

STUDY ON EXTRACTION FROM CESIUM IN CONTAMINATED SOIL PACKED IN FLEXIBLE CONTAINER BAG AND ADSORPTION USING RICE HUSK

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*Corresponding Author, Received: 15 June 2019, Revised: 15 Nov. 2019, Accepted: 17 Feb. 2020

ABSTRACT: A large amount of radioactive cesium was diffused by the accident at Fukushima Daiichi nuclear power station. Most of the diffused radioactive cesium deposited on Fukushima soil, and most of the contaminated soil was recovered by the stripping work. The contaminated soil including the radioactive cesium is currently placed in a flexible container bag and stored in a temporary storage facility. In the future, the contaminated soil is going to be burned at the intermediate storage facility. However, the storage facilities are insufficient and a disposal method has an agenda. In order to solve these problems, it is demanded to reduce the contaminated soil by decreasing the dose of radioactive cesium in the contaminated soil. Therefore, in this study, the test equipment simulating the actual flexible container bag is primarily made. Secondly, the two methods are combined; one is the extraction method using the electrophoresis, and another is the adsorption method using an adsorbent in order to decrease the concentration of cesium included in the simulated contaminated soil. As the adsorbent, the rice husk is focused on. Its material cost is reasonable and it can be acquired in bulk. Two types of the electrophoresis test are carried out, one with the use of the rice husk and another with the use of zeolite. The test with the zeolite is positioned as a control test for the test with the rice husk. It is clarified that the adsorption effect of rice husk for cesium is similar to that of zeolite.

Keywords: Radioactive cesium, Electrophoresis, Rice husk, Zeolite

1. INTRODUCTION

The huge tsunami caused by the Great East Japan Earthquake brought devastating damage to the Pacific coast of the Tohoku and Kanto regions. Even now, about eight years have passed since the tsunami disaster, and the reconstruction of Fukushima Prefecture has not been completed due to the serious nuclear accident of the diffusion of a large amount of radioactive materials at the Fukushima Daiichi Nuclear Power Plant of Tokyo Electric Power Company. Among the released radioactive materials, the radioactive cesium is still detected in a wide range in Fukushima Prefecture since it is released in large quantities and has a long half-life as in [1]. In addition, it is known that it is difficult to extract cesium due to the elective fixation of cesium by the clay mineral in soil as in [2]. The soil distribution map in Fukushima prefecture is shown in Fig.1 as in [3], [4]. From Fig. 1, the soil in Fukushima prefecture has a relatively large amount of clayey soil, and cesium is likely to be incorporated into the soil under these circumstances. Fig. 2 shows the abundance of radioactive cesium in multiple soils when one year has passed since the nuclear accident as in [5]. It can be seen that almost all of the radioactive cesium is fixed in the soil as a fixed state. It has been

confirmed that a large amount of fixed radioactive cesium is fixed between the layers, called as Frayed Edge, in which mineral particles such as vermiculite are involved. The vermiculite is broadly distributed in the soil of Fukushima prefecture. Therefore, the development of effective removal technology of cesium from vermiculite is an urgent issue. The biggest issue in the decontamination project in Fukushima prefecture is how to treat the contaminated soil generated by decontamination. Since much of the deposited radioactive cesium exists in the surface layer of about 10 cm of the contaminated soil, the radiation dose has been reduced by the surface decontamination such as the peeling of the topsoil. Large amounts of collected contaminated soil are temporarily stored in flexible container bags in temporary storage areas in Fukushima prefecture. The contaminated soil enclosed in the flexible container bags is scheduled to be sequentially delivered to intermediate storage facilities in Fukushima prefecture in the future. However, it is not easy to carry out a large amount of contaminated soil from the temporary storage place to the intermediate storage facility, in fact, only about 2.18 million m³, which is about 15.6% of about 14 million m³ of the transported objects which should be transported to the intermediate storage facility, has been carried out of the

temporary storage place. Furthermore, the contaminated soil transported to intermediate storage facility will be sorted by a sieve, and incinerated at a high temperature of 800 ° C or higher as in [6]. However, not only the transportation cost of a large amount of contaminated soil but also the incineration cost has not been clarified. Therefore, it is necessary to establish a technology for reducing the volume of contaminated soil by removing cesium from the contaminated soil in the flexible container bags at a temporary storage place. The technology can reduce the radiation dose of the contaminated soil without transporting it to an intermediate storage facility. Thus, in this, study, the simulated flexible container bag is produced on the assumption of the removal of cesium in the flexible bag at the temporary storage place, and the test is conducted with the sand in which vermiculite and Toyoura standard sand are mixed as a simulated contaminated soil. As a cesium removal method from the contaminated soil, and it is verified whether cesium in the soil can be moved and adsorbed to adsorbents by means of the electrophoresis method. The purpose of this study is to examine the effective cesium extraction conditions and the possibility of volume reduction of contaminated soil through the obtained results of

various tests.

