

Decontamination of Radioactive Cesium Released from Fukushima Daiichi Nuclear Power Plant – 13277

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ABSTRACT

Peculiar binding of Cesium to the soil clay minerals remained the major obstacle for the immediate Cs-decontamination of soil and materials containing clay minerals like sludge. Experiments for the removal of Cesium from soil and ash samples from different materials were performed in the lab scale. For soil and sludge ash formed by the incineration of municipal sewage sludge, acid treatment at high temperature is effective while washing with water removed Cesium from ashes of plants or burnable garbage. Though total removal seems a difficult task, water-washing of wood-ash or garbage-ash at 40 °C removes >90% radiocesium, while >60% activity can be removed from soil and sludge-ash by acid washing at 95 °C.

INTRODUCTION

The 9.0 magnitude earthquake of March 11, 2011, is remembered for the destruction of Fukushima Daiichi Nuclear Power Plant and release of 630,000–770,000 TBq (terabecquerel) radioactive substances to the environment [1]. As a result, the hydrosphere, lithosphere, atmosphere, and the biosphere of a wide area centering the Fukushima Prefecture are contaminated with mostly the volatile radioisotopes like Iodine and Cesium. Recently taken aerial map of the evacuated area shows radiation level of 1.48 million Bq/m², the source of which, after months of the disaster, are mostly the radioactive isotopes of cesium, Cs-134 and Cs-137. Cesium is third in the order of radioisotope release probability, noble gases and Iodine being the top two, and Cs-137 is an exceptional nuclide possessing both strong decay energy ($\beta\gamma$ 1.176 MeV) and long half-life (30.2 y) [2]. Thus the presence of Cs-137 in the environment is hazardous causing internal exposure (via air and food chain) and external exposure to gamma-rays released during its decay to stable Ba-137 [3].

Following the radioactive fallout and Chernobyl disaster, there have been detail studies on Cs-contamination countermeasures. However, the peculiar interaction of Cs with various soils has attracted more interest, though studies on Cs removal like chemical extraction, use of microorganisms, and phytoremediation were also performed with limited success: mostly low and slow removal [4-7]. Therefore, only effective measure for controlling mobility of radiocesium and its entry to the food chain is the topsoil removal [6]. The task of scrubbing the surface soil is certainly difficult and more difficult is long term safe-storage of the contaminated soil. Also, when contaminated wastes like trees, grasses, household garbage and tsunami-generated debris are incinerated, the mass is generally reduced to less than 5%, and proportionally the radioisotopes also get concentrated. In such case, removal of Cs from ash becomes necessary prior to the disposal. In order to accelerate the Fukushima-decontamination mission, we are studying the possibility of removing the radiocesium, the major cause of recent environmental radioactivity, from ash and soil of various genres.

MATERIALS AND METHODS

Soil, sludge ash and ash samples with or without radiocesium contamination were collected from various areas of Japan including those from the areas surrounding damaged Fukushima Daiichi Nuclear Plant. For the samples with radiocesium (Cs-134 & Cs-137) contamination, the initial activities were analyzed using Berthold model LB2045 NaI-Gamma Scintillator (NaI-Scintillator) and SEIKO EG&G model ORTEC GEM25P4-70 Germanium Semiconductor Detector (Ge-Detector). And the initial Cs-133 concentration in non-contaminated samples were analyzed by microwave assisted dissolution using Perkin Elmer model Multiwave 3000 microwave system followed by Cs analysis using Perkin Elmer model NexION 300D ICP-MS.

Washing out the radioactive isotopes of Cs from soil and ash samples was started using water at room temperature to 95 °C. For the samples releasing high % Cs, the conditions were optimized with water as solvent. However, for the samples with negligible release with water, soil and sludge ash, a number of reagents were tested. The Cs release was evaluated by the difference between initial Cs-133 or radiocesium activity and the concentration or activity released to the solvent. Once the best condition is set, the samples after Cs-extraction were again analyzed for the residual Cs in order to evaluate the effective decontamination factor.

