Fundamental study on extraction of cesium from soil

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ABSTRACT

Large amounts of radioactive materials were spread over a wide range by the accident of Fukushima Daiichi nuclear power plant occurred on March 11, 2011. Currently, the decontamination of radioactive materials discharged by this accident is urgently needed. However, the efficient and effective decontamination technology is not established. The current state is that the completion of final decontamination is nowhere in sight because the disposal volume is enormous. It is necessary to achieve the extraction of the cesium that firmly fixed to the clay mineral in soil and the volume reduction of the disposal materials so as to base our prediction on the decontamination. The authors focus attention on the fact that the cesium is solubility and exists as a monovalent cation in the solution. Through the fact, the method that the cesium ion in soil migrates to the cathode plate connected with the negative side if a DC power supply due to electrophoresis and is captured by the adsorbent sandwiched between the soil and the cathode plate is proposed. First, in this study, the test with a small chamber was conducted to examine the extraction characteristic of cesium and the adsorption property of an adsorbent material. Secondly, the adsorption property of the adsorbent material for cesium through the electrophoresis adsorption test was investigated by more practically test with a large-scale chamber which is extended from the test with a small chamber. From the test with a small chamber, it is turned out that there is not most changes in extraction characteristics even if the passage of time is changed, and that the used adsorbent has a very high adsorption ability. From the test with a large-scale chamber, it is found that the adsorption effect of the large-scale test is inferior to the small one due to the decrease of energizing performance.

Keywords: decontamination, radioactive material, electrophoresis, cesium, HAp

1 INTRODUCTION

Large amounts of radioactive materials were spread over a wide range by the accident of Fukushima Daiichi nuclear power plant occurred on March 11, 2011. (TEPCO, 2012) The major decontamination method of contaminated soil that is currently carried out is the stripping of topsoil. (K, Wakasugi and N, Haraguchi, 2014) However, the contaminated soil amounts to 23 cups of Tokyo Dome (28,790,000 m³) at the maximum so as to decrease the radiation dosage of the soil under 5mSv a year. The current decontamination method is not suitable since the securing of interim storage facility or temporarily site for the decontaminated soil is faced to difficulty as well as the unclear plan in terms of final disposal of the decontaminated soil.

If the volume reduction of contaminated soil is concerned, it is desirable that just radioactive material is removed without removing the whole soil. At the present, some decontamination methods are proposed. For example, only the radioactive substance is removed from the washing water after the contaminated soil is washed by water. (K, Ide et al., 2012) The other is a sort of separation method in which the volume reduction is realized by the incineration of combustible material after organic substance is mechanically separated from the soil. (Shimizu Corp) However, in these methods, the time and costs are expected to be enormous because the contaminated soil is once at least collected.

In the washing method, a variety of adsorbent are proposed to remove only the radioactive substance from the washing water. Though the cesium adsorption material such as a prussian blue sheet is proposed, unclear cost may bring about less economy.

Cesium is well known to be water-soluble material. (A, Nakao, 2012) Thus, in this study, cesium is adsorbed by an adsorption material with the help of electrophoresis method in order to accomplish not only the decontamination but also volume reduction of contaminated soil. It is noted that the volume of adsorption material which can adsorb cesium is much smaller than that of contaminated soil. However, in this method, there are some technical problems such as the
extraction of cesium which is firmly fixed to the clay mineral in soil and the efficient adsorption of cesium from the contaminated soil. Furthermore, it is difficult to extract the cesium which remains submerged in soil for a while from contaminated soil. Thus, in this study, the property of cesium extraction is also examined as the time between the addition of cesium to soil and the start of test is varied.

Secondary, in this study, it is aimed to investigate the property of cesium extraction from contaminated soil through the tests with a large-scale device and an adsorption sheet.

2 EXPERIMENT AND ANALYSIS

The electrophoresis is the phenomenon that charged particles or molecules in solution move in the inside of an electric field. The electrodes are placed in solution and a direct current using the power is applied to them. By doing so, the difference of electrical potential is occurred between the electrodes, and the electric field is formed in solution. If charged particles or molecules are placed in the electric field, they move toward the pole which has opposite electrical charge to it. In this study, most tests are conducted by using this electrical phenomenon. The experimental outline is explained below.

First, Toyoura sand is laid at the bottom of experimental acrylic chamber (60 mm, 70 mm, and 80 mm of cuboid) to simulate the decontamination of land contaminated by radioactive cesium. Secondly, 38.1 mg of cesium is added into the sand. After that, the anode connected with the positive side of a DC power supply. A carbon rod is connected with the conductor, and is embedded into the bottom of Toyoura sand. Furthermore, the adsorption sheet is put on sand, and the aluminum plate connected with the negative side of a DC power supply. Finally, 70 mL of electrolyte (ammonium acetate) is poured into the chamber to simulate the decontamination of land contaminated by the radioactive cesium, and 50 mA of current is applied to the conductor. (see Fig.1) (A. Nakao and N. Yamaguchi, 2011) It is noted that 50 mA of current is maintained constant by a DC power supply apparatus. In this manner, cesium is adsorbed by an adsorption material with the help of electrophoresis method. After the continuous current tests, cesium contained in Toyoura sand and the electrolyte is extracted from the sand and the electrolyte by stirring machine (4 times of 10 minutes). The remained cesium is analyzed by AAS (Atomic Absorption Spectrometer) to measure its remained amount of Toyoura sand and the electrolyte. Through the comparison between the remained amount of cesium in Toyoura sand and the electrolyte and the additive amount of cesium, the difference between them is defined to the adsorbed amount by the adsorption sheet.

