Fig. 7.3** Mass loss (*open circle*) and radiocesium loss of  $^{134}\text{Cs}$  (*closed circle*) and  $^{137}\text{Cs}$  (*closed square*) at various combustion temperature

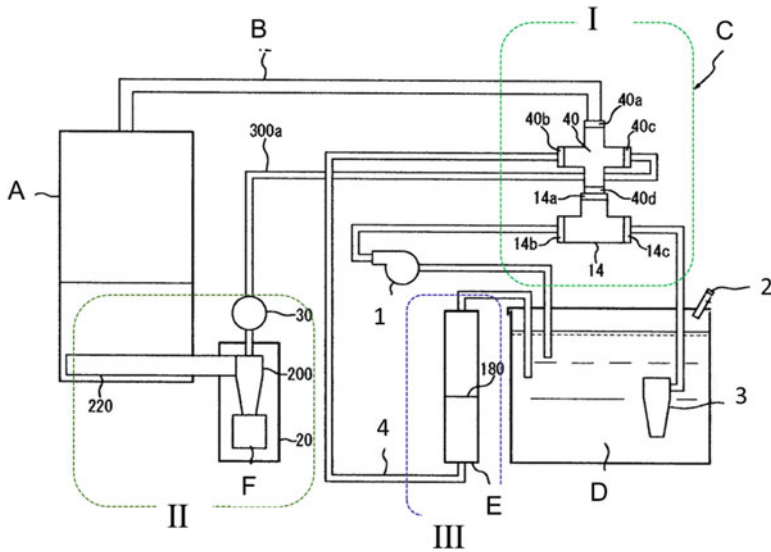


to 98 % of radiocesium evaporated during the combustion tests. These results indicated radiocesium in forestry wastes vaporized by the combustion, and the evaporated radiocesium was trapped efficiently by water.

### 7.3.2 Development of Decontamination System for Forestry Waste

In Fukushima, the non-industrial wastes including contaminated materials are burned at about 900 °C in the waste incineration plant equipped with the smoke extraction apparatus such as the desulfurization equipment and the bag filter for fly ash. The desulfurization of exhaust gas is processed generally by the absorption of sulfurous acid gas ( $\text{SO}_2$ ) with aqueous dispersion of limestone ( $\text{CaCO}_3$ ), which has the possibility to trap the evaporated radiocesium; however, the desulfurization equipment is not designed for the radiocesium absorption. Fly ashes are filtrated by the bag filter made of poly(ethylene tetrafluoride) with 0.4  $\mu\text{m}$  of mesh size.

The safety decontamination system for forestry wastes was designed as shown in Fig. 7.4 [16]. The design criteria of this system were the compact size and the flexible attachment to connect with the existing small combustion furnace (100 kW scale) in sawmill and wood market yard. The developed system consisted of three modules, the smoke extraction apparatus by water (I), the combustion ash coagulate apparatus (II) and the radiocesium filtration unit from the sewage



**Fig. 7.4** Design of combustion system consisted of furnace (A), smoke tube (B), water scrubber absorbed smoke (C), water tank (D), sewage water filtrate column (E) and ash collecting apparatus (F)

water (III). The furnace (A) connected with the smoke extraction apparatus by jet stream of water (C) through the smoke tube (B), water supplied from the water tank (D), the combustion ash was collected by the ash enclosure apparatus (F) and the radiocesium in the sewage water was filtrated by the absorption column unit (E).

The woodstove model 1630CB (Morsϕ, Finland) connected with the water scrubber (14) through the smoke tube and three channel connector (40). About 600 L of water stored in water tank (D) pumped up and compressed by motor (1), and water jet (2 L/s) flowed into the scrubber from 14b and flowed out from 14c induced the reduced pressure at 14a. The smoke from the woodstove was absorbed in the scrubber from 14a and mixed with water jet in the scrubber. The mixed smoke and water flowed in the water tank through the wet cyclone (3) where the radiocesium in smoke dissolved in water and the excess pressured air flowed out through the air filter made of wool dyed by Prussian blue (2).

After the combustion, the water-extracted smoke was decontaminated by radiocesium absorption filter made of wool dyed by Prussian blue (18) through the column (E) absorbed by the scrubber through three mouth connector (40b). The combustion ash including radiocesium was collected and separated particles by air cyclone (200), and the separated ash particles were packed automatically under the reduced pressure by the ash enclosure (F: ATA Co, Japan) connected with the scrubber through three mouth connector (40c).

The outlook of combustion system was shown in Fig. 7.5. The smoke extraction apparatus (1) consisted of the water tank (A), the water motor (B), the scrubber (C)





**Fig. 7.5** Photographs of the smoke extraction system (1), the ash enclosure instrument (2) and its inside view (3)

and the three mouth connection to furnace (D) and the front view of ash enclosure (2) with control panel (E) and its inside consisted of air cyclone (F) and ash packing instrument (G) were shown in Fig. 7.5.

### 7.3.3 Demonstration Test of Combustion for Forestry Wastes

The decontamination experiments were carried out at Fukushima Forestry Research Center in March 2014. Two combustion tests using 2.3 kg of pine needles with 1.0 kg of cedar bark and 2.5 kg cedar bark with 0.4 kg of cedar sapwood were burned with slow temperature increment from 400 to 700 °C for 1 h. The mass and radiocesium concentration in forestry wastes used for the combustion tests were listed on Table 7.1. About 550 L of water was used for the smoke extraction. During the demonstration tests, the surrounding temperature was about 4–6 °C; the initial temperature of water was about 5 °C and became 45 °C after the combustion tests. After the combustion test, about 5 L of water was lost by evaporation. From these values, the heat transfer from smoke to water was 2.9 kWh, which corresponded to 200 kWh scale combustion furnace, such as wood chip boiler and incinerator. No radiocesium was detected (the lower limit of 0.2 Bq/kg) in the air filter where the exhausted steam passed from this system during the decontamination.

Immediately after the combustion tests, the clear water changed the black soot-suspended water with pH 7.2. The sewage water absorbed the acidic compound caused by the decomposition of wood components and the soot. The suspended soot in sewage absorbed on the surface of water tank overnight; the optical clear and pale yellow sewage water was obtained. The smoke tube with 5 m length took off from the system and separated to pieces; the soot absorbed in smoke tube was washed by 100 L of water. The sewage water (50 Bq/L, about 545 L) and the soot-washed water (soot suspended water, 60 Bq/L, about 100 L) were decontaminated by the filter system with 300 g of Prussian blue-dyed wool filter. After 1 h filtration, no radiocesium was detected by Ge semiconductor detector with 0.2 Bq/L of the lower limit. The decontaminated water was recyclable in this system.

**Table 7.1** Mass and radiocesium concentration of materials used for the combustion test and obtained after the combustion

Raw materials of combustion			Collected materials after combustion		
Materials	$^{134}\text{Cs} + ^{137}\text{Cs}$	Mass	Materials	$^{134}\text{Cs} + ^{137}\text{Cs}$	Mass
	Bq/kg	kg		Bq/kg	kg
Pine needle <sup>a</sup>	22,000	2.3	Ash	440,000	0.14
Cedar bark <sup>a</sup>	10,800	1.0	Soot in water <sup>b</sup>	290,000	>0.0015
Cedar bark <sup>c</sup>	15,000	2.5	Soot in flue <sup>d</sup>	60	100
Sapwood <sup>c</sup>	50	0.4	Sewage water <sup>e</sup>	50	545

<sup>a</sup>Materials used for the first combustion test

<sup>b</sup>Soot suspended in sewage water absorbed on water tank, collected from the water tank surface

<sup>c</sup>Materials used for the second combustion test

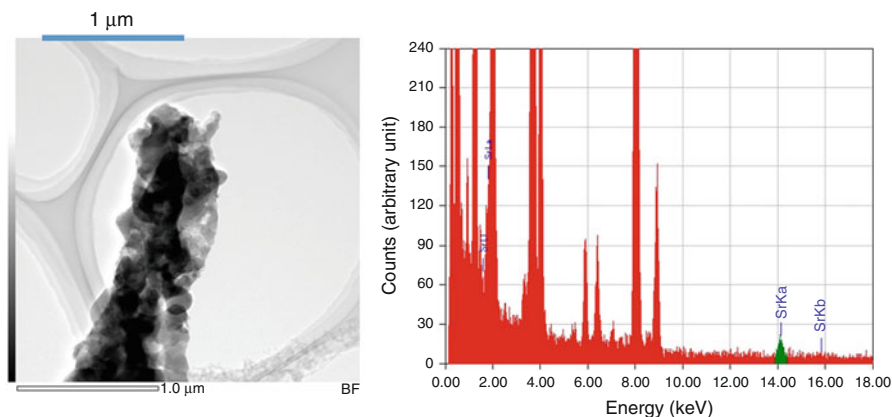
<sup>d</sup>Soot absorbed in smoke tube washed by 100 L of water

<sup>e</sup>Sewage water after filtration of suspended soot

The ash was collected by the enclosure under the reduced pressure and was packed and sealed automatically in the antistatic polyethylene bag under vacuum. After sealing the ash, the package of ash was easily handled without further contamination. The mass and radiocesium concentration of ash, sewage water, separated soot and washed soot from the smoke tube were shown in Table 7.1. The ratio of mass of ash against the raw materials was 22.2 %, which indicated that the combustion proceeded in imperfect condition. The soot suspended in sewage water and absorbed in smoke tube also suggested the imperfect combustion. The collected ash included white powder and black charcoal particles caused by the imperfect combustion.

