

STUDY ON EXTRACTION AND ADSORPTION OF CESIUM FROM VERMICULITE MIXTURE SAND

Shota NISHIOKA¹, Keiichiro SHIBATA², Hidenori YOSHIDA²

Naomichi MATSUMOTO² and Yoshihiro SUENAGA²

¹ Faculty of Engineering, Kagawa University, Japan

*Corresponding Author, Received: 11 June 2018, Revised: 31 July 2018, Accepted: 27 Aug. 2018

ABSTRACT: A large amount of radioactive materials were diffused by the accident at Fukushima Daiichi nuclear power station of Tokyo electric power company, and decontamination has been continued for about six years in Fukushima. The contaminated soil that is stripped on the ground and is collected should be reduced in volume at an intermediate storage facility. However, it takes a long time to operate the facility. The ministry of the environment shows the guidelines that it is possible to dispose the radioactive waste below 8000Bq/kg of radiation dose in an ordinary process. Therefore, it is more desirable that the radiation dose should be reduced below 800Bq/kg in flexible containers filled with contaminated soil than the reduction of radiation dose in the intermediate storage facility. Thus, in this study, the method in which only radioactive materials are collected from the contaminated soil in the flexible containers is proposed. The extraction of radioactive cesium from the soil is investigated so as to check the performance and availability of the proposed method. As a result, it is confirmed that it is possible to collect a certain amount of cesium from the cohesive soil like vermiculite in which cesium is strongly fixed.

Keywords: Cesium, Vermiculite, Ammonium acetate, Electrophoresis, Zeolite

1. INTRODUCTION

A serious nuclear accident at the Tokyo electric power company's Fukushima Daiichi nuclear power station caused the spread of large amounts of radioactive materials. Among released radioactive substances, iodine 131, cesium 134, cesium 137 and strontium 90 have serious influences on the human body and the environment in terms of release amount and half-life. In particular, cesium 137 has a large release amount of 1.5×10^{16} Bq and its half-life is as long as about 30 years. Moreover, the detection of radiation still continues over a wide range of Fukushima.

Cesium fixed in clay minerals in soil is known to be difficult to remove from the soil. The soil in Fukushima prefecture is relatively abundant in viscous soils. In general, the viscous soils absorb the cesium well from the environmental point of view. In addition, it has been confirmed that most of the radioactive cesium is fixed in mineral particles called vermiculite (weathered biotite) which is unevenly distributed in the soil of Fukushima, and it is necessary to establish the efficient removal method of cesium from vermiculite.

In Fukushima, the stripping on topsoil has been carried out for the decontamination of cesium in the soil.

The Ministry of the Environment estimates that

the amount of generated contaminated soil is about 16 million m³ to 22 million m³ after the volume reduction of the gathered one when all the soil in decontamination area of Fukushima is stripped. It is currently considered difficult to secure an intermediate storage facility in which these large contaminated soils will be managed over a long period of time. Therefore, the disaster waste safety assessment study meeting organized by the Ministry of the Environment proposed that the polluted soil whose radiation dose is less than 8000 Bq / kg can be reused as construction materials such as embankment. This propose indicates that a certain amount of cesium from the contaminated soil in the temporary storage bag are removed without waiting for the construction of intermediate storage facilities.

As a technology for removing cesium, the method in which the volume of contaminated soils can be reduced by burning the burnable materials after separating soil and organic matter mechanically and with high precision is proposed. Other method in which contaminated soils are classified into fine particles fixed with cesium and regenerated soil by washing the soils is proposed. However, in these methods, the contaminated soils are decontaminated in large-scale facilities such as intermediate storage facilities which is difficult to construct in the present situation due to securing their construction sites. Therefore, it is necessary to

reduce the radiation dose of contaminated soil in temporary storage space.

In this study, the artificial soil mixed vermiculite and Toyoura standard sand was prepared as the soil to which cesium could be easily adhered, and a stirring test was conducted using an ammonium acetate aqueous solution as an extraction solution. Based on the results obtained in these cesium extraction tests, electrophoresis tests were conducted at different current values. In the test, it was aimed to investigate whether it is possible to transfer cesium from vermiculite to the adsorbent and to investigate whether it is possible to reduce the radiation dose of contaminated soil in the flexible container at the temporary houserom.