Explaining the adsorption sheet in a little more detail, the sheet contains a combination of hydroxyapatite (HAp) and unwoven cloth. The HAp is sandwiched between the unwoven cloth and its content ratio of the sheet is more or less 10%. The thickness of the HAp sheet is more or less 4mm. The HAp has many functions including an ion adsorption property, an ion exchange property, a catalytic characteristic, an ion transmission characteristic, etc. (H, Shigeta et al., 2013) Then, in this study, the ion exchange properties and adsorption characteristic are focused on. The developed HAp sheet is used for the adsorption of the cesium ion.

In the second stage, the adsorption characteristic of the HAp sheet for cesium through the electrophoresis adsorption test is investigated by more practically test with a large-scale chamber which has 1,000 mm of width, 700 mm of depth and 300 mm of height, which is extended from the test with a small chamber. In the experiment with a large-scale acrylic chamber, first of all, a carbon rod connecting to the anode of direct current battery with the conductor is embedded at the bottom of the chamber and 100mm away from the side of the chamber. Toyoura sand is filled until the carbon rod is hidden. Next, cesium (38.1 mg) is added into the 100 mm by 100 mm region of the sand. Then, the HAp sheet (600 mm by 900 mm) is laid on the sand. As an
electrolyte, an aqueous solution of ammonium acetate (3 L) is poured into the chamber, and the steel plate (500 by 800 mm) (the cathode plate) connected with the negative side of a DC power supply is laid on the upper side of the adsorption sheet. 50 mA of current is applied to the conductor as well as the small chamber test. After the continuous current tests, the sand around which cesium is added is collected. The cesium is extracted by the wash of the sand with stirring machine (4 times of 10 minutes stir). Then, the remained amount of cesium in the sand and electrolyte in the chamber after the test is analyzed by an AAS (Atomic Absorption Spectrometer). The addition point of the cesium is point E shown in Figure 2. The analytical sample is gathered from 9 divisions surrounding point E (see Figure 2). The size of a gathered division is 50 mm by 50 mm.

3 RESULTS AND DISCUSSION OF IMMERSION TEST

In order to confirm the adsorption ability of the HAp sheet for cesium in the experiment, it is necessary to determine the quantity of cesium contained in the sand. Moreover, the cesium contained in the sand should be extracted so as to determine it. Thus, the cesium (38.1 mg) is added to the sand (200 g) in the test with a small chamber, and the immersion test for 24 hours is conducted. In the immersion test, acetic acid ammonium is employed as a solution, and 70 mL of the acetic acid ammonium is added into the sand. The concentration of the acetic acid ammonium is 29.6 g of acetic acid ammonium dissolved in 1 L of distilled water. After the immersion test, the cesium contained in Toyoura sand and the solution is extracted by the wash of the sand with stirring machine (4 times of 10 minutes stir). The amount of cesium extracted by AAS. The following shows the adsorption property of HAp sheet and the validity of proposed decontamination method are discussed after showing the test results.

Table 1 shows the cesium extraction amount of two tests, one is the test in which the immersion test with 100 mL of ammonium acetate is started just after cesium is added into Toyoura sand (immediate case), and another is the test in which the immersion test with 100 mL of ammonium acetate is started after a month of adding cesium into Toyoura sand (a month later case). Comparing two results, there is a little difference between them since the average cesium extraction amounts are 33.65 mg of the immediate case and 34.33 mg of a month later case, respectively. Hence, the cesium extraction rate is calculated with the average cesium extraction amount, and is listed in Table 1 as well as the cesium extraction amount. They are 88.33 % of the immediate case and 90.11 % of a month later case, respectively. From this fact, it afford to say that most cesium added into Toyoura sand can be extracted.

Table 1. The amount of cesium extraction.

| Addition time | First (mg) | Second (mg) | Third (mg) | Average (mg) | Extraction rate (%) |
|---------------|------------|-------------|------------|--------------|---------------------|
| Immediate     | 34.21      | 32.36       | 34.39      | 33.65        | 88.33               |
| 1 month later | 33.98      | 35.35       | 33.67      | 34.33        | 90.11               |

That is to say, the cesium added into Toyoura sand can be extracted by ammonium acetate even if the time after the addition of cesium into Toyoura sand passes.