The mass balance of radiocesium before and after the combustion was evaluated. The initial amount of radiocesium in the raw materials was 98,920 Bq; the amount of radiocesium in the collected materials was 95,285 Bq. About 95 % of radiocesium was recovered by this combustion system. The difference between total amount of radiocesium before and after the combustion was caused by the uncertainty of initial concentration due to the inhomogeneity of radiocesium distribution in pine needles and bark, and the radiocesium remained as soot in the woodstove, smoke tube and water tank.

The transmission electron microscopic observation and EDX spectrum of white ash were shown in Fig. 7.6. The main component of white ash was calcium oxide from X-ray diffraction analysis. EDX spectrum analysis indicated the existence of boron (0.187 keV,  $\text{BK}\alpha$ ), magnesium (1.25 keV,  $\text{MgK}\alpha$ ), silica (1.74 keV,  $\text{SiK}\alpha$ ), phosphor (2.01 keV,  $\text{PK}\alpha$ ), manganese (5.89 keV,  $\text{MnK}\alpha$ ), iron (6.38 keV,  $\text{FeK}\alpha$ ), copper (8.0 keV,  $\text{CuK}\alpha$ ), zinc (8.63 keV,  $\text{ZnK}\alpha$ ) and strontium (14.1 keV,  $\text{SrK}\alpha$ ) addition to calcium (3.69 keV,  $\text{CaK}\alpha$ ). Mg, P, Mn, Zn and Ca were the base element of plants, and B, Si, Fe, Cu and Sr came from the soil contamination of plants. The existence of radiocesium was not clear due to the low concentration in ash, because the estimated radiocesium concentration was about 12 ppb evaluated from 440,000 Bq/kg. The main component of calcium oxide formed the solid solution



**Fig. 7.6** Transmutation electron microscopic image (*left*) and EDX spectrum (*right*) of ash

with these elements. The water-soluble radiocesium from 5 g of ash was extracted by 4 L of water stirring for 5 h at room temperature. After the filtration of insoluble ash, the filtered water contained 260 Bq/L of radiocesium, which indicated 47 % of radiocesium in ash was water soluble. This result suggested that the storage of the ash from forestry wastes should be done with the extreme care not to leak the water-soluble radiocesium to the environment.

## 7.4 Conclusion

The mass balance of radiocesium in forestry wastes by combustion was evaluated with the laboratory-scale combustion tests and the demonstration combustion tests. About 30–35 % of radiocesium in cedar bark evaporated by the combustion under air flow condition at temperature above 500 °C. Most evaporated radiocesium was trapped efficiently by water.

Based on the laboratory combustion test, the decontamination system for the combustion of forestry wastes was developed. The decontamination system consisted of three modules, the smoke extraction apparatus by water, the combustion ash coagulate apparatus and the radiocesium filtration unit from the sewage water.

The demonstration combustion test for forestry wastes using the developed decontamination system was carried out. No gaseous radiocesium was detected in the exhausted air from this system during the decontamination of forestry wastes. About 80 % of mass of forestry waste decreased by the combustion, and 95 % of radiocesium was collected safely by the developed system. The ash caused by the combustion of forestry waste contained about 45 % of water-soluble radiocesium.

**Open Access** This chapter is distributed under the terms of the Creative Commons Attribution Noncommercial License, which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

## References

1. MECSSST; Ministry of Education, Culture, Sports, Science and Technology (2011) 6th air dose monitoring by aircraft. [http://radioactivity.nsr.go.jp/ja/contents/7000/6749/24/191\\_258\\_0301\\_18.pdf](http://radioactivity.nsr.go.jp/ja/contents/7000/6749/24/191_258_0301_18.pdf)
2. Nakanishi T, Tanoi K (eds) (2013) Agricultural implications of the Fukushima nuclear accident. Springer, Tokyo
3. Yoshida H (2012) Contamination analysis of radionuclide in soils and plants caused by Fukushima nuclear power plant accident. *Chem Eng* 6:250–257
4. Kikawada Y, Hirose M, Tsukamoto A, Nakamachi K, Oi T, Honda T, Takahashi H, Hirose K (2015) Mobility of radioactive cesium in soil originated from the Fukushima Daiichi nuclear disaster; application of extraction experiments. *J Radioanal Nucl Chem* 304(1):27–31
5. Matsuda N, Mikami S, Shimoura S, Takahashi J, Nakano M, Shimada K, Uno K, Hagiwara S, Saito K (2015) Depth profiles of radioactive cesium in soil using a scraper plat over a wide area surrounding the Fukushima Dai-Ichi nuclear power plant, Japan. *J Environ Radioact* 139:427–434
6. Yoshida H (2014) Transportation and restraint of radiocesium in forest near the populated area. *Green Power* 2:14–15
7. Kuroda K, Kagawa A, Tonosaki M (2013) Radiocesium concentrations in the bark, sapwood and heartwood of three tree species collected at Fukushima forests half a year after the Fukushima Dai-ichi nuclear accident. *J Environ Radioact* 122:37–42
8. Yoshihara T, Matsumura H, Hashida S, Nagaoka T (2013) Radiocesium contaminations of 20 wood species and the corresponding gamma-ray dose rates around the canopies at 5 months after the Fukushima Nuclear Power Plant accident. *J Environ Radioact* 115:60–68
9. Ogawa H, Ito H, Yokota K, Arai S, Masumoto K, Yoshida H (2015) Radiocesium distribution and changes of the wood in Sugi and Hinoki caused by the accident of Fukushima Daiichi Nuclear Power Plant. In: Proceedings of the 16th workshop environmental radioactivity, KEK, Japan, vol 2015-8, pp 302–309. <http://ccdb5fs.kek.jp/tiff/2015/1525/1525004.pdf>
10. Ogawa H, Ito H, Murakami K, Kumata A, Hirano Y, Yokota K, Yoshida H (2014) Radiocesium distribution in Japanese Cedar trees at one year after Fukushima Dai-ichi nuclear power plant accident. In: Proceedings of the 15th workshop on environmental radioactivity, KEK, Japan, vol 2014-7, pp 252–260. <http://ccdb5fs.kek.jp/tiff/2014/1425/1425007.pdf>
11. Mahara Y, Ohta T, Ogawa H, Kumata A (2014) Atmospheric direct uptake and long-term fate of radiocesium in trees after the Fukushima nuclear accident. *Sci Rep* 4:7121–7127
12. Internet news, Fukushima Minyu, October 11, 2013. <http://www.minyu-net.com/osusume/daisinsai/serial/131011/news3.html>
13. Internet news, Fukushima Minpo, May 5, 2015. [http://www.minpo.jp/pub/topics/jishin2011/2013/02/post\\_6181.html](http://www.minpo.jp/pub/topics/jishin2011/2013/02/post_6181.html)
14. Ozawa T (2004) Thermal analysis. In: Sorai M (ed) Comprehensive handbook of calorimetry and thermal analysis. JSCA, Wiley, Chichester
15. Tsuge A, Outani H, Watanabe C (eds) (2006) Pyrolysis-GCMS of highpolymers, Techno-system, Tokyo
16. Tokyo Metropolitan University, Closed smoke extract system, Japanese Patent 2013-224831

# Chapter 8

## Remediation Technology For Cesium Using Microbubbled Water Containing Sodium Silicate

Yoshikatsu Ueda, Yomei Tokuda, and Hiroshi Goto

**Abstract** Remediation of materials contaminated with a radioactive material such as  $^{137}\text{Cs}$  is important for public health and environmental concerns. Here, we report the effectiveness of aqueous sodium metasilicate (SMC) prepared using a microbubble crushing process for the removal of radioactive  $^{137}\text{Cs}$  from contaminated materials. We have already reported that almost 80 %  $^{137}\text{Cs}$  removal was achieved for a nonwoven cloth sample in which multiple washings using low SMC concentrations were effective. In addition, the volume of the waste solution can be reduced by neutralizing the SMC and using gelation to remove the radioactive material. We also attempt to clarify the mechanism of SMC operation by measuring its electrical properties. Decontamination is shown to be more efficient with SMC than with sodium hydroxide, even for washing granule conglomerates.

**Keywords** Radioactive cesium • Microbubble • Sodium metasilicate • Cs-137

### 8.1 Introduction

The accident at the Fukushima Daiichi nuclear power plant in 2011 following the Great East Japan Earthquake resulted in the dispersal of radioactive Cs into the environment and the contamination of an extensive area of soil. Various decontamination methods have been developed and applied in Fukushima Prefecture [1–4], but optimum methods for remediation of materials under specific contamination conditions still need to be developed. Radioactive Cs adsorbs on soil particles through ion exchange with potassium [5, 6]. Our research focused on using aqueous

---

Y. Ueda (✉)

Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji,  
Kyoto 611-0011, Japan

e-mail: [yueda@rish.kyoto-u.ac.jp](mailto:yueda@rish.kyoto-u.ac.jp)

Y. Tokuda

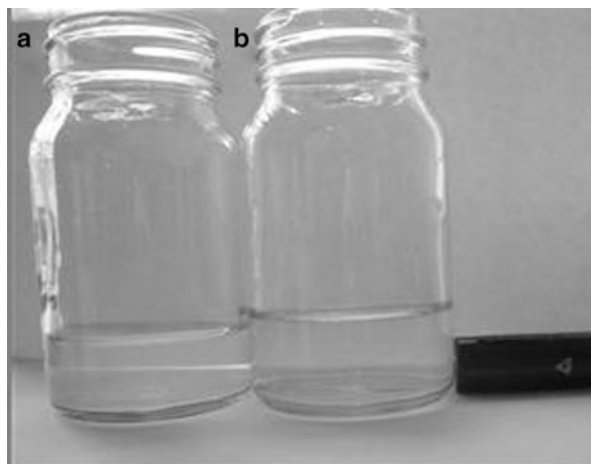
Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

e-mail: [tokuda@noncry.kuicr.kyoto-u.ac.jp](mailto:tokuda@noncry.kuicr.kyoto-u.ac.jp)