2. CESIUM IN SOIL

Cesium exists as a monovalent cation in soil and is adsorbed to the soil particles which is charged with a negative in soil. Additionally, cesium is easily adsorbed in and on the clay particles whose size is small. It is the 2: 1 layered silicate constituting a clay mineral that cesium adheres to the soil. The 2: 1 layered silicate is a generic term of the minerals in which the relation between the thickness of silicon tetrahedral sheet and those of aluminum octahedral sheet is 2: 1. In a silicon tetrahedron sheet and an aluminum octahedron sheet, either sheet or both of the sheets become insufficient in positive charge when a part of silicon or aluminum is replaced with another element having a small amount of positive charge. After that, the negative charge is appeared by the lack of positive charges in the sheet, and the cations are adsorbed to neutralize the interlayers of the sheet. The layer charge shows high selectivity to cesium ions as in [7]. This is because the size of cavity called a six-membered ring formed by oxygen atoms on the basic plane of a silicon tetrahedral sheet is approximately equal to the ionic radius of cesium ion. In addition, the bonding strength to the six-membered ring increases as the hydration energy decreases, which means that cesium ion has the highest bonding strength. However, the potassium ion occupies the six-membered ring because the abundance of potassium ion is decisively large in the soil (see the top of Fig. 3). The end of the clay mineral layer is frayed by

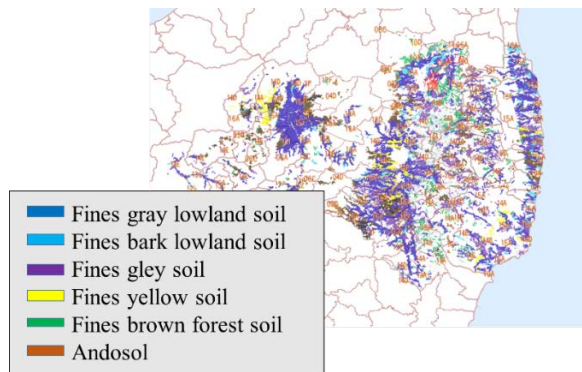


Fig. 1 Soil distribution map in Fukushima prefecture

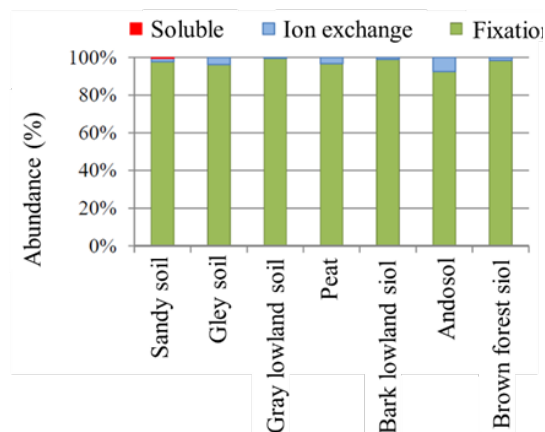


Fig. 2 Abundance of cesium in the soils

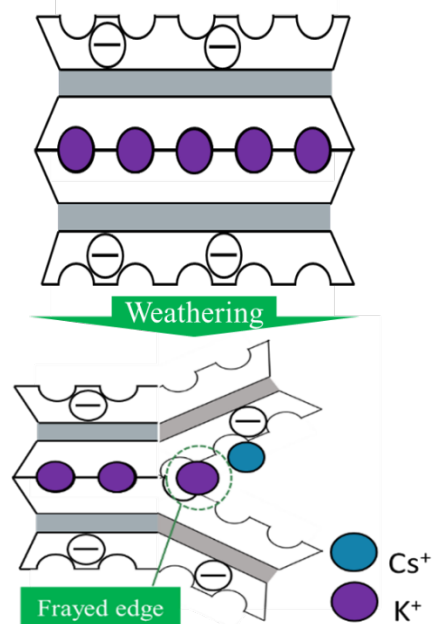


Fig. 3 Top part of 2:1 type of lamellar silicate and bottom part of the Frayed edge

weathering of soil, and the potassium ion is released. As a result, the region into which other cations can penetrate is formed and called as frayed edge site (see the bottom of Figure 3). It is difficult to replace cesium ions fixed to the frayed edge site with other cations as in [8].