2. MATERIALS AND METHODS

2.1 Materials

In this study, the soil mixed with Toyoura standard sand (Fig.1) and vermiculite (Fig.2) was used as an experimental soil to which cesium was added.

The Toyoura standard sand is composed with the soil particle of the uniform grain size. Moreover, it is very smooth, and the soil grains hardly stick each other. Therefore, the difference between experimental samples can be neglected under the same condition, and the reproducibility of experiments are secured.



Fig.1 Toyoura standard sand.

The vermiculite is the silicate mineral that mainly consists of the oxidized silicon, magnesia and aluminum oxide. It is also called leech stone in Japan since it expands at high temperature. The common uses of vermiculite include soil improvement and livestock food in agricultural and horticultural fields, refractory materials and lightweight concrete in the construction field, disposable hand warmer and friction materials. It has been confirmed that the vermiculite is unevenly distributed in the soil of Fukushima, which is a major obstacle to the decontamination of radioactive cesium. Cesium present as a monovalent cation in soil adsorbs to negatively charged soil particles in the soil. It also has the property of selectively adsorbing to clay particles of

small particle size. Cesium is fixed to the soil by the 2: 1 type layered silicate (Fig.3) such as vermiculite among the minerals constituting the clay mineral. The weathering of the soil swells so that the terminal part of the layer of clay mineral gets frayed and releases potassium ion. As a result, a portion where other cations can enter can be formed. This is called a frayed edge (Fig.4). The cesium ion fixed to this frayed edge becomes difficult to replace by other cations. In this study, 0.7 mm, 1.0 mm, 2.0 mm of grain size of vermiculite was utilized.



Fig.2 Vermiculite (particle size 0.7mm, 1.0mm, 2.0mm from the left).

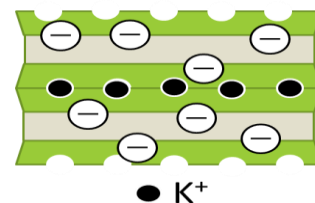


Fig.3 2: 1 type layered silicate schematic.

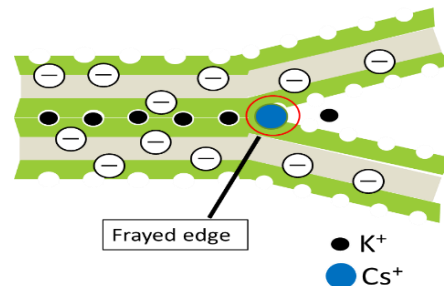


Fig.4 Schematic diagram of the frayed edge in 2: 1 type layered silicate.

The cesium extraction test using decomposed granite soil was conducted by Miyazaki (2016), but the test result tended to vary on account of the size of weathered granite soil. Therefore, in this study, the experimental results with high reproducibility can be secured by preparing the mixed soils mentioned above, because only the Toyoura standard sand and the vermiculite are employed as a soil sample. In the experiment, it was decided to carry out a cesium extraction test on the mixed soil

with the Toyoura standard sand and the vermiculite.

Powdered zeolite (Fig.3) was used as an adsorbent for cesium in the electrophoresis test. The skeleton structure of zeolite is silicon and aluminum bonded via oxygen. In the skeleton structure, the periphery of silicon is electrically neutral and the surroundings of aluminum are negatively charged since aluminum and silicon share oxygen with each other. Therefore, the cations are required in the framework to compensate for the negative charge. Since the cation is easily exchanged with other metal ions, the zeolite is known to have ion exchange properties.



Fig.5 Powdered zeolite.

An aqueous ammonium acetate solution as an extraction solution for extracting cesium in the soil and as an electrolyte in the electrophoresis test was used. It is known that the ammonium ion of ammonium acetate shows a high ion exchange reaction with cesium ions fixed in the clay mineral. Based on this fact, it is suitable for the extraction of cesium in the mixed soil. From the study of Miyazaki (2016), the higher the concentration of the ammonium acetate aqueous solution used as the extraction solution and electrolyte, the higher the extraction rate of cesium. Since, however, the contaminated soil in which the radiation dose is decreased below the reference value is reused, the ammonium acetate aqueous solution in concentrated form cannot be employed. Therefore, 5% concentration of ammonium acetate aqueous solution (concentration 3.0%) of a saturated aqueous ammonium acetate solution (concentration 59.7%) having a low concentration and an excellent extraction rate.