H. Goto

Kureha Trading Co., Ltd., 1-2-10, Horidomecho, Nihonbashi, Chuo-ku, Tokyo 103-0012, Japan

**Fig. 8.1** Photographs of aqueous sodium metasilicate irradiated by a green laser after storage for one-half year. The metasilicate was dissolved in water (a) without crushing, and (b) with crushing [1]. The black object in the lower right corner is the green laser



sodium metasilicate as a new detergent and possible decontamination agent. We examined the mechanism and principle of the change in the chemical reaction characteristics of aqueous sodium metasilicate after microbubble and ultrasonic treatments. We found that, because aqueous sodium metasilicate is not a surfactant, it has a low environmental load and does not exhibit foaming characteristics. It can be used with hard, soft, or sea water and is a “peeling detergent” in terms of its cleaning activity, which differentiates it from dissolving detergents such as organic solvents. As a peeling detergent, aqueous sodium metasilicate is suitable for foaming, jet streaming, high-pressure ultrasonic wave, and spray cleaning. A microbubble crushing process [7, 8] can also be used to suppress precipitation during long-term storage [9] (see Fig. 8.1).

Coprecipitation can be used to decrease the volume of the waste solution produced because sodium metasilicate turns into a gel that traps Cs when neutralized with acid [10]. Coprecipitation followed by gel formation can be used to separate the  $^{137}\text{Cs}$  gel from the soil, yielding a decontaminated waste product.

## 8.2 Experimental

### 8.2.1 Preparation of Aqueous Sodium Metasilicate

A 0.47 mol/kg solution of sodium metasilicate nonahydrate ( $\text{Na}_2\text{O}_3\text{Si}\cdot 9\text{H}_2\text{O}$ ) was prepared by dissolution in filtered water (manufactured using G-20B; Organo Corporation). A microbubble generator (capable of generating  $>20,000$  microbubbles/mL) was manufactured by Kyowa Engineering and used to interfuse microbubbles into the solution. Ultrasonic irradiation (40 kHz; ultrasonic wave generator UT-1204U and ultrasonic transducer UI-12R3; Sharp Corporation) was employed to crush the bubbles, and the resulting solution, aqueous sodium metasilicate prepared

with a microbubble crushing process (abbreviated here as SMC), was used as the nonsurfactant aqueous detergent. Purified water and aqueous sodium hydroxide with the same pH as SMC (pH = 13.1) were prepared for comparison. To analyze the structure of the sodium metasilicate in SMC and understand the dissolution stability, we measured the electrical conductivity and dissolved oxygen content every 5 min during the microbubble crushing process. We also compared the change in conductivity of SMC after 6 h.

### 8.2.2 *Cleaning Method*

Depending on the individual diameters and buoyancy, microbubbles only remain in water for several minutes. They can remain in an aqueous environment for longer times, however, if an ultrasound treatment is used to reduce their size [11]. An ultrasound pretreatment of aqueous sodium metasilicate to form SMC and reduce the bubble size does not decrease the eduction rate of aqueous sodium metasilicate and offers the possibility of sustained cleansing. In this experiment, we conducted a cleaning test in a standing solution so that we could focus on the chemical cleansing effects due to the synergy between aqueous sodium metasilicate and microbubbles as opposed to focusing on the physical cleansing effects [1].

Granule conglomerates and nonwoven cloths were used as the materials to be cleaned. The ~150-g granule conglomerate samples were collected from soil in a hot spot (~500,000 Bq/kg) at the Fukushima Agricultural Technology Centre. These pieces of nonwoven cloth (made of polypropylene) were used in farm work at farms exposed to the fallout from the nuclear accident in Fukushima Prefecture. The cloths had an average weight of 2.65 g, and the average amount of  $^{137}\text{Cs}$  exhibited approximately 1633 Bq/sample (616,226 Bq/kg) of radioactivity.

The granule conglomerate and nonwoven cloth samples were immersed in 100 mL of several SMC concentrations for 20 h. Twelve granule conglomerate samples were prepared. These samples were divided into four groups of three samples. One group was washed in NaOH, one in normal sodium metasilicate, and the remaining two were washed in 10- and 100-wt% solutions of SMC. The 28 cloth samples were divided into 4 groups of 7 samples, and 1 group was washed in water, while the other 3 groups were washed in 1-, 10-, and 100-wt% solutions of SMC. To examine the effects of multiple washings, samples were tested after 6 h of immersion before the second and third washes. After these immersion tests, the samples were dried at 40 °C for 40 h until they were free of moisture [2].

To reduce the volume of waste solution, hydrochloric acid (HCl) was added to neutralize the detergent solutions after washing, which resulted in gelation. The gel and clear supernatant were then separated by filtration, and the radiation intensities (counts per second, cps) of the gel and supernatant were measured. We tried to remove  $^{137}\text{Cs}$  from SMC solutions by neutralization. We prepared three samples of 10 and 100 wt% SMC solutions, and then neutralized and filtered them. We measured the radiation intensity and compared the results of the two remediation methods.

### 8.2.3 Radiation Measurement

The background radiation intensity of the nonwoven cloth specimens was measured using the germanium semiconductor detector at the Radioisotope Research Center, Kyoto University. The main unit of the detector is made from high-purity germanium (GMX-18200-S; EG&G Ortec), with a germanium crystal that is 102 cm<sup>3</sup> and a relative efficiency of 22.3 % (efficiency ratio of a 3'' × 3'' NaI (TI) (76 × 76 mm) crystal relative to that of the <sup>137</sup>Cs 662 keV gamma ray). The entrance window is a 0.5-mm-thick beryllium plate, which allows the detection of X-rays 3 keV or higher in energy, as well as high-energy gamma rays. The energy resolution was 0.54 keV for <sup>55</sup>Fe 5.9-keV (Mn K $\alpha$ ) X-rays and 1.8 keV for <sup>60</sup>Co 133-MeV gamma rays. A special container (100 mL) was used to analyze the nonwoven cloth specimens. The removal ratio was defined as the ratio of the radiation intensity from the sample after and before immersion, as shown in Eq. 8.1.

$$\text{Removal ratio [\%]} = \frac{\text{After immersion [cps]}}{\text{Before immersion [cps]}} \times 100 \quad (8.1)$$

## 8.3 Results

### 8.3.1 Electrical Properties of SMC

Figure 8.2 shows the measured electrical conductivity and dissolved oxygen content during the SMC-making process. The electrical conductivity of each sample was measured every 5 min. In Fig. 8.3, we show real-time electrical conductivity data sampled 6 h after the data in Fig. 8.2. The results show that SMC is almost stabilized after 10 min, but compared with the real-time data, 1 h of microbubble crushing was required to stabilize the electrical conductivity.

### 8.3.2 Washing the Granule Conglomerate

The removal ratios of <sup>137</sup>Cs from the granule conglomerate using SMC (10 and 100 wt%), NaOH, and aqueous sodium hydroxide (Fig. 8.4) show that, while the decontamination efficiency of SMC was low, it was still more than 10 times higher than using sodium hydroxide at the same pH. Furthermore, the higher efficiency of SMC compared with sodium metasilicate without the microbubble treatment confirms the effectiveness of SMC. One of the characteristics of SMC is that the concentration of dissolved oxygen does not increase after aeration. Hence, a large number of adsorption pits (sites) are probably present, similar to zeolites. Thus, cesium ions present in water will be incorporated into the silicate. In addition, the



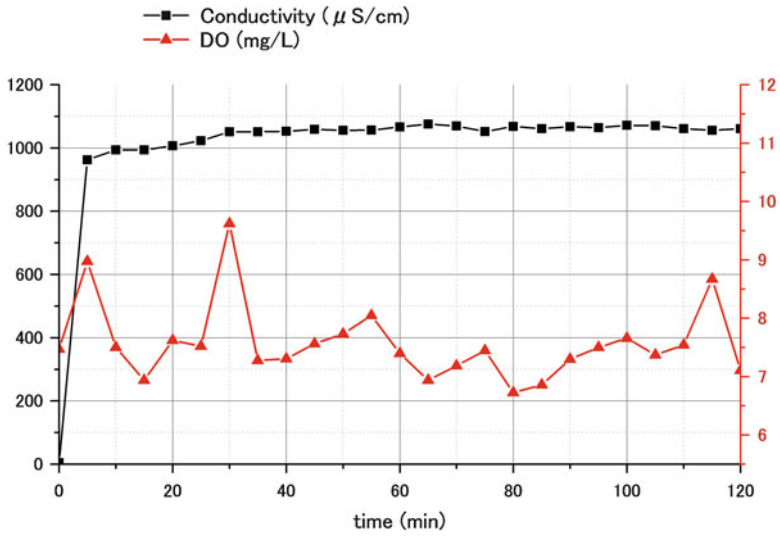


Fig. 8.2 Electrical conductivity and dissolved oxygen content during the microbubble crushing process