3. ADSORBENTS

3.1 Rice husk and Rice husk powder

A large amount of rice husk is generated in the process of threshing and hulling after harvesting, and 2 million tons are discarded every year. In this study, the cesium adsorption ability of rice husks is focused on in order to effectively utilize it as a resource. Various researches on the adsorption ability for cesium of rice husk have been studied as in [9], [10]. For example, the research by Shozugawa et al. states that radioactive cesium is trapped by viscous fungi on the rice husks as in [11]. The possibility as a new adsorbent to replace zeolite is examined by using rice husk as an adsorbent in an electrophoretic test. Raw rice husk and commercially available rice husk powder as shown in Photo 1 are used in the test.



Photo 1 Rice husk (left) and Rice husk powder (right)

3.2 Zeolite

Zeolite is a clay mineral with regular tubular pores and cavities. Zeolite crystals have adsorption properties and ion exchange properties because they have many pores. In particular, it is known that the zeolite has high ion exchange properties against cesium. Thus, the zeolite is selected so as to exam



Photo 2 Powdered zeolite

the adsorption ability of the rice husk through the results of adsorption tests as a comparative material for rice husk. In the test, powdered rice husk is used (see Photo 2).

4. TEST METHOD

4.1 Electrophoresis

In this study, the electrophoretic method is employed in order to transfer cesium ions extracted from clay minerals in soil. The cesium ions transferred to the cathode are adsorbed by an adsorbent placed in front of the cathode. An electrophoretic phenomenon is the movement of charged particles in a liquid medium under an electric field. Cesium ions are transferred to the cathode side by using the electrophoretic phenomenon, and are adsorbed in or on the zeolite or rice husk which are placed in front of the cathode side.

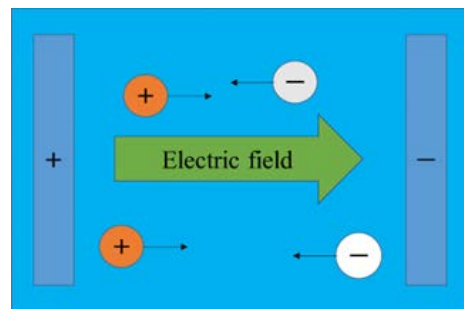


Fig. 4 Mechanism of electrophoresis

4.2 Electrophoresis test

The experiment device which simulates the flexible bag packing the soil contaminated by radioactive cesium is produced in the course of conducting the electrophoresis test. First, a simulated contaminated soil is prepared by adding 1 mL of the cesium standard solution so as to assume a real contaminated soil. The simulated soil consists of vermiculite and standard sand. Next, the simulated contaminated soil is placed in an acrylic container bag, and a carbon rod (diameter of 15 mm and length of 40 mm) serving as an anode is placed vertically in the center of the soil. Additionally, the simulated contaminated soil is placed in a simple container that combines filter paper and holding cloth (mesh size 37 μm) to prevent mixing with the adsorbents. Moreover, the simulated contaminated soil is immersed in ammonium acetate aqueous solution (3.0% of concentration, 60 - 70 mL) and the adsorbent is placed in front of an aluminum plate so as to enclose the simulated contaminated soil (see Fig. 5). After an energization for a specified time, the soil is collected and washed out

by stirring. The extracted amount of cesium contained in the solution and soil after the test is quantified by an atomic absorption spectrophotometer for the solution separated through filtration. The extraction rate is determined by the following equation (1).

$$\text{Extraction ratio (\%)} = \frac{\text{extracted amount (mg)}}{\text{added amount (mg)}} \times 100 \quad (1)$$