RESULTS AND DISCUSSION

The initial Cs concentration in the ash and soil samples and the maximum released concentration are listed in Table 1. Depending on the sample type, the Cs-133 concentration was measured in a range of 1.0 to 6.2 mg/kg. Also, the contaminated samples contain combined Cs-134 and Cs-137 in a range of 1.5-50 kBq/kg. The decontamination experiment was started by washing the samples with water at ambient temperature. Based on the literature, Cs once trapped on clay mineral sites is difficult to move. Therefore, the wood ash or garbage samples those contain least or no clay minerals, Cs release is expected to be easier compared to the sludge ash and soil samples.

Table 1. Initial Cs concentration in the samples studied and the maximum concentration released at the optimized conditions.

Sample	Cs-133 (mg/kg)		Cs-134 & Cs-137 (kBq/kg)	
	Initial	Released	Initial	Released
Iitate	4.5	3.6	50	35
Nihonmatsu	3.8	3.0	-	
Kooriyama	3.2	2.8	-	
Sludge ash-1	2.4	1.96	-	
Sludge ash- 2	1.0	0.82	7.1	5.85
Household garbage ash	6.1	5.05	1.5	1.43
Wood ash -1	1.4	0.98	-	
Wood ash -2	6.2	5.0	38	36.5

The release was gradual for wood ash-1 upon increasing the temperature from 25 °C to 90 °C, as shown in Figure 1a. Because wood ash-1 is the mixture of bottom ash and fly ash collected by a

cyclone dust collector, the release could not be improved by increasing the washing volume. Based on this Cs release pattern, the wood ash-2, fly ash collected by a bag filter during the incineration of radiocesium contaminated wood bark, was washed with water. In this case, the release was only slightly dependent on temperature, Figure-1b. For this sample, as given in Table 1, the radiocesium release was >95% at 40 °C, in contrary to some lower Cs-133 release. This difference is attributed to the difference in the Cs-133 and Cs-134, Cs-137 analysis. The Cs-133 was measured using ICP-MS, in which case more the presence of counter ions, more is interference and higher is the analytical error. The initial concentration was measured using microwave dissolution method, hence solubilizing almost all components, whereas the final solution contains only components dissolved to water and remained after neutralizing to pH <7 prior to the analysis. Thus, the measurement error is certainly different for initial and final sample. Irrespective of the results observed for Cs-133, the radiocesium decontamination of wood ash has been successfully observed by simply washing with water in a ratio of 1:10, at ambient to slightly higher temperature of 40 °C. The same optimized condition for wood ash was applicable for the >95% radiocesium release from the household garbage ash.

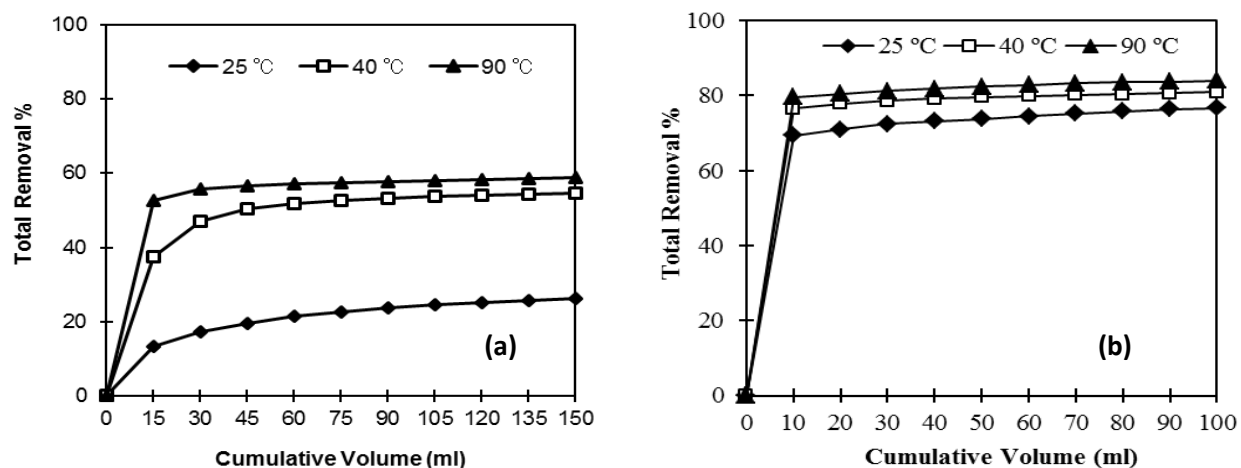


Figure 1. Cs-133 release with water (5 ml/min) from wood ash-1, ash overall (a) and wood ash-2, fly ash (b).