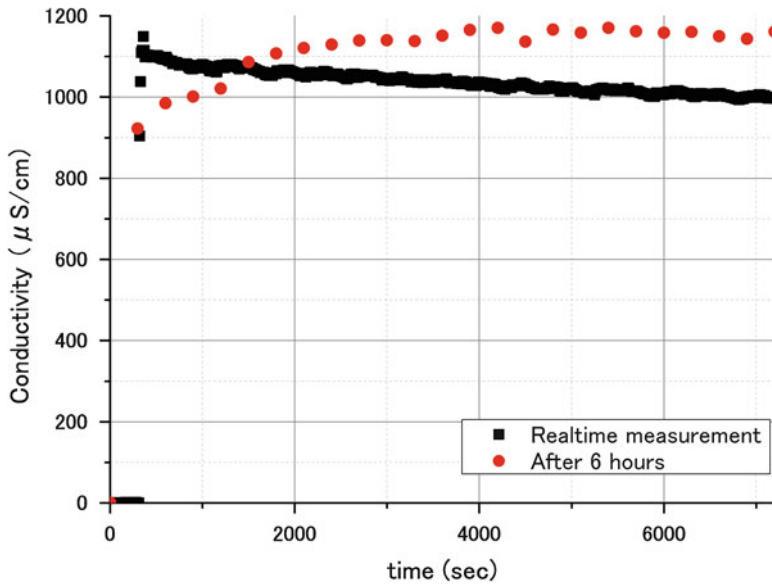
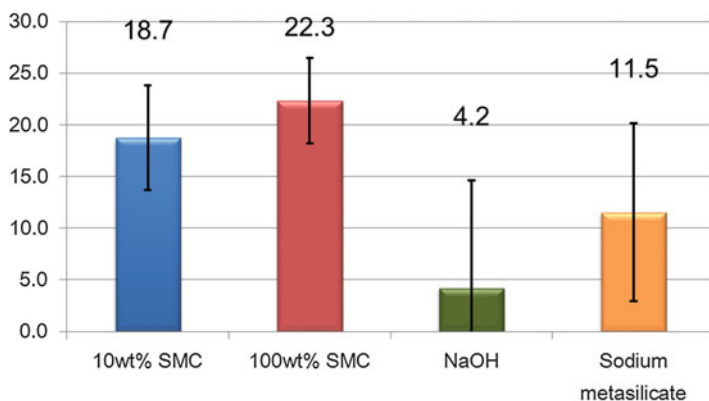


Fig. 8.3 Plot of conductivity versus time during the microbubble crushing process



**Fig. 8.4** Average removal ratios of  $^{137}\text{Cs}$  from the granule conglomerate samples using 10- and 100-wt% SMC, NaOH, and sodium metasilicate

**Table 8.1**  $^{137}\text{Cs}$  removal ratios of using purified water and SMC for the nonwoven cloth samples\*

Washing	Pure water	1-wt% SMC	10-wt% SMC	100-wt% SMC
First	0	44.5	59.5	77.5
Second	–	34.5	27.5	51.4
Third	–	20.6	–	–

\*Pure water was used for the first washing, whereas 10- and 100-wt% SMCs were used for the second washing

decontamination efficiency increased because the alkaline solutions dissolved the granule conglomerate.

### 8.3.3 Washing the Nonwoven Cloth

The cleaning performance of SMC at various concentrations is compared in Table 8.1, which lists the average removal ratios for multiple washings with SMC concentrations of 1, 10, and 100 wt% compared with pure water [2].

As expected, almost no  $^{137}\text{Cs}$  was removed by washing with pure water, but significant decontamination occurred as soon as SMC was introduced. Since the nonwoven cloth samples were previously used in agricultural fields, they also contained traces of fertilizers and other organic materials. As mentioned previously, sodium metasilicate detergent is used for washing because it has a capacity for breaking down organic materials via saponification, which is a result of its alkaline nature. We anticipate that we will be able to increase the efficiency of this detergent using microbubbles and ultrasound treatments. Organic components such as sebum and oil that are contaminated with  $^{137}\text{Cs}$  are likely to be eluted from the nonwoven

cloth owing to the alkalinity of SMC. The data in Table 8.1 also show that even with 1 wt% SMC, the removal ratio is 60 % of that obtained with 100 wt% SMC after the first washing. This result shows that the amount of detergent used for remediation can be reduced to a low concentration.

In the case of multiple washings, the background radiation intensity decreased considerably after the third washing using a highly concentrated (10 or 100 wt%) SMC solution. Therefore, a 1 wt% SMC solution was used for further analysis. The removal ratios after each wash with the 1 wt% solution, listed in Table 8.1, were 64 % for the second wash and 71 % for the third wash, indicating that even at a concentration of 1 wt%, significant decontamination of nonwoven cloth materials can be achieved after multiple washings. Though there was only a slight decrease in the removal ratios compared with higher wt% SMC solutions, we believe that using 1 wt% SMC is an effective washing method for even higher levels of contaminants because the need for further decontamination of materials in the Fukushima Prefecture still exists.

### 8.3.4 Remediation of $^{137}\text{Cs}$ by Neutralizing SMC

Reduction in the waste solution volume obtained after using SMC was also investigated. We prepare three samples each of 10 and 100 wt% SMC waste solution. Solutions were neutralized by HCl and the gels separated from the filtered solution. By measuring the radiation intensity then normalizing the readings, we were able to compare the gels and filtered solutions (Fig. 8.5).  $^{137}\text{Cs}$  was captured

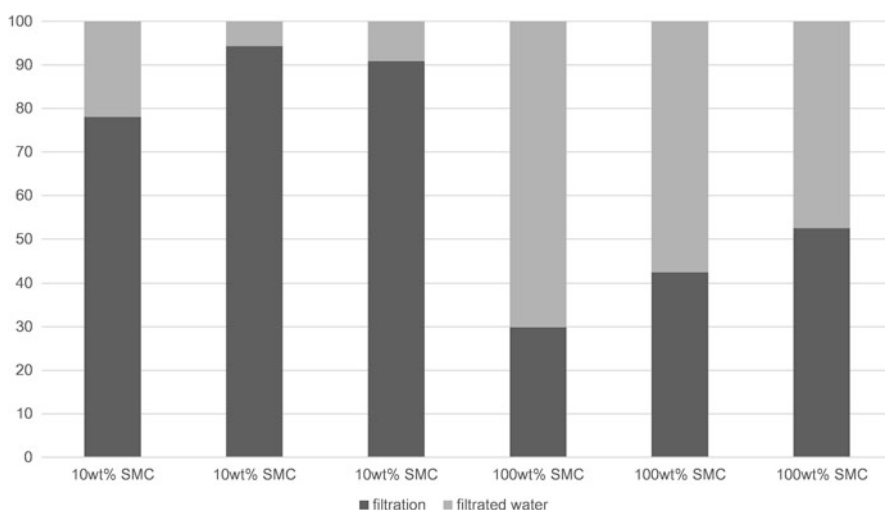


Fig. 8.5 Remediation of  $^{137}\text{Cs}$  by neutralizing SMC (10 and 100 wt%)

in the gel after coprecipitation [1, 2]. Hence, each concentration of SMC has the ability to capture Cs effectively. We discovered, however, that the 100 wt% SMC solution had an opposite ability compared with the other solutions. It is because sodium metasilicate can leave its captured ions in water. We need much additional experimentation to determine the optimum conditions for capturing Cs in SMC gels. We are currently trying to neutralize the SMC by alcohol and cleanup  $^{137}\text{Cs}$  from waste solutions.

## 8.4 Conclusions

We have examined the cleaning performance of SMC by comparing the radioactivity of waste solutions before and after washing contaminated granule conglomerates and nonwoven cloth samples. A study of the changes in the chemical characteristics of SMC was also undertaken.  $^{137}\text{Cs}$  particulates attached to a nonwoven cloth sample were removed effectively by SMC cleaning. After cleaning, the remaining dissolved aqueous sodium metasilicate from the SMC had a better treatment capacity (after neutralization) than standard aqueous solutions. Thus, the use of SMC should contribute significantly to the decontamination work currently being undertaken in urban and rural areas where decontamination cannot be performed by using water alone. We are currently attempting to measure the chemical structure of SMC by SPring-8. We will be able to report the results of this new study in the near future.

**Acknowledgments** This work was financially supported by Kyoto University, The Japan Association of National Universities, Japan Association for Chemical Innovation (JACI), ITOCHU Foundation, and the Collaborative Research Program of Institute for Chemical Research, Kyoto University (No. 2013-63). We thank N. Nihei, S. Fujimura, T. Kobayashi, Y. Ono, M. Tosaki, and T. Minami for helpful discussions and experimental preparation. We appreciate the SMC samples (JPAL) provided by Kureha Trading Co. Ltd. The synchrotron radiation experiments were performed at the BL14B2 beamline of the SPring-8 facility with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2015A1662).