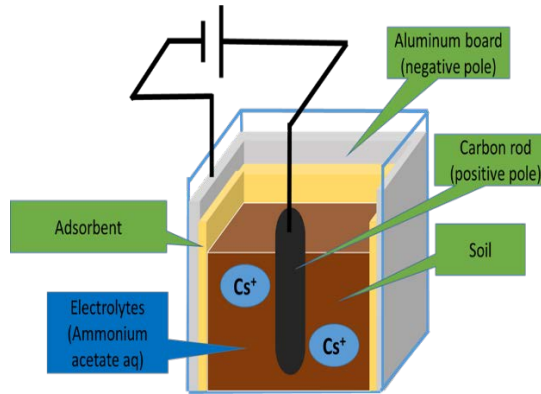


Fig. 5 Test device

5. TEST RESULTS

The volume ratio of standard sand to vermiculite contained in simulated contaminated soil is 1: 1, and the mass of simulated contaminated soil is 120 g. The current values during the electrophoresis test are 25, 50, and 100 mA, and the energizing time is 48 hours. The results of tests using three types of adsorbents are shown in graphs, respectively. Each test is conducted three times to ensure a reproducibility, and the average value for three batches is listed in the graphs. The test conditions are shown in Table 1.

Table 1 Test conditions

Soil	Standard sand: 114 g, Vermiculite: 6 g
Electrolyte	Ammonium acetate aqueous solution (3.0 %): 60-70 mL
Sample	Cesium standard solution: 1mL
Adsorbents	Zeolite 10 g
	Rice husk 3 g
	Rice husk powder 10 g
Curing time	168 hours
Energizing time	48 hours
Current value	25, 50, 100 mA (under 40 V)

5.1 Test results of zeolite

Fig. 6 shows the test results when zeolite is used as the adsorbent. The vertical and horizontal axes of the graph represent the extraction ratio of cesium and the current value, respectively. The results of the test with and without zeolite are compared. As a result of the test, the extraction rate of cesium decreases with increasing of the current value regardless of the presence or absence of the adsorbent. It is found that about 20% of the added cesium is extracted, which can help the volume reduction of the contaminated soil. On the other hand, about 80% of the added cesium remains in the soil. These facts indicate the difficulty of extracting cesium from the soil. Before the electrophoretic test is carried out, the curing period of 168 hours is set to fix the cesium sufficiently to the soil. Most of the cesium is adsorbed to the vermiculite during the curing period, which makes it difficult to extract the cesium from the vermiculite. Alternatively, the most effective extraction of the cesium from the soil appears when the current value is 25 mA in the electrophoresis test. It is found that the extraction of cesium is inhibited if the current value becomes too high. This is caused by the re-adsorption of cesium, temperature rise, the promotion of evaporation of electrolyte, etc. The investigation of the cause should be examined in the future. Considering the practical operation, it can be said that the low current value is advantageous from the viewpoint of running cost. Suppose the difference between the extraction ratios of specimens with and without zeolite is the adsorption ability of zeolite for cesium, the adsorption ability hardly changes with increasing or decreasing current value. In other words, it is found that the current value has little significant influence on the adsorption ability.