Cs removal from sludge ash and soil was not as easy as for other ash samples. Water washing of these samples at any temperature was ineffective. Then washing with organic acids, complexing reagents like EDTA and potassium, iron or ammonium salts also could not yield effective result. Treating with high concentration mineral acids showed the positive response, though high % release was far to achieve, suggesting the necessity of some variation in the experimental parameter. Naturally, Cs in soil is mostly bound to the frayed edge sites (FES) of the soil clay minerals, which is considered almost irreversible [8,9]. Therefore, setting the condition that effectively loosens the FES is necessary.

For the ease of handling and availability to post use disposal, mineral acids are considered the most suitable options for the purpose of Cs-decontamination in mass scale. Therefore, taking nitric acid (HNO₃) or sulfuric acid (H₂SO₄) as solvent, first variation was made on soil-solvent mixing temperature. Mixtures of dried soil and 0.5 M acid in 1:50 ratio were heated for 1 h at

various temperatures. As shown in Figure 2, the Cs-133 release is increasing with the rising temperature. Also, slightly higher release was observed in sulfuric acid compared to nitric acid solution. Along with the temperature, acid concentration was important for Cs-133 release. In the concentration variation study, the release was higher in sulfuric acid than in nitric acid.

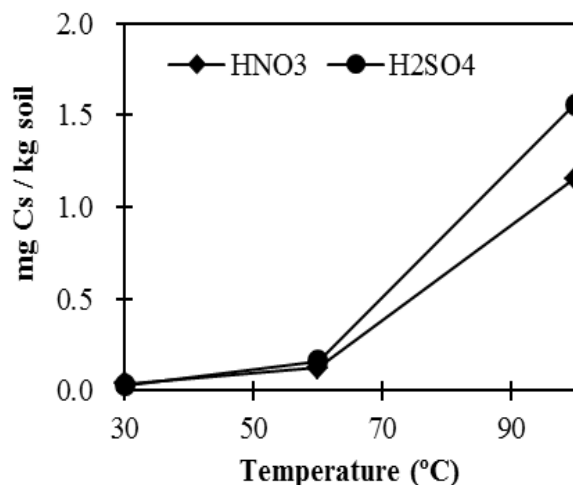


Figure 2. Effect of temperature on release of Cs-133 with 0.5 M acid solutions at 1:50 ratio.

In the optimized condition of 0.5 M mineral acid, 95 °C and 1 h mixing, the Cs extraction test of soil samples collected from Koriyama and Nihonmatsu, places in Fukushima Prefecture, was also performed. Though the appearances of three soil samples were different, Cs-133 was released in comparative order in the same experimental conditions. In addition, about 70% radiocesium release, higher than the Cs-133, was observed for contaminated Iitate-soil, a brown forest type soil. Higher release of radiocesium than the Cs-133 release, as in the case of wood ash samples, is expected to be due to the interference of co-existing ions on Cs-133 analysis using ICP-MS.

Decontamination of two kind of municipal sewage sludge ash was also performed taking 0.5 M nitric acid in 1:50 ratio at 95 °C and 1 h mixing, or in flow. Sludge ash-1 was calcium rich, while sludge ash-2 was Iron rich and contained some Cs-radioisotopes. In each case, substantial release of Cs was observed, Table 1.

CONCLUSION

Environmental Cs-decontamination is a vague topic as the conditions vary based on the substrate. For contaminated burnable materials like plants and tsunami-debris, incineration followed by washing the ash sharply reduces the volume and eases the disposal of the ash. Similarly, the sewage sludge of contaminated areas centering the Fukushima Prefecture contains substantial concentration of radiocesium via the rain-drained soil particles, therefore needs immediate attention. In addition, removal of radiocesium from the collected contaminated surface soils would certainly eases the delayed disposal issue.

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