**Open Access** This chapter is distributed under the terms of the Creative Commons Attribution Noncommercial License, which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

## References

1. Ueda Y, Tokuda Y, Goto H, Kobayashi T, Ono Y (2014) Removal of radioactive Cs using aqueous sodium metasilicate with reduced volumes of waste solution. *ECS Trans* 58(19):35
2. Ueda Y, Tokuda Y, Goto H, Kobayashi T, Ono Y (2013a) Removal of radioactive Cs from nonwoven cloth with less waste solution using aqueous sodium metasilicate. *J Soc Remed Radioact Contam Environ* 1:191

3. Ueda Y, Tokuda Y, Fujimura S, Nihei N, Oka T (2013b) Cesium transfer from granule conglomerate using water containing nano-sized air bubbles. *ECS Trans* 50(22):1
4. Ueda Y, Tokuda Y, Fujimura S, Nihei N, Oka T (2013c) Removal of radioactive Cs from gravel conglomerate using water containing air Bubbles. *Water Sci Technol* 67:996
5. Raskin I, Ensley BD (eds) (2000) *Phytoremediation of toxic metals: using plants to clean up the environment*. Wiley, New York
6. Willey N (ed) (2007) *Phytoremediation: methods and reviews*. Humana Press, Totowa
7. Agarwal A, Ng WJ, Liu Y (2011) Principle and applications of microbubble and nanobubble technology for water treatment. *Chemosphere* 84:1175
8. Stride E (2008) The influence of surface adsorption on microbubble dynamics. *Philos Trans R Soc A* 366:2103
9. Suwabe J (2010) Manufacturing method of a water-based cleaning agent. Japanese Patent (Kokai), 2010-1451
10. Merrill RC, Spencer RW (1950) Gelation of sodium silicate; effect of sulfuric acid, hydrochloric acid, ammonium sulfate, and sodium aluminate. *J Phys Colloid Chem* 54:806
11. Takahashi M, Kawamura T, Yamamoto Y, Ohnari H, Himuro S, Shakutsui H (2003) Effect of shrinking microbubble on gas hydrate formation. *J Phys Chem B* 107:2171

# Chapter 9

## Extractability and Chemical Forms of Radioactive Cesium in Designated Wastes Investigated in an On-Site Test

Yoko Fujikawa, Hiroaki Ozaki, Xiaming Chen, Shogo Taniguchi, Ryouhei Takanami, Aiichiro Fujinaga, Shinji Sakurai, and Paul Lewtas

**Abstract** In the aftermath of the 2011 accident at Fukushima Daiichi Nuclear Power Plant (F1 hereafter), municipal solid waste (MSW) contaminated with radioactive cesium (rad-Cs hereafter) has been generated in 12 prefectures in Japan. The Japanese Minister of Environment classified MSW that contained rad-Cs in the concentration more than 8,000 Bq/kg as “designated (solid) waste (DSW hereafter), and prescribed the collection, storage and transportation procedures. When MSW containing rad-Cs was incinerated, rad-Cs was concentrated in fly ash, and the ash often fell into the category of DSW. We have investigated a technique that can reduce the volume of the rad-Cs-contaminated fly-ash by extracting rad-Cs with aqueous solvents such as water and oxalic acid and concentrating rad-Cs in a small amount of hexacyanoferrate (or ferrocyanide, designated as Fer hereafter) precipitate. Since DSW could not be transported to the outside laboratory, we have conducted on-site tests at places where DSW were generated to investigate the applicability of the extraction – precipitation technique.

The present report is a summary of our most recent on-site test conducted in 2014. Also presented is the re-evaluation of the results of our past on-site test from the viewpoint of leaching of rad-Cs and heavy metals in the fly ash. An apparent decrease in leaching of rad-Cs from fly ash was observed by incinerating sewage sludge with soil. Fly ash from a melting furnace contained more water-soluble rad-Cs than that from a fluidized-bed incinerator. Some incinerator fly ash appeared to

---

Y. Fujikawa (✉)

Kyoto University Research Reactor Institute, Asahiro-nishi, Kumatori-cho, Sennan-gun, Osaka 590-0458, Japan

e-mail: [fujikawa@rri.kyoto-u.ac.jp](mailto:fujikawa@rri.kyoto-u.ac.jp)

H. Ozaki • X. Chen • S. Taniguchi • R. Takanami • A. Fujinaga

Osaka Sangyo University, 3-1-1 Nakagaito, Daito city, Osaka 574-8530, Japan

S. Sakurai

Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai-shi, Osaka 599-8531, Japan

P. Lewtas

Edith Cowan University, 270 Joondalup Drive, Joondalup, WA 6027, Australia

© The Author(s) 2016

T. Takahashi (ed.), *Radiological Issues for Fukushima's Revitalized Future*,

DOI 10.1007/978-4-431-55848-4\_9

produce rad-Cs in colloidal form when extracted with oxalic acid, resulting in the lower removal of rad-Cs from the extract by Fer method.

**Keywords** Ferrocyanide (hexacyanoferrate) • Radioactive cesium • Designated waste • Leaching • Water • Oxalic acid

## 9.1 Background Information on the Aftermath of the F1 Accident

Four years have passed since the 2011 Eastern Japan Great Earthquake Disaster and the F1 accident that resulted in the first case of widespread contamination of the general environment with rad-Cs in Japan. Millions of people have continued to live in the zone that received rad-Cs fallout higher than the level of background global fallout observed in the middle latitudes of the northern hemisphere [1, 2]. Public and semi-public services indispensable for daily life, e.g. supply of electricity and potable water, sewage treatment, garbage collection, public transportation, etc., had been reconstructed relatively quickly after the 2011 disaster (e.g. [3, 4]). Among these services in the affected areas, potable and sewage water treatment and garbage collection have produced drinking water treatment sludge, sewage sludge, and incinerator ashes containing elevated concentration of rad-Cs. Both disposal and reuse have become difficult for such wastes, resulting in sludge and ashes piling up in many treatment facilities.

The government of Japan has proposed to construct landfills with special leachate collection and treatment systems along with a radiation monitoring system for the disposal of wastes with rad-Cs concentration higher than 8,000 Bq/kg (so-called DSW). But so far the plan has stalled due to public criticism. We have summarized the situation in our previous reports [5, 6], and the situation has remained unchanged concerning the final disposal of DSW.

## 9.2 Strategy of Volume Reduction and Stabilization of Municipal Solid Waste and Designated Waste in Japan

Under the circumstances delineated above, the volume reduction of various wastes contaminated with rad-Cs is of paramount importance. The thermal treatment, with emphasis on incineration, has been the topmost strategy for stabilization and volume reduction of municipal and industrial wastes in Japan [7]. Also, thermal treatment has been a recommended option for volume reduction of combustible radioactive wastes for a long time [8]. Consequently, incineration has been planned and conducted on vegetation and paddy straw removed in the course of the cleanup work and sewage sludge contaminated with rad-Cs from the area with high rad-Cs

fallout, resulting in generation of bottom ash and fly ash possessing diverse leaching characteristics of rad-Cs and non-radioactive hazardous components.

In Japan, various pretreatment procedures have been studied and administered for incinerated MSW before burying the waste in landfills [9, 10]. The purpose of the pretreatment had been to accelerate the waste stabilization, namely to prevent the leaching of toxic elements, hazardous organic substances and dissolved and/or suspended organic matters related with BOD and COD values, from the waste. Among such procedures was the washing of ashes with acid or water (e.g. [11, 12]). The washing effectively removed the major elements from MSW incineration ashes and also reduced the leachability of toxic elements from the washed residues. In a full-scale acid extraction process, washed ash became a stabilized cake to be buried in a landfill, solid salt was recycled to soda production plants, condensed water was recycled in the plant as cooling water and no wastewater was discharged from the plant [11]. More recently, a group of researchers and engineers proposed the “wash out waste” (WOW) system in which solid waste was inactivated by washing before landfilling, resulting in rapid stabilization of the buried waste and early closure of the landfill [13]. The WOW system can reduce the possibility of long-term contamination of the environment by landfill leachate, and may also help gain public support for the siting of landfills.

After the F1 accident and the concomitant pollution of MSW with rad-Cs, waste-washing technology has drawn the attention of researchers and private companies again. The nature of Cs in incinerated (or in some case smelted) ashes and the decontamination technology to remove rad-Cs from the wastes or waste extracts have been investigated [5, 6, 14–16]. Parajuli et al. [14] pointed out that the percentage of water-soluble rad-Cs is much smaller in sewage ash compared to that in wood and garbage ash, probably because of clay minerals of pedogenic origin present in the sewage sludge. Saffarzadeh et al. [15] studied the behaviour of Cs in bottom ash using stable Cs salts in a pilot incinerator, and reported that Cs in bottom ash could be most commonly found in the silicate glass matrix. Kozai et al. [16] studied the mineralogical components of sewage sludge ashes and reported that the majority of rad-Cs was in the HCl-soluble phase, and was probably contained in iron oxides.

The fly ash washing technique to eliminate rad-Cs has been also studied by some private companies, and the initial and running cost of the technology has been estimated [17]. In the processes developed by the companies, the use of Fe compounds to remove rad-Cs from the washing solution was a prerequisite. A report by the Institute of National Environmental Studies [18] defined the category of rad-Cs containing wastes for which washing processes can be applied and the performance requirements as well as radiation safety standard of the washing system.



### 9.3 Principle of Ferrocyanide Coprecipitation for Cs Removal

The principle of the Fer method for removal of Cs is reviewed in literatures [19–21], as well as in our previous report [5, 6]. In brief, the method utilizes the extremely high affinity of the Cs cation to insoluble Fer compounds. The insoluble Fer compounds are prepared by reacting soluble Fer salts (K, Na or H compounds) with metal (Fe, Cu, Zn, Ni, Cd, Mn, etc.) ions in solution.

There are three different ways to use Fer in order to remove Cs: (1) addition of soluble Fer salts and metal elements to waste solution (in situ formation of Fer solid), (2) addition of freshly prepared insoluble Fer metal complex slurry to waste solution and (3) use of Fer-metal adsorbents in solution. The distribution ratio of Cs to insoluble Fer compounds is high in the order of method (1) > (2) > (3). Throughout our experiment, we have used method (1) (in situ method) as much as possible, and have used method (2) (addition of the fresh Fer solid) when method (1) could not be used, e.g. when Zn concentration in the solution is very high and Zn-Fer was going to be the prevalent Fer solid to be formed.