2.2 Cesium extraction test method

In this study, the experimental sample should be put into solution for the quantitative analysis for cesium with atomic absorption spectrometry. Therefore, it is necessary to separate the cesium in the soil into the solution after the electrophoresis test. In addition, it is difficult to separate only cesium from the adsorbent after the test into a solution. Thus, in order to confirm the adsorption effect for cesium on the adsorbent by electrophoresis, it is necessary to separate cesium into solution and to compare the difference of

cesium between the tests with and without the adsorbent. As a separation method, 100 mL of the ammonium acetate aqueous solution whose concentration is same as that used in the test was added to the soil after the test. Then, it is agitated for 10 minutes at 300 rpm of a rotation speed using a stirrer. Moreover, it is sieved with a sieve of 38 μm . Stirring is performed for 40 minutes in total by repeating the solid-liquid separation step of filtering to solution and soil four times. The amount of cesium contained in the solution after the test and the soil is quantified for the solution separated by filtration with each stirring using an atomic absorption spectrometer.

2.3 Electrophoresis test

As a test soil assuming contaminated soil, vermiculite mixed sand with cesium is placed in a test container and a carbon rod (D 15 mm, L 40 mm) to be an anode is installed on the bottom of the container. It is immersed in an aqueous solution of ammonium acetate which is an electrolyte, and an adsorbent is placed on an assumed contaminated soil. The adsorbent was placed in the simple container which consists of a filter paper and a holding cloth for an easy access after testing. Finally, an aluminum plate (W 30 mm, L 90 mm) is installed to serve as a cathode from the top of the adsorbent (Fig.4). Since cesium exists as a cation in solution, it moves to the aluminum plate which is the cathode by energization and is adsorbed by the adsorbent.

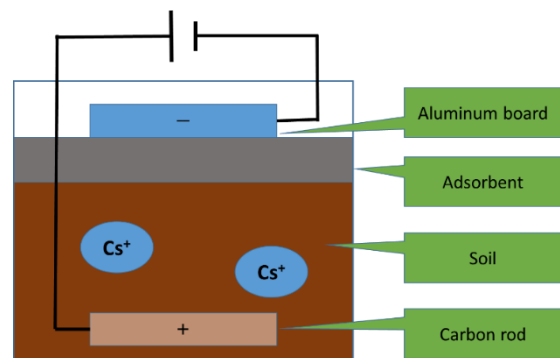


Fig.6 Schematic drawing of electrophoresis test

3. RESULTS AND DISCUSSION

3.1 Cesium adsorption of vermiculite

In order to confirm the adsorption performance of vermiculite to cesium, the results of cesium extraction test using aqueous ammonium acetate solution as an extraction solution are shown. The purpose of the extraction test is to confirm whether cesium can be efficiently extracted from

vermiculite by using aqueous ammonium acetate solution. In addition, the tests are conducted under the conditions where cesium is more easily to be fixed, such as the curing tests in which the curing period of the assumed contaminated soil is varied or the wet state is kept. According to the test results, the compounding ratio of vermiculite and sand for the mixed sand is determined. As a result, 20 g of mass and 0.7, 1.0, and 2.0 mm of particle size of the vermiculite are determined.

In this test, cesium is extracted by washing with stirring. 1 mg of cesium is added to the vermiculite or mixed sand in the test container. 0 hour and 168 hours of curing period are set, 100 ml of ammonium acetate aqueous solution as extraction solution is poured into the assumed contaminated soil, and the washing out by stirring is carried out. The concentration of the ammonium acetate aqueous solution is set to 3.0%, and the stirring is carried out for 10 minutes at 300 rpm of a rotation speed. Four sets of the stirring is conducted, that is to say, 40 minutes stirring is totally carried out. In some tests, the distilled water is added into the assumed contaminated soil before the addition of cesium into the soil so as to reproduce the real condition in Fukushima. In this study, each test is conducted three times under the same condition to ensure a reproducibility.

In the cesium extraction test with 0.7 mm of vermiculite particle size, Fig. 7 shows that about 20% of cesium can be extracted by washing out with distilled water immediately after the addition of cesium. However, compared with Fig. 8, the extraction ratio is reduced to 10% or less due to long curing period. This is because the cesium is not completely absorbed in the flied edge of vermiculite immediately after the addition of cesium. However, the cesium is sufficiently adsorbed in the flied edge of vermiculite due to the long curing period. This face suggests that the washing out with the distilled water against the curing contaminated soil is ineffective.

