Effective Extraction of Radioactive Cesium from Various Pollutants with a Detergent Solution Including Mg$^{2+}$ and K$^+$

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Radioactive cesium (Cs) is extracted effectively from various polluted samples such as soil, silt, and burned ash by washing with a detergent solution comprised of KCl, MgCl$_2$, and a hydroxyethyl cellulose in a 5% H$_2$SO$_4$ aqueous solution. Repeatedly washing extracts more than 65% of the radioactive Cs.

Keywords: radioactive cesium, soil, silt, burned ash, detergent solution

1. Introduction

Radioactive Cs has severely contaminated the soil in Fukushima and neighboring prefectures due to the accident at the Fukushima Daiichi Nuclear Power Plant. These contaminants must be removed as quickly as possible and stored in controlled areas.

Several methods have been reported to extract radioactive Cs from the soil.$^{1,2}$ However, serious drawbacks of these methods include processing at high temperatures and expensive equipment. Recently, we reported that washing with a detergent composed of an acid, an alkali metal or alkali earth metal ion, and a cellulose derivative effectively extracts radioactive Cs from soil (92% extraction).$^3$

Silt, which is clastics (particle size < 75 µm) collected through sifting soil, readily adsorbs a great mass of radioactive Cs.$^4$ Thus, the development of an effective extraction technique for radioactive Cs in silt is strongly desired.

Radioactive Cs is also found in burned ashes produced by the incineration of radioactive pollutants, but the incineration process transfers most of the radioactive Cs to fly ash. Vast quantities of fly ash have been generated to date, causing issues with storage space.$^5$ Hence, an effective extraction technique for radioactive Cs in fly ash must also be developed.

Here we report the extraction behavior of radioactive Cs from silt, burned ash, and soil using a detergent solution that includes Mg$^{2+}$ and K$^+$ ions.

2. Experimental Methods

2.1 Radiation Measurements

The concentration of radioactive Cs in each sample was determined by 3-inch × 3-inch NaI(Tl) scintillation gamma-ray spectrometry (EMF-211, EMF Japan, Kawachinagano, Japan). The photon energies at pulse heights were calibrated using the photon peaks of $^{137}$Cs (661.7 keV) and $^{40}$K (1460.8 keV). The radioactive Cs concentrations of the pollutants were determined by a $^{137}$Cs standard radiation source sample (19,565 Bq/kg).

2.2 Sample Preparation

A soil sample with radioactive Cs was collected in Iwaki-shi, Fukushima in March 2013. Bottom ash and fly ash with radioactive Cs were taken from Koriyama-shi, Fukushima in July 2013. The sewage sludge-burned ash with radioactive Cs was gathered in Miyagi in July 2013. Each sample was sifted through a stainless-steel sieve (mesh size: 2 mm) several times to remove stones, branches, and dead leaves. The total concentrations of $^{134}$Cs and $^{137}$Cs in the soil, bottom ash, fly ash, and sewage sludge-burned ash were 19,200 Bq/kg, 13,000 Bq/kg, 28,000 Bq/kg, and 7,200 Bq/kg, respectively.
2.3 Preparation of Silt

Silt was collected by sifting the soil sample from Iwaki-shi, Fukushima using a stainless-steel sieve (mesh size: 75 µm). Gamma-ray spectrometry indicated that the total concentration of $^{134}$Cs and $^{137}$Cs in the silt was 49,300 Bq/kg.

2.4 Preparation of the Detergent Solution

The detergent solution (500 mL) was comprised of KCl (40–80 g), MgCl$_2$ (50–100 g), hydroxyethyl cellulose (200–300 mPas) (5 g), and concentrated sulfuric acid (25 g). The salts and sulfuric acid were purchased from the Junsei Chemical (Tokyo, Japan), while hydroxyethyl cellulose was purchased from the Tokyo Chemical Industry (Tokyo, Japan).

2.5 Extraction of Radioactive Cs from Polluted Samples with the Detergent Solution

Radioactive samples (100 g) and the detergent solution (500 mL) were placed into a separable flask (1 L) and stirred for 5 h at 300 rpm and 30 ºC. The polluted samples and the solution were then separated by vacuum filtration. After drying the remaining solid, the radioactive Cs concentration was measured by gamma-ray spectrometry (sample weight: 50 g, measuring time: 20 min).