### 9.4 The Waste Volume Reduction When Ferrocyanide Coprecipitation Technique Was Used

We have been working on a technique that extracts rad-Cs from DSW (especially rad-Cs contaminated fly ash) with water or hot oxalic acid, and selectively removes rad-Cs from the extract as a small amount of precipitate utilizing the Fer coprecipitation technique. The focus of our research has been to achieve the efficient removal of rad-Cs from the waste extracts having a complex composition. So far, we have found that more than 95 % of rad-Cs could be removed from the extracts of MSW under an optimized combination of pH, Fer concentration and type of metal-Fer complex formed in the extract. A high Zn concentration in the extract suppressed the removal of Cs by the Fer precipitation method [5, 6].

The waste volume reduction  $d$  [%] and the ratio of rad-Cs concentration in the precipitate to that of the original waste  $Q_{Cs}/C_0$  are estimated by the following equation:

$$d = 100 \left( 1 - \frac{pV}{M} \right) \quad (9.1)$$

$$\frac{Q_{Cs}}{C_0} = \frac{100}{100 - d} rE \quad (9.2)$$

where  $M$ : weight [kg] of MSW extracted by  $V$  [L] of the solvent,  $p$  [kg/L]: weight of Fer precipitate formed per unit volume of the extract,  $Q_{Cs}$  [Bq/kg]: rad-Cs concentration [Bq/kg] in Fer precipitate,  $C_0$  [Bq/kg]: rad-Cs concentration in original MSW,  $r$ : ratio of rad-Cs removed from the extract of MSW by Fer technique, and  $E$ : ratio of rad-Cs extracted from MSW with solvent.

We estimated the volume reduction  $d$  (%) experimentally by a cold run using fly ash of sewage sludge obtained from the area unaffected by rad-Cs from the F1 accident [22]. The procedures are as follows:  $M$  [kg] of fly ash samples was extracted with  $V$  [L] of oxalic acid or distilled water, 100  $\mu\text{g/L}$  of Cs-133 (stable isotope of Cs) as CsCl salt was added to the extract as a spike, and Fer coprecipitation was conducted to remove Cs from the extract. After the coprecipitation, the precipitate was separated from the liquid by centrifugation (6,400 g, 4 °C, 15 min), freeze dried and weighed to estimate the value of  $p$  [kg/L]. The Cs concentration in the supernatant after Fer coprecipitation was determined by ICP-MS to estimate the Cs removal ( $r$  in Eq. 9.2). The  $d$  (%) values for actual DSW used in our on-site test were not obtained due to the shortage of time during the test.

The results obtained are summarized in Table 9.1. When concentration of Fer added for the removal of Cs was 0.1 mM, the theoretical  $d$  (%) value is 99.3 % for oxalic acid extract and 99.99 % for water extract, under the assumptions that the solid-to-liquid ratio of the extraction of waste was 1 g/2.5 mL, that the extract was diluted by a factor of 100 when the extracting reagent was 1 M oxalic acid (factor of 2 when the reagent was water) before subjecting it to Fer coprecipitation and that the Fer solid is anhydrous. As shown in the table, the observed  $d$  (%) values were generally higher than 99.9 % for the water extract and were close to the theoretical value. On the other hand,  $d$  (%) values were low for oxalic acid extract especially when Fer coprecipitation was conducted at circumneutral or alkaline pH. The original oxalic acid extract had low pH (c.a. 1), and as we added NaOH to increase the pH of the solution, the precipitates of metal hydroxides were formed. It was also noted that the oxalic acid extract of fly ash KO had a lower volume reduction compared to that of fly ash O under the same pH values. This is ascribed to the high amount of Fe contained in the extract of fly ash KO [6], starting to precipitate around pH 3. In summary, for the oxalic acid extract, higher waste volume reduction is achieved by conducting the Fer coprecipitation at pH value as low as possible so that the formation of metal hydroxide precipitate can be suppressed.

Overall, the results in Table 9.1 indicate that Fer coprecipitation leads to significant reduction in the amount of the waste (more than 1/1,000 for waste extracted with water, or nearly 1/100 for waste extracted with oxalic acid), under appropriate operating conditions. The waste residue after the extraction contains a low concentration of rad-Cs, and, since the extractable rad-Cs was removed from the residue, the long-term contamination of the environment caused by leaching of rad-Cs from the buried waste residue is expected to be negligible. Combined with proper management (e.g. storage) of the small volume of rad-Cs concentrated waste, the siting of the final disposal site of DSW is expected to become much easier.

**Table 9.1** Volume reduction of the waste by extraction-precipitation method (results of cold run)

Extracting reagent	Fer [mM] <sup>a</sup>	Fly ash O				Fly ash KO			
		pH	<i>d</i> % <sup>b</sup>	<i>r</i>	$(Q_{Cs}/C_0)/E$	<i>d</i> % <sup>b</sup>	<i>r</i>	$(Q_{Cs}/C_0)/E$	
Distilled water <sup>c</sup> 1 g/2.5 mL solid to liquid ratio	0.1	3	n.a.	0.959	n.a.	99.9<	0.952	667<	
		4	99.933	0.946	1,401	99.916	0.990	827	
		5	99.9<	0.958	671<	99.935	0.959	1,031	
		6	99.9<	0.933	653<	99.985	0.995	4,642	
		7	99.961	n.a.	n.a.	99.963	0.992	1,851	
		8	99.848	0.988	454	99.965	1.000	1,999	
		10	99.911	0.985	63	99.713	0.993	242	
	0.5	5	99.9<	0.974	682<	99.970	0.989	2,305	
	1.0	5	99.9<	0.942	659<	99.961	0.999	1,793	
	1 M oxalic acid <sup>d</sup> 1 g/2.5 mL solid to liquid ratio	0.1	3	98.66	0.999	74	82.33	0.998	6
4			94.41	0.996	18	77.45	0.998	4	
5			90.32	0.969	10	74.04	0.957	4	
6			86.58	0.978	7	78.65	0.937	4	
7			83.69	0.960	6	70.65	0.963	3	
8			77.82	0.926	4	63.43	0.962	3	
10			76.79	0.924	4	76.11	0.919	4	
0.5		5	97.68	0.998	43	69.35	0.985	3	
1.0		5	88.07	0.988	8	69.74	0.928	3	

<sup>a</sup>When 0.1 mM of Fer was added to the extract resulting in  $Fe_4[Fe(CN)_6]_3$  or  $Ni_2[Fe(CN)_6]$  precipitate, the weight of the precipitate is 29 or 34 mg/L respectively (excluding the weight of the hydrated water)

<sup>b</sup>Theoretically, volume reduction *d* (%) is 99.3 % for oxalic acid extract and 99.99 % for distilled water extract based on the weight of the anhydrous Fer solid

<sup>c</sup>The extract was diluted by a factor of 2 before subjecting it to the Fer coprecipitation

<sup>d</sup>The extract was diluted by a factor of 100 before subjecting it to the Fer coprecipitation

## 9.5 Objectives of the Present Study

The extraction-coprecipitation method described above can be an ultimate solution for volume reduction of DSW. The waste volume reduction *d* (%) in Eq. 9.1 is an important factor in assessing the effectiveness of the method, but also important is the relative concentration of the rad-Cs in the precipitate compared to that in the original waste. Higher values of  $Q_{Cs}/C_0$  imply that rad-Cs is concentrated more efficiently in the precipitate compared to the waste residues after the extraction, thereby defining the overall effectiveness of the method.

The starting point of our study has been to identify the factors that are likely to govern the rad-Cs removal (i.e. *r* in Eq. 9.2) from DSW extracts by Fer coprecipitation technique, and to optimize coprecipitation conditions for Cs removal. Based on this perspective, we evaluate the results of our most recent (fiscal year 2014) on-site test using DSW in the present report.

Leachability of rad-Cs in the DSW (i.e.  $E$  in Eq. 9.2) is another important factor that governs the effectiveness of the extraction-coprecipitation method. We therefore evaluated the results of our 2013 and 2014 on-site tests to examine the leaching of rad-Cs from sewage sludge ashes. Also important are the leaching characteristics of heavy metals. High leaching of Fe and Ni from waste is convenient in our study since these metals can be effectively used for the formation of insoluble Fe precipitate. On the other hand, high leaching of Zn is inconvenient because Zn forms insoluble Fe precipitate when soluble Fe salt is added to the solution, but the removal efficiency of Cs by Zn-Fe is low [6]. In this context, in the present report, we also examine the leaching of heavy metals from the fly ash samples.

## 9.6 Experimental

### 9.6.1 Reagents

All reagents used in our study were of analytical grade unless specified otherwise.

### 9.6.2 Procedures of Cold Run

We used MSW fly ash samples unaffected by the F1 accident to clarify the effect of extracting procedures on the extraction efficiency of various elements (including non-radioactive cesium) from the sample. In particular, we compared the use of 0.1 and 0.5 M hot oxalic acid extraction procedures on fly ash from a melting furnace treating sewage sludge from Western Japan. Since the sample was not contaminated with rad-Cs from the F1 accident, the extraction could be conducted in the university laboratory, and the concentration of various elements in the extracts could be determined using ICP-MS (model 7700 series, Agilent Technologies).