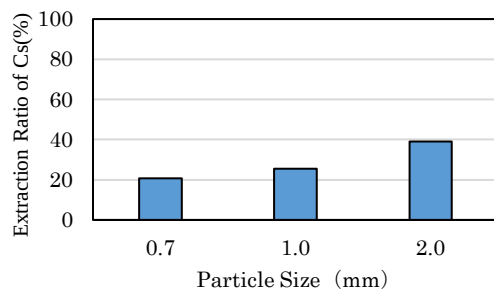


Fig. 7 Extraction ratio of cesium by washing out with distilled water (curing period 0 h).

Figure 9 shows the result of washing out the curing vermiculite with an ammonium acetate aqueous solution. Comparing Fig. 8 with Fig. 9, it can be seen that the extraction ratio of cesium is improved by about 20% by washing with ammonium acetate. Therefore, it was confirmed that the ammonium acetate aqueous solution was effective and efficient extraction of cesium for the curing contaminated soil.

In the cesium extraction test with 1.0 mm of the vermiculite particle size, the cesium extraction ratio is slightly higher than that of 0.7 mm of the vermiculite particle size. The surface area per gram of vermiculite is larger when the particle size is smaller. The vermiculite having 0.7 mm of the particle size contacts cesium more widely than the others, and trend high performance of cesium adsorption.

For the vermiculite having 2.0 mm of the particle size, the extraction ratio is higher than the other two. As mentioned above, the extraction amount of cesium depends on the surface area per gram of vermiculite. However, it is found that the extraction rate by the extraction with distilled water shows about 20% drop due to curing in the case of 2.0 mm particle size.

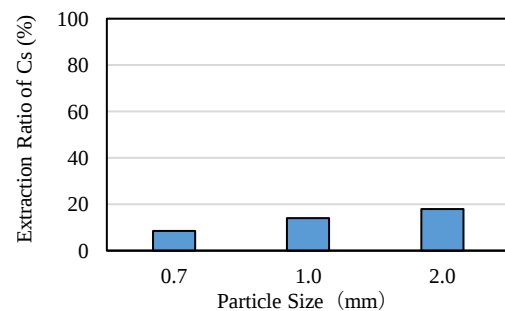


Fig. 8 Extraction ratio of cesium by washing out with distilled water (curing period 168 h).

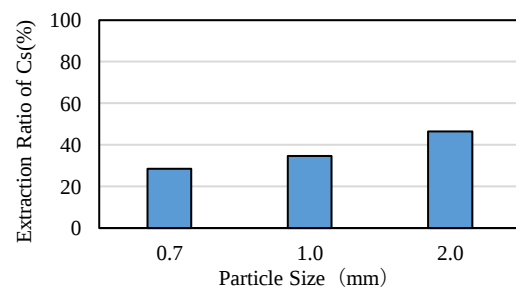


Fig. 9 Extraction ratio of cesium by washing out with ammonium acetate aqueous solution (curing period 168 h).

From the results of these tests, it is confirmed

that it is difficult to extract cesium in the case of smaller size is difficult to extract cesium in the case of smaller size of vermiculite particle and to extract cesium with distilled water from cured contaminated soil. In these tests, it is found that the vermiculite having 0.7 mm of particle size adsorbs a lot of cesium. Thus, in this study, the vermiculite having 0.7 mm of particle size is mixed with the Toyoura standard sand and employ an ammonium acetate aqueous solution as an extraction solution.

3.2 Extraction of cesium from mixed sand

The vermiculite mixed sand is prepared based on the results obtained from the tests in which the cesium is extracted from only vermiculite. The vermiculite with 0.7 mm particle size is employed in order to prepare the mixed soil. The total mass of the mixed soil in the cesium extraction test and electrophoresis test are set to 50 g and 120 g, respectively. The mixing ratios of vermiculite to standard sand are three cases; 3, 5, 10%.

As can be seen from Fig. 10, the lower the cesium extraction rate is, the higher the mixing ratio of vermiculite to standard sand is. Under the condition of constant volume of standard sand, the more the cesium is adsorbed, the higher the mixed ratio of vermiculite to standard sand is.

