

# STUDY ON REMOVAL OF CESIUM FROM CONTAMINATED SOIL BY ELECTROPHORESIS USING POTASSIUM ACETATE AS ELECTROLYTE

\* Ayane Yanaka<sup>1</sup>, Keiichiro Shibata<sup>2</sup>, Naomichi Matsumoto<sup>3</sup> and Hidenori Yoshida<sup>3</sup>

<sup>1</sup> Graduate School of Engineering, Kagawa University, Japan; <sup>2</sup> Kajima Corporation, Japan, <sup>3</sup> Faculty of Engineering and Design, Kagawa University, Japan

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**ABSTRACT:** 9 years have passed since a large amount of radioactive materials were diffused by the nuclear accident at the Fukushima Daiichi Nuclear Power Station of Tokyo Electric Power Company. The decontamination works have almost been completed, and some of the contaminated soil whose topsoil was stripped and collected was transported to the intermediate storage and incineration facilities. However, the contaminated soil containing the radioactive cesium stored in the temporary storage place has not decreased significantly. Additionally, the transportation of the intermediate storage and incineration facilities have an agenda from the viewpoint of cost. Therefore, it is needed to investigate the method of decontamination by which the radiation dose of contaminated soil can be reduced below 8000 Bq/kg at the temporary storage place. Considering the decontamination in the actual temporary storage place, electrophoresis is the simple method as a decontamination method, and it is desirable to utilize zeolite with ion-exchange property as an inexpensive adsorbent. Ammonium acetate has been considered to be effective as an electrolyte because it has ammonium ion that has high ion-exchange reaction with cesium ion. However, an efficient decontamination cannot be achieved since the adsorption of cesium ions to zeolite is inhibited by ammonium ions. The purpose of this study is to discuss the efficient removal of cesium by using zeolite as an adsorbent and potassium acetate as an electrolyte through the electrophoresis test. From the test results, it is turned out that potassium acetate is suitable to extract cesium efficiently in electrophoresis.

*Keywords: Radioactive materials, Cesium, Zeolite, Electrophoresis, Extraction*

## 1. INTRODUCTION

The nuclear accident at the Fukushima Daiichi Nuclear Power Station of Tokyo Electric Power Company occurred due to the effect of the huge tsunami by the Great East Japan Earthquake, and a large amount of radioactive materials were diffused extensively widely around Fukushima Prefecture. Most of the released radioactive materials were radioactive cesium. Radioactive cesium has a long half-life and affects over a long period of time as in [1]. Vermiculite is widely distributed in soils in Fukushima Prefecture and has interlayers called frayed edge. Since radioactive cesium is selectively fixed to the interlayers of mineral particles such as vermiculite, it is difficult to extract cesium which is once fixed. Since most of the accumulated radioactive cesium exists in the surface soil of the contaminated soil as in [2], the surface decontamination work has been carried out by stripping the surface soil. The contaminated soil collected by the stripping of the topsoil is enclosed in a flexible container bag and temporarily stored in the temporary storage place. At present, 9 years have passed since the occurrence of the accident, the decontamination works have almost been

completed. Additionally, some of the contaminated soil enclosed in flexible container bags have been transported to the intermediate storage facilities in Fukushima Prefecture successively since 2015. However, the contaminated soil containing the radioactive cesium of about 6.67 million m<sup>3</sup> remains to be stored in the temporary storage place. Furthermore, the contaminated soil transported to an intermediate storage facility is sorted through sieves, and incinerated at a high temperature above 800 °C or higher as in [3]. Therefore, it is expected that not only the transportation cost of a large amount of contaminated soil but also the incineration cost will be enormous. According to the basic policy by the Ministry of the Environment, since it is shown that the contaminated soil with radiation dose below 8000 Bq/kg is reused as construction materials as in [4], the reuse of low dose of soil as construction materials can reduce the volume of contaminated soil. To achieve the volume reduction of the contaminated soil, it is desired to reduce the dose to 8000 Bq/kg or less by the partial removal of the radiation cesium for the contaminated soil exceeding 8000 Bq/kg at present. It is necessary to remove only radioactive cesium efficiently in order to reduce the dose of soil in the

flexible container bag stored in the temporary storage place.

As one of the means for efficiently realizing the removal of only the radioactive cesium, the technique using the electrophoresis is mentioned as a candidate. By using this method, cesium ions, which are cations, can be extracted from the soil using a solution which also serves as an electrolyte and an extract, and transferred to the cathode by electric force. Ammonium or potassium salts are necessary for the extraction of cesium ions in soil, and ammonium acetate is known to have relatively higher extraction performance than potassium acetate as in [5]. Therefore, ammonium acetate with ammonium ion which has high ion exchange reactivity with cesium ion seems to be effective as an electrolyte for the electrophoresis. However, it is reported that the adsorption of cesium ions on zeolite is inhibited by the presence of ammonium ions when zeolite is used as an adsorbent as in [6]. Potassium acetate is slightly inferior in the extraction performance, but from the viewpoint of the cesium adsorption ability of zeolite and the volume reduction of contaminated soil containing radioactive cesium, it is expected that the cesium adsorption capacity of zeolite can be increased by using potassium acetate as an electrolyte and extraction solution.