The three different extraction procedures were tested on the fly ash sample from the melting furnace. (1) One procedure was vacuum extraction (or continuous extraction), in which a 5 g fly ash sample placed on an i.d. 47 mm membrane filter holder (fitted with pore size 0.45  $\mu\text{m}$  PTFE filter) was continuously eluted with hot oxalic acid (50 mL solution/40 min) supplied via a peristaltic pump for total 120 min. The filter holder was connected to a vacuum flask, and vacuum was applied periodically so that the extracting reagent (0.1 or 0.5 M hot oxalic acid) was passed through the filter while the fly ash sample was always soaked in the oxalic acid. The percolate was collected every 40 min, and was analyzed by ICP-MS. By using the vacuum extraction method, re-adsorption of once extracted components to the waste material, as well as temporary oversaturation of extracted metals in the solution phase, could be minimized. This procedure was also practicable in the on-site test. (2) Conventional batch extraction (2.5 g of fly ash in 75 mL of 0.1 or 0.5 M hot

oxalic acid), with 200 rpm of shaking in a 90 °C hot bath, was conducted. (3) Also tested was a batch exchange extraction method, an intermediate method between continuous extraction and batch extraction. With this method, 2.5 g of fly ash was extracted with 25 mL of 0.1 M or 0.5 M hot oxalic acid with continuous shaking (200 rpm) in a hot bath for 1 h, centrifuged for solid–liquid separation ( $6,400 \times g$ , 4 °C, 15 min), and the supernatant was removed and saved for the subsequent analysis by ICP-MS. Then 25 mL of 0.1 or 0.5 M hot oxalic acid was added to the solid waste again and the same extraction procedure repeated twice. The batch exchange method turned out to be laborious and was not practicable in the on-site test compared to the other two methods.

With hot oxalic acid extraction, a precipitate was sometimes formed in the extract after it was cooled to room temperature. In such cases, the extract was centrifuged, the precipitate was dissolved in dilute  $\text{HNO}_3$  and the supernatant and the dissolved precipitate were analyzed separately by ICP-MS.

To determine the total element concentration in the fly ash, 100 mg of the fly ash sample, pulverized to pass a 150 mesh sieve, was digested by mineral acids in a pressurized Teflon vessel placed in a microwave oven model MARS5000 (CEM Co., US). The acids used were 5 mL of concentrated 68 %  $\text{HNO}_3$ , 1 mL of 70 %  $\text{HClO}_4$  and 4 mL of 38 % HF. All the acids used were AA-100 grade from Tama Chemicals Corporation (Japan). The sample was acid decomposed under 70 psi pressure for 10 min. after 20 min. of ramp time. After the decomposition, 6 mL of 4.1 w/v percent boric acid was added to the digested sample to dissolve the fluoride precipitated with Ca, etc. as well as to neutralize HF left in the solution. With this procedure, a clear solution with no visible suspended particles was obtained. The solution was diluted and analyzed by ICP-MS. The results obtained were used to calculate the percentages of the elements extracted by 0.1 or 0.5 M oxalic acid from the fly ash per total amount of the elements in the original fly ash.

### ***9.6.3 Determination of Radioactive Cs and Non-radioactive Metals in the On-Site Test***

On-site analysis of rad-Cs was conducted using a portable Ge detector from Princeton Gamma Technology (P-type, relative efficiency 20 %), and a Ge detector from ORTEC (model Trans-Spec, p-type, relative efficiency 40 %), in 2013 and 2014, respectively. Ge detectors were pre-calibrated for absolute full-energy peak efficiency for the solid samples packed in commercially available U-8 vessels (i.d. 50 mm, height 68 mm) as well as for a 30 mL volume of aqueous solution in a 50 mL polypropylene bottle, and were used to quantitate rad-Cs in waste extracts and waste materials. A NaI detector (model AN-OSP-NAI, Hitachi-Aloka-Medical, pre-calibrated for determination of rad-Cs) was also used to quantitate Cs-134 and Cs-137 in waste materials.

Concentrations of metals in the extract obtained at the on-site test were determined using a portable voltammetry instrument (model PDV6000plus from Modern Water, UK) coupled with an autosampler. In 2014, Fe and Zn were determined. Determination of Fe was conducted using a glassy carbon working electrode, acetate buffer as a supporting electrolyte, deposition potential  $-1,600$  mV and stripping step potential range of  $-1,100$  to  $50$  mV. Determination of Zn was conducted at a mercury-film-coated glassy carbon working electrode, acetate buffer as a supporting electrolyte, deposition potential  $-1,300$  mV and stripping step potential range of  $-1,200$  to  $50$  mV.

#### ***9.6.4 Extraction Procedures Used in the On-Site Test***

The rad-Cs-contaminated fly ash samples from sewage treatment in the area affected by the F1 accident were extracted and analyzed for rad-Cs in the plant where they were produced (the on-site test). The information for the waste materials used for the on-site test is summarized in Table 9.2, together with extracting reagents tested on the samples. We used a distilled-water extraction [23] and a hot oxalic acid (0.1 M) extraction [24] that had previously been applied to the removal of rad-Cs from contaminated MSW. Also tested were 5 M HCl extraction and 0.5 M hot oxalic acid extraction in an attempt to achieve higher leaching of rad-Cs for some samples.

The extraction of rad-Cs containing waste materials was conducted using the vacuum extraction (continuous extraction) procedure in the on-site test conducted in 2014. This procedure was used because the results of three different extraction methods for uncontaminated waste showed that the batch extraction may be affected by loss of the extracted elements due to re-adsorption and/or precipitation processes as will be discussed in the Sect. 9.7. The extraction in 2013 was conducted by batch extraction.

#### ***9.6.5 Ferrocyanide Coprecipitation Procedures Used at the On-Site Test***

The treatment of the extract by Fer precipitation technique was conducted as follows: The pH of the waste extract containing rad-Cs was adjusted to the desired values (shown later in Sect. 9.7) using NaOH and HCl. Potassium ferrocyanide ( $K_4[Fe(CN)_6]$ , K-Fer hereafter) was used as a soluble Fer salt source. Since metal hydroxides (ineffective for Cs removal) rather than metal-Fer complexes could be formed in the solutions when pH values are in neutral to alkaline regions, a slightly acidic pH was used for Fer precipitation. After the addition of K-Fer, Ni-Fer or Fe(III)-Fer precipitate (prepared in a separate bottle) to the extract, the sample was

**Table 9.2** Designated waste samples subjected to the on-site test

Sample code	Type of waste material	Period of waste generation	Period of time when on-site test was conducted	rad-Cs concentration [kBq/kg] <sup>a</sup>		Extracting reagent tested
				Cs-134	Cs-137	
IF1	Incinerator fly ash <sup>b</sup>	October, 2013	October, 2013	4.0	8.5	Distilled water <sup>c</sup> and 0.1 M hot oxalic acid
IF2	Incinerator fly ash <sup>d</sup>	October, 2014	October, 2014	2.7	8.1	Distilled water, 0.1 M hot oxalic acid, 0.5 M hot oxalic acid, and 5 M HCl
IB	Incinerator bottom ash <sup>e</sup>	October, 2013	October, 2013	0.6	1.2	Distilled water <sup>c</sup> and 0.1 M hot oxalic acid
MF1	Fly ash from melting furnace <sup>f</sup>	May, 2013	October, 2014	14.5	45.4	Distilled water, distilled water (pH3), 0.1 M hot oxalic acid and 0.5 M hot oxalic acid
MF2		October 2013	October, 2013	32.0	67.4	Distilled water and 0.1 M hot oxalic acid
MF3		September, 2014	October, 2014	6.2	19.5	Distilled water (pH3), 0.1 M hot oxalic acid and 0.5 M hot oxalic acid

<sup>a</sup>Radioactivity at the time of the experiment<sup>b</sup>Sewage sludge and the cover soil were incinerated together in a fluidized bed incinerator at 850 °C. Volume reduction by incineration was approximately 67 %<sup>c</sup>The solution pH was adjusted to 3 during the extraction by titrating with HCl<sup>d</sup>Only sewage sludge was incinerated. Volume reduction of the sludge by incineration was approximately 95 %<sup>e</sup>Incinerated soil was discharged as a bottom ash of the fluidized bed incinerator<sup>f</sup>Sewage sludge was smelted at 1,200 °C. Volume reduction of the sludge by the smelting was approximately 97 %

centrifuged at  $2,600 \times g$  at  $4\text{ }^{\circ}\text{C}$  for 20 min. or stood still until the precipitate was settled. When more than a few liters of the extract were treated, 30 mg/L of cationic polymeric flocculant (polymethacrylic ester, C-303 or C-512 from MT AquaPolymer Inc., Japan) was added to facilitate the settling of fine precipitates.