4 RESULTS AND DISCUSSION OF ABSORBENT TEST

The powdered hydroxyapatite (HAp) which has a high adsorptive performance was used in previous study. However, it is difficult to set and collect the powdery type in an actual decontamination of ground. In order to remove such difficulty, the adsorption sheet (the HAP sheet) which is utilized exclusively for a decontamination is developed. In this chapter, the adsorption property of the HAp sheet and the validity of proposed decontamination method are discussed after showing the results of 48 hours continuous current test. Ammonium acetate is employed as electrolyte in continuous current test as well as the extraction test.

Table 2 shows the cesium residual amount after current tests with the HAP sheet and the powdered HAp. Hence, the cesium residual rate is calculated with the cesium extraction amount, and is listed in Table 2 as well as the cesium residual amount. The cesium residual rate is more or less 5 % in the test with the HAP sheet. There is a little difference in the cesium residual rates of the HAp sheet and the powdered HAp. From this fact, it is found that the developed HAP sheet has a high adsorptive performance as well as the powdered HAp.

Table 2. Residual amount of cesium.

| Powdered HAp | HAp Sheet (1) | HAp Sheet (2) | HAp Sheet (3) | Ave.HAp Sheet |
|--------------|---------------|---------------|---------------|---------------|
| Residual amount (mg) | 0.53 | 1.87 | 1.95 | 2.25 | 2.20 |
| Residual rate (%) | 1.40 | 4.90 | 5.12 | 5.90 | 5.31 |

5 RESULTS AND DISCUSSION OF THE LARGE-SCALE ELECTROPHORESIS ADSORPTION TEST

In this chapter, in order to discuss the adaptability of proposed decontamination method to a practical test, the large-scale electrophoresis adsorption test is conducted. The test results are examined after showing the results of 48 hours continuous current test. In the case that cesium was added at point E (see, Fig.2), relatively large amount of cesium is detected at point D, point E, point G and point H. On the contrary, it is
hardly detected at point A, point B, point C, point F and point I. (see Table3). Since an electric current flows from the upper of chamber to the lower left of chamber shown in Fig.2, the cesium which was added at the point E moved around this point such as point D, point G and point H. The total amount of residual cesium in Toyoura sand was 20.22 mg, which is 53 % of added cesium before the start of electrophoresis adsorption test. The result indicates that the HAp sheet can adsorb the cesium added in Toyoura sand in the large-scale test as well as the small one, but that the adsorption performance of the proposed method for cesium in the large-scale test is inferior to the small one. Even if the cesium added at point E diffuses widely from point E, the sample which was analyze by AAS (Atomic Absorption Spectrometer) is limited around point E. As the residual amount of cesium may exist at the place other than these analyzed points, the analyzed points should be increased.

| Table 3. The amount of cesium extraction.          | First (mg) | Second (mg) | Third (mg) | Average (mg) |
|--------------------------------------------------|------------|-------------|------------|--------------|
| Point A                                          | 0          | 0           | 0          | 0            |
| Point B                                          | 0          | 0           | 0          | 0            |
| Point C                                          | 0          | 0           | 0          | 0            |
| Point D                                          | 1.43       | 3.75        | 2.47       | 2.55         |
| Point E                                          | 7.46       | 11.11       | 10.57      | 9.71         |
| Point F                                          | 0          | 0           | 0          | 0            |
| Point G                                          | 2.20       | 2.51        | 2.57       | 2.43         |
| Point H                                          | 9.00       | 3.75        | 3.86       | 5.53         |
| Point I                                          | 0          | 0           | 0          | 0            |
| Total                                            | 20.09      | 21.1        | 19.47      | 20.22        |
| Extraction rate (%)                              | 52.73      | 55.38       | 51.10      | 53.07        |

6 CONCLUSIONS

Though the decontamination of radioactive materials is urgently needed due to the accident of Fukushima Daiichi nuclear power plant, the efficient and effective decontamination technology is not established. Thus, the authors proposed a new decontamination method in which radioactive materials can be removed on the basis of electrophoresis since cesium is water-soluble material and exists as a cation in soil. However, there are some engineering problems such as the advisability of cesium extraction from soil as time advances and the adsorption characteristic of the developed adsorption sheet for a large-scale test. Thus, first, the immersion test was conducted to investigate the advisability of cesium extraction from soil as time advances after the embeddedness of cesium in soil. Secondary, the absorbent test was conducted to exam the applicability and availability of the developed adsorption sheet to the adsorption of cesium in a large-scale test.

In the immersion test, the cesium added into Toyoura sand can be extracted by ammonium acetate as an abstraction solution even if the time after the addition of cesium into Toyoura sand passes. In the large-scale test, it was recognized that cesium can be absorbed by electrophoresis. However, compared with the small test, the large-scale test had a deteriorating adsorption effect due to a decrease in electrical conductivity. It is a future task to improve the efficiency of the large-scale test. For the improvement, it is necessary to carry on further tests in which the content of the HAp in the adsorbed sheet, the amount of electrolyte or the energization time is changed. In this study, Toyoura sand whose quality rarely varies was used because we gave priority to reproducibility in the tests. It is necessary to investigate the adsorption property of HAp sheet for cesium to various soils in near future to cope with ground soil, field, marine soil, lake soil, etc.

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