The extraction ratio of cesium in the case of only the vermiculite and the mixed sand is considered. Comparing Fig. 9 with Fig. 10, there is not much difference between only the vermiculite and the mixed sand in terms of the extraction of cesium.

Figure 11 shows the result of cesium extraction of assumed contaminated soil in the case of 120 g of the mixed sand for electrophoresis test. Comparing Fig. 10 with Fig. 11, it can be seen that there is not much difference between 50 g case and 120 g case in terms of the extraction ratio of cesium. This is because the volume ratio of vermiculite and standard sand hardly changes between them even if their total amount of mixed sand are different. Thus, more or less same cesium extraction ratio are obtained in both cases.

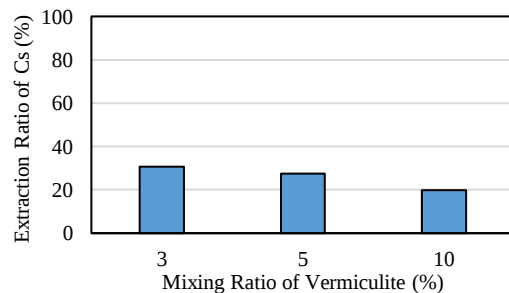


Fig. 10 Extraction ratio of cesium in vermiculite

mixed sand 50 g (curing period 168 h).

From the above test results, the addition of 5% of vermiculite for 120 g of the mixed soil is determined in the electrophoresis test.

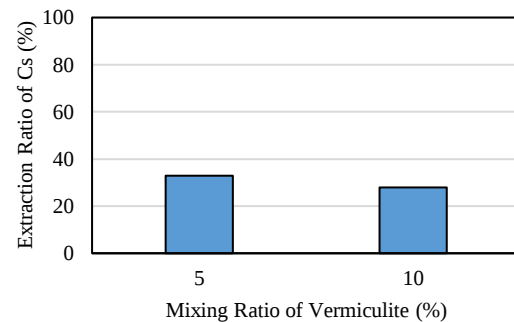


Fig. 11 Extraction ratio of cesium in vermiculite mixed sand 120 g (curing period 168 h).

3.3 Electrophoresis test

In the electrophoresis test, the vermiculite having 0.7 mm particle size, which adsorbs cesium most, is employed based on the results of cesium adsorption a performance test of vermiculite. In the assumed contaminated soil used for the electrophoresis test, 1 mg of cesium is added after setting the moisture content to 30% wet state, and the curing period is 168 hours.

In the electrophoresis test, the aqueous solution of ammonium acetate is employed as an electrolyte, and the test is carried out under the conduction conditions of 48 hours of the energization time, 25V or less of voltage, and 0.005, 0.010, 0.015, 0.025, 0.050 or 0.100 A of current. As a result, the most effective condition in which the cesium moves from the assumed contaminated soil to the adsorbent is selected. The adsorption effect is evaluated through the comparison of the cesium extraction ratio in the case of presence or absence of the adsorbent. In this stage, the difference of the cesium extraction ratio between two cases of gives us the adsorption performance of absorbent for cesium.

As can be seen from Fig. 12, it is confirmed that a certain amount of cesium is adsorbed to the zeolite which is employed as an absorbent in this study at 0.015 A or more of current. The cesium is considered to be unmoving because 0.010 A or less of current is not enough or the cesium to move. Compared Fig. 11 to Fig. 12, it is found that extraction ratio of cesium is decreased by carrying on the electrophoresis test. This is thought that the cesium which is not fixed moves to the frayed edge of vermiculite by current application.