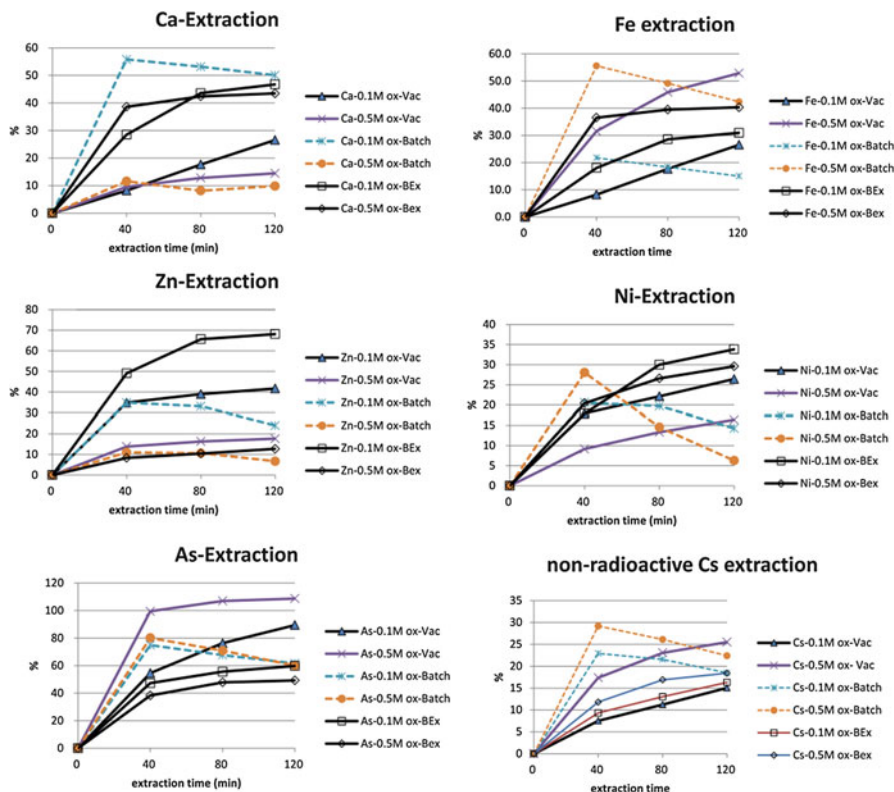
## 9.7 Results and Discussion

### 9.7.1 *Extraction of Metal Elements from Fly Ash Sample in the Cold Run*

Extractions of stable (non-radioactive) Ca, Fe, Zn, Ni, As and Cs from fly ash (collected from a melting furnace treating sewage sludge from Western Japan) with 0.1 and 0.5 M hot oxalic acid are compared in Fig. 9.1. Clearly, the percentages of metal extraction differed considerably depending on the concentration of oxalic acid as well as on the extraction procedures (continuous, batch and batch exchange). With the batch extraction procedure, we observed a high extraction percentage at an earlier time (40 min), followed by a decrease in the extraction percentage. This is probably explained by re-adsorption or re-precipitation (or co-precipitation) of once extracted elements. In contrast, the continuous extraction showed a gradual increase in extraction percentages with time. The extraction percentages by continuous extraction at 120 min of extraction time were similar to those obtained by batch extraction at 40 min for non-radioactive Cs and Fe. The batch exchange procedure method showed a gradual increase in the extraction percentages of the elements with time and was more similar to the continuous extraction than simple batch extraction. For both batch and batch exchange procedures, there could have been temporary oversaturation of the extracted elements in the solution after 40 min of extraction with hot oxalic acid. In the case of the batch exchange method, the oversaturated elements, if any, should have been precipitated during the centrifugation to exchange the supernatant. In simple batch extraction, unlike batch exchange extraction, supernatant was not exchanged, and the aliquot of the supernatant collected for analysis should contain the oversaturated element (if any). In any case, the batch exchange procedure was laborious compared to the continuous extraction and simple batch methods. Also, the centrifugation we conducted for solid-liquid separation in the batch exchange procedure every 40 min caused a temporary decrease in the extraction temperature, making it difficult to interpret the obtained results.

The oxalic acid concentration of the extract also affected the extraction efficiency of elements (in Fig. 9.1, only the results of Ca, Fe, Zn, Ni, As and Cs are shown). Briefly, in the case of continuous extraction, 0.5 M hot oxalic acid was more effective than 0.1 M hot oxalic acid in extracting non-radioactive Cs, Fe, Mg, Al, Mn, As, Se, Sr and Ba. On the other hand, for Zn, Ca, Co, Ni and Cu, 0.1 M hot oxalic acid was more effective than 0.5 M hot oxalic acid (in the case of continuous





**Fig. 9.1** Comparison of extraction rate of various elements with continuous (vacuum extraction), batch extraction, and batch exchange extraction methods for fly ash from a melting furnace. Here, 0.1 M ox – Vac: continuous extraction with 0.1 M hot oxalic acid, 0.5 M ox – Vac: continuous extraction with 0.5 M hot oxalic acid, 0.1 M ox-Batch: batch extraction with 0.1 M hot oxalic acid, 0.5 M ox-Batch: batch extraction with 0.5 M hot oxalic acid, 0.1 M ox – BEx: batch exchange extraction with 0.1 M hot oxalic acid, and 0.5 M ox – BEx: batch exchange extraction with 0.5 M hot oxalic acid

extraction). Oxalic acid dissolves Fe and some other metals preferentially through the ligand-promoted dissolution process [25], and the lower pH of 0.5 M oxalic acid compared to 0.1 M oxalic acid enhances the dissolution of elements in general. At the same time, with 0.5 M oxalic acid, metal oxalates having low solubility can be more easily formed than with 0.1 M oxalic acid. We consider that the concentrations of Zn, Ca, Co, Ni and Cu in the 0.5 M oxalic acid extract were solubility controlled by the metal oxalates. Although the solubility values of metal oxalates freshly formed at high temperature (90 °C) may be hard to obtain, solubility determined for pure metal oxalates can be used as reference values. According to the literature [26], oxalates of Zn, Co, Ni and Cu have very low solubility at 20 °C. This information supports our inference that Zn, Co, Ni and Cu concentrations were solubility controlled. Since the concentration of Ca in the extract is high (between 67

and 600 mg/L in 0.5 M oxalic acid extract), it is no wonder that the Ca concentration was controlled by the solubility of calcium oxalate.

Based on the results above, we applied the continuous extraction method at the on-site test in 2014, in order to obtain more scientific estimates of the leaching of rad-Cs from the contaminated fly ash. We noted, however, that the behavior of non-radioactive Cs during the extraction was relatively simple, i.e. Cs was not precipitated with oxalic acid and therefore its extraction was higher in 0.5 M oxalic acid than in 0.1 M oxalic acid, and the highest extraction could be achieved with 40 min of batch extraction. From a practical point of view, by using 0.5 M hot oxalic acid in simple batch extraction mode, the majority of Cs that can be extracted with the reagent by the continuous method will be released from the solid phase, although there is a chance that the behavior of non-radioactive Cs we have investigated in this section and that of rad-Cs in fly ash samples are different, depending on the original chemical form of Cs.

### ***9.7.2 Extraction of rad-Cs from Contaminated Fly Ash Samples***

The results are summarized in Table 9.3. The results indicate rad-Cs leaching from melting furnace fly ash (MF1, MF2 and MF3) is high. At least 40 % was extracted with distilled water, and the percentage of the rad-Cs extraction was close to 100 % when 0.5 M hot oxalic acid was used. Notably, the percentages of rad-Cs extraction were not much affected by the pH values of the extract. For example, distilled water extracts of MF3 had pH values around 7 (refer to Table 9.3), and rad-Cs extraction was higher than 60 %. The distilled water extracts of MF2 had lower pH values (around 1) compared to MF3, and the rad-Cs extraction was only 40 %, lower than the distilled water extracts of MF3 with pH value 7. The lower extraction percentages for MF2 are partly attributable to the lower solid-to-liquid ratio (1 g/2.5 mL) of extraction compared to 1 g/75 mL for MF3, implying that a thorough washing with larger volume of liquid leads to higher leaching.

As discussed in the preceding section, stable Cs extracted by distilled water from fly ash of the melting furnace treating sewage sludge from Western Japan was only 5 % of the total Cs contained in the ash. Interestingly, rad-Cs in the fly ash MF1, MF2 and MF3 from the similar melting furnace was more water soluble compared to the stable cesium in the other fly ash of similar origin.

The extractability of rad-Cs was lower for incinerator fly ash (IF1 and IF2) compared to fly ash from the melting furnace (MF1, MF2 and MF3). The ashes collected in different periods, IF1 and IF2, also exhibited quite different leaching of rad-Cs, Fe and Zn. When extracted with distilled water, rad-Cs extraction percentages were only ca. 1 % for IF1, whereas it was 10 % or higher for IF2. The IF2 ash also had higher amount of extractable Fe and Zn compared to IF1. The IF1 ash was obtained when sewage sludge was incinerated together with soil, while IF2

**Table 9.3** Results of rad-Cs extraction by various extracting reagents

Sample code	Extracting reagent	Extraction time	pH	Fe (mg/g-soil)	Zn(mg/g-soil)	Percentage of Cs extracted	Extracting procedures and solid/solution ratio		
IF1	Distilled water (titrated to pH3)	1 h	3.0 (8.9 before pH adjustment)	–	–	2.1 %	Batch, 1 g/2.5 mL		
		2 h	3.9	–	–	0.4 %			
		3 h	3.5	–	–	0.7 %			
	0.1 M hot oxalic acid	1 h	4.2	0.08	0	1.3 %			
		1 h	1.0	0.63	0.002	11 %			
	0.5 M hot oxalic acid	2 h	–	–	–	11 %			
		3 h	–	–	–	10 %			
		1 h	0	–	0.023	24 %			
	5 M HCl	2 h	–	–	–	20 %			
		3 h	–	–	–	25 %			
40 min		5.8	0.0	–	14 %				
IF2	Distilled water	80 min	6.9	0.0	–	14 %	Continuous, 1 g/30 mL		
		40 min	5.5	0.0	0.2	12 %			
	Distilled water (pH3)	80 min	6.7	0.0	–	12 %			
		120 min	6.8	–	–	19 %			
	0.5 M hot oxalic acid	40 min	1.2	43.4	13.4	39 %			
		80 min	0.7	–	–	61 %			
	Distilled water	120 min	0.7	–	–	66 %			
		1 h	3.0 (5.1 before pH adjustment)	–	–	0 %			
	IB	Distilled water	2 h	3.1	–	–		0 %	Batch, 1 g/2.5 mL
			3 h	3.3	–	–		6 %	
1 h			1.5	0.01	0.0	2.9 %			