The extraction percentage of radioactive Cs was calculated as (E: extraction percentage, CA: concentration after washing, CB: concentration before washing):

$$ E = \left( \frac{C_B - C_A}{C_B} \right) \times 100 $$

The distribution ratio of radioactive Cs was calculated as (D: distribution ratio, E: extraction percentage, $V_s$: volume of solid phase, $V_L$: volume of liquid phase):

$$ E = \frac{D}{D \times \left( \frac{V_s}{V_L} \right) } $$

3. Results and Discussion

3.1 Effect of the Detergent Components on the Extraction of Radioactive Cs in Soil

Recently, we reported that washing can significantly reduce the concentration of radioactive Cs in soil. Here, we initially examine the extraction behavior of radioactive Cs from soil (concentration: 19,200 Bq/kg) with a new detergent solution. Figure 1 shows the effects of adding KCl and MgCl$_2$ (at a total concentration of 0.53 or 1.06 mol) into the solution increases the extraction percentage from 23% to 38%, whereas adding solely MgCl$_2$ (100 g, 1.06 mol) increases the extraction percentage to 51%. Interestingly, adding both MgCl$_2$ (50 g, 0.53 mol) and KCl (40 g, 0.53 mol) while keeping the total molar amount of the salts constant results in the highest extraction of radioactive Cs (56% extraction). These observations demonstrate that the addition of both MgCl$_2$ and KCl extracts radioactive Cs from soil effectively, and imply that the size and charge are distributed amongst the cavities in the soil. Hence, the K$^+$ ion can compensate for the insufficient exchange of the Cs$^{3+}$ ion with the Mg$^{2+}$ ion due to size and charge incompatibilities between the soil cavities and the Mg$^{2+}$ ion.

The calculated distribution ratio of radioactive Cs by this method is 0.14 (E: 0.56, $V_s$: 55.6, $V_L$: 500). This value is much higher than those obtained by other methods using 0.5 mol/L nitric acid aq. ($^{1}$) (0.014) and 0.5 mol/L oxalic acid aq. ($^{2}$) (0.017), clearly confirming that our method is superior.

3.2 Extractions of Radioactive Cs in Soil, Silt, and Burned Ash

Figure 2 shows the changes in the radioactive Cs concentration in soil, silt, and burned ash as functions of the number of wash cycles using a detergent solution (500 mL) containing KCl (40 g), MgCl$_2$ (50 g), and hydroxyethyl cellulose (5 g) in a 5% H$_2$SO$_4$ aqueous solution. Each cycle consists of washing the soil, silt, or burned ash with the detergent solution for 5 h at 30 ºC.

After five wash cycles, the radioactive Cs concentration in silt is reduced from 49,300 to 2,800 Bq/kg (94% extraction), demonstrating that this method effectively extracts radioactive Cs in silt. Similarly, this method extracts 95% of the radioactive...
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Cs from soil after five wash cycles.

Washing the bottom ash thrice using the aforementioned procedure reduces the radioactive Cs concentration from 13,000 to 1,100 Bq/kg (92% extraction). Similarly, three washings reduce the radioactive Cs concentration in fly ash from 28,000 to 800 Bq/kg (97% extraction). Unlike in soil and silt where radioactive Cs is absorbed strongly inside the cavity, radioactive Cs in bottom ash and fly ash can exist on the surface as cesium chloride. Consequently, radioactive Cs in the latter two pollutants can be extracted easily.

However, it is more difficult to extract radioactive Cs from contaminated sewage sludge–burned ash. Washing the sewage sludge–burned ash thrice under the above conditions reduces the radioactive Cs concentration from 7,200 to 2,500 Bq/kg (65% extraction). This moderate extraction percentage may be because the organic and inorganic matters in the sewage sludge–burned ash adsorb Mg$^{2+}$ and K$^+$, inhibiting the effective exchange of radioactive Cs ions with Mg$^{2+}$ and K$^+$ ions.

4. Conclusions

We successfully extracted radioactive Cs from contaminated soil, silt, and burned ash. Washing the contaminated soil with an initial concentration of 19,200 Bq/kg thrice at 30°C with a detergent solution, which contains KCl, MgCl$_2$, and a cellulose-based dispersant in a 5% H$_2$SO$_4$ aqueous solution, reduces the radioactive Cs concentration to ≤ 8,000 Bq/kg. This method can be used to treat radioactive contaminants in many materials such as soil, silt, and burned ash (e.g., bottom ash, fly ash, and sewage sludge–burned ash).

References