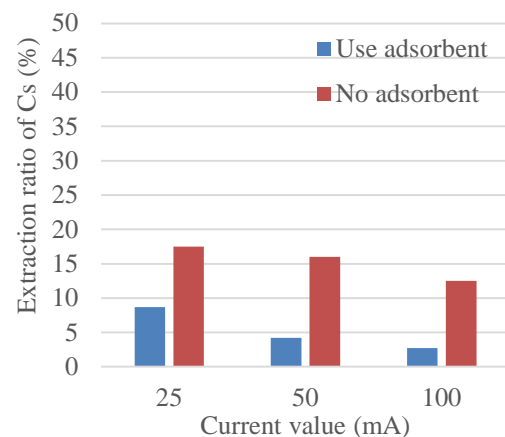


Fig. 6 Extraction ratio of Cs using zeolite

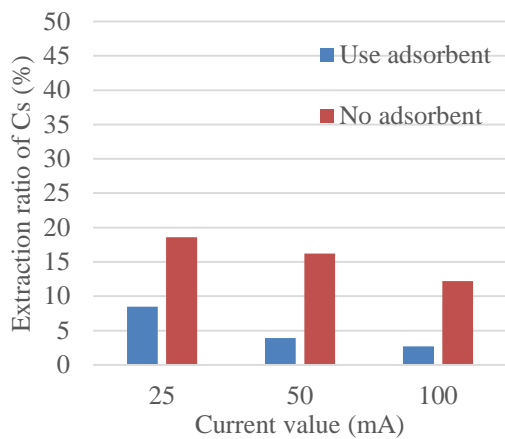


Fig. 7 Extraction ratio of Cs using rice husk

5.2 Test results of rice husk

Fig. 7 shows the test results when the rice husk is used as the adsorbent. The test results are very similar to those of zeolite. The smaller the current value, the larger the extraction ratio r , and the current value has little significant influence on the adsorption ability of rice husk. It is clarified that the rice husk has almost the same adsorption capacity for cesium as the zeolite. It is noted that the used amount of adsorbent is 10g of zeolite and 3g of the zeolite. There is a difference in mass since the apparent volumes of both adsorbents are tried to be equalized. Thus, from the viewpoint of mass, the rice husk has higher adsorption capacity per unit volume than the zeolite. As these results, it may be most useful to use raw rice husk as adsorbent from the viewpoint of both volume reduction and processing cost of rice husks when the amount of adsorbent and adsorption performance is focused on.

5.3 Test results of rice husk powder

Fig. 8 shows the test results when the rice husk

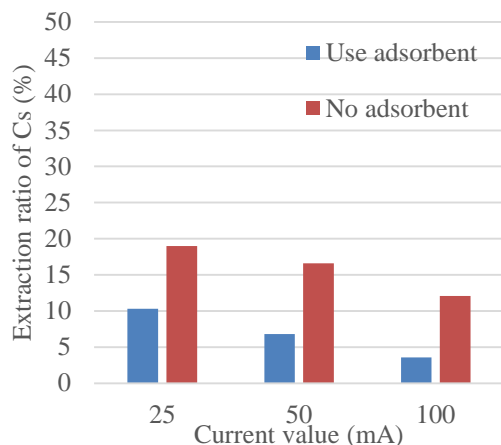


Fig. 8 Extraction ratio of Cs using rice husk powder

powder is used as the adsorbent. The test results are similar to those of zeolite and rice husk. The mass of the adsorbent is 10g of rice husk powder as well as zeolite, and the rice husk powder has the more or less same adsorption ability as zeolite. The adsorption to cesium is largely due to the micropore distribution of the adsorbent and the constituent elements. In the future, it is necessary to investigate the cause by comparing the micropore distributions with using a facility such as a BET specific surface area measurement device.

6. CONCLUSIONS

- In this study, the experiment device which simulates the flexible bag packing the soil contaminated by radioactive cesium is produced, and the electrophoresis tests are conducted under various conditions in order to investigate appropriate transfer conditions of cesium to the adsorbents (zeolite, rice husk and rice husk powder).
- The extraction rate of cesium is the highest at the minimum current value (25 mA) when the cesium is extracted by electrophoresis without an adsorbents.
- The adsorption rate of cesium at 50 mA of current value shows the maximum value to compare with the other current value (25, 100 mA) when the zeolite is used as the adsorbent. However, the difference due to the current is not so large.
- The adsorption rate of cesium at 50 mA of current value also shows the maximum value to compare with the other current value (25, 100 mA) when the rice husk or the rice husk powder are used as the adsorbent, the difference due to the current is not so large. The test results with zeolite, rice husk and rice husk powder as an absorber for cesium are similar, which shows that their adsorption properties for cesium are more or less same.
- It is not clear whether there is a clear correlation between the mass and the amount adsorbed, but it is venture to discuss them here. It can be seen that the rice husk adsorbs the cesium in a smaller amount. It is considered that the adsorption principle of rice husk is one of the factors that enables rice husk to adsorb cesium in a smaller amount than rice husk powder.
- Some of the cesium can be trapped by viscous fungi that attach to the rice husk surface. The reason why the adsorbent performance of rice husk powder is inferior to that of rice husk can be that the adsorption property mentioned above is lost during the powder processing from rice husk to powder form.
- It is identified that a rice husk is an excellent adsorbent for cesium because the powder processing is not necessary and the required amount is small.

7. ACKNOWLEDGMENTS

This work was supported by Japan Society for the Promotion of Science, the Grants-in-Aid for Scientific Research (C) (Grant number: 18J12343).

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