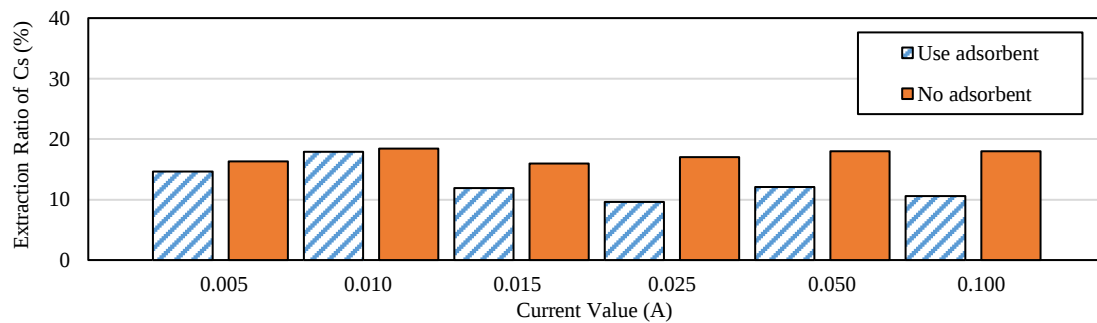


Fig. 12 Cesium extraction ratio (adsorbent: zeolite) in vermiculite mixed sand for 48 hours electricity test.

4. CONCLUSION

The decomposed granite used in our previous studies was heterogeneous in particle size, and there was variability in the result of cesium extraction for each test. The vermiculite which exists a lot in Fukushima soil fixes cesium and causes the removal of cesium from the soil difficult. Therefore, in this study, the vermiculite is employed as an assumed contaminated soil. The aim of this study is to examine the possibility of decontamination of contaminated soil in a flexible control bag through the extraction of cesium test and electrophoresis test with thinking much of reproducible conditions.

First, in order to investigate the cesium adsorption ability of vermiculite used in this study as an assumed contaminated soil, the extraction test in which some size of vermiculite particle are used is conducted under various conditions. The distilled water and ammonium acetate aqueous solution are utilized as an extraction solution to extract cesium from the vermiculite. As a result, it is found that the smaller the particle size is, the more the cesium is absorbed in the vermiculite due to the larger surface area of the particle. In the extraction of cesium test with using 0.7 mm of vermiculite particle size and the distilled water, it is found that the extraction ratio is about 20% without the curing period and about 10% under the curing. Furthermore, it is clarified that extraction of cesium with the distilled water is difficult. However, using an aqueous solution of ammonium acetate as an extraction solution, the extraction ratio of cesium in the case of 0.7 mm of the vermiculite particle size is about 30% without respect to the curing period of an assumed contaminated soil after adding cesium into it. Therefore, it is confirmed that more cesium can be extracted by using ammonium acetate aqueous solution even if the curing period is provided.

Based on the above test results, the cesium extraction test on mixed soil of vermiculite and Toyoura standard sand is conducted. In this test, the extraction of cesium from the assumed contaminated soil with using 0.7 mm of vermiculite particle size is examined. From the tests, it is found that the extraction ratio of cesium decreases as the mixing ratio of vermiculite is higher.

In the electrophoresis test, it is turned out that a certain amount of cesium is adsorbed to the zeolite which is employed as an adsorbent in this study at 0.015 A or more of current. In addition, it is also confirmed that extraction ratio of cesium declines by carrying out energization. However, there is no need to remove all the cesium from the contaminated soil, so we need to consider how much cesium should be adsorbed by an adsorbent like zeolite. As for future tasks, the containers assuming actual flexible container bags will be prepared and the electrophoresis test is conducted to investigate the amount of adsorption of cesium which is added into the soil in the container.

5. REFERENCES

- [1] Mukai H, Hatta T, Kitazawa H, et al, "Speciation of Radioactive Soil Particles in the Fukushima Contaminated Area by IP Autoradiography and Microanalyses", *Environmental Science & Technology*, Vol. 48, No. 22, 2014, pp.13053-13059.
- [2] Ministry of the Environment, "The basic concept of the safe use of recycled materials of the removed soil", 2016, pp.1-8.
- [3] Tokyo Sangyo Co., Ltd, "Decontamination and reduction system of radioactive substances", 2014, pp.2-10.
- [4] Ministry of the Environment, "About efforts of technology demonstration projects such as decontamination and volume reduction", 2016, pp.1-7.
- [5] Atsushi Nakao, Noriko Yamaguchi, "Move-ment of radioactive substance in soil", *Soil fertilizer compilation*, No.23, 2011, pp.85-93.
- [6] Hidenori Yoshida, et al, "Fundamental study on extraction of cesium from soil", *Environmental Geotechnical Engineering Symposium paper*, Vol.11, 2015, pp.453-460

Copyright © Int. J. of GEOMATE. All rights reserved, including the making of copies unless permission is obtained from the copyright proprietors.