The purpose of this study is to discuss the efficient extraction and adsorption of cesium by using zeolite as an adsorbent and potassium acetate as an electrolyte through the electrophoresis test.

## 2. THE BEHAVIOR OF CESIUM IN SOIL

Cesium exists as monovalent cation in soil and is adsorbed to the soil particles which carry a negative charge in soil. Cesium selectively adheres to soil composed of clay minerals mainly of 2:1 type layered silicate among the minerals constituting clay minerals. The 2:1 type layered silicate is a generic name of minerals having a 2:1 relationship between the lamination of silicon tetrahedral sheets and the lamination of aluminum octahedral sheets. A silicon tetrahedron sheet is a tetrahedron formed by surrounding silicon atoms with four oxygen atoms, and an aluminum octahedron sheet is a tetrahedron formed by surrounding aluminum atoms with six oxygen atoms in two dimensions. In a silicon tetrahedral sheet or an aluminum octahedral sheet, when some silicon or aluminum elements are replaced by other elements having a small amount of positive charge, the amount of positive charge is not sufficient in either sheet or both sheets as in [7]. After that, negative charge appears due to lack of positive charge, and the interlayers are neutralized by the adsorption of cations. The interlayer charge shows high adsorption selectivity for cesium ions. This is

because the size of the cavity called six-membered ring formed by oxygen atom on the basal surface of a silicon tetrahedral sheet is approximately equal to the ionic radius of cesium ions. As the hydration energy decreases, the binding force to the six-membered ring increases, and in particular, the cesium ion has the highest binding force. However, potassium ions occupy the six-membered ring because an abundance of potassium ion in the soil is overwhelmingly large (see Fig. 1). Potassium ions are released by the fray at the end of the layer in clay minerals accompanied by soil weathering (see Fig. 2). As a result, a region in which other cations can penetrate is formed. This is called frayed edges. It is difficult that cesium ion fixed in the frayed edge is displaced by other cations as in [8].

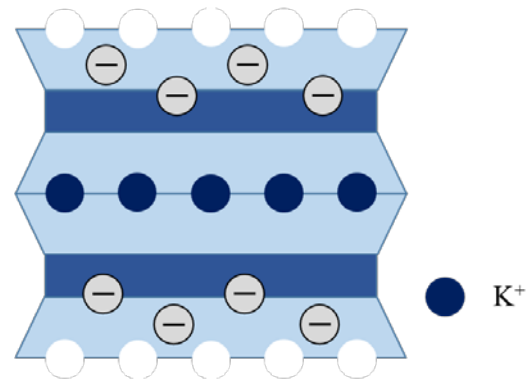


Fig. 1 The 2:1 layered silicate

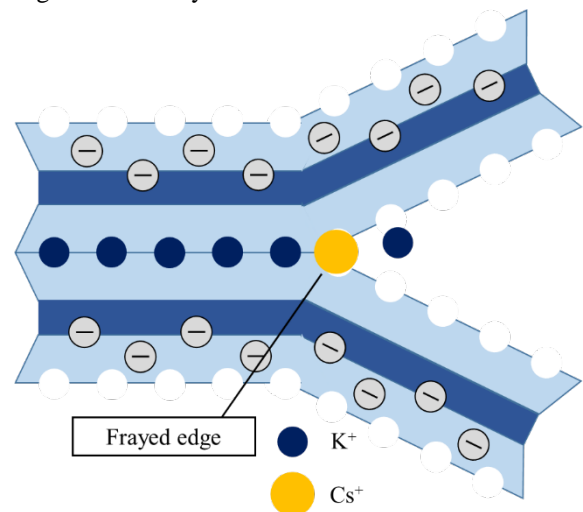


Fig. 2 Frayed edge

## 3. TEST METHOD

### 3.1 Electrophoresis

In the electrolyte used in electrophoresis, charged particles in the solvent move under the electric field generated by the application. In the

electric field, cations and anions transfer to the cathode side and the anode side, respectively. Cesium ions, which are cations, are transferred to the cathode side by utilizing the electrophoretic phenomenon, and the transferred cesium ions are adsorbed on zeolite which is placed between the soil and the cathode.

### 3.2 Electrophoresis test

Electrophoresis test is conducted using potassium acetate aqueous as an electrolyte and extraction solution. Electrolyte and extract solutions are prepared at three different concentrations (1.0 %, 1.5 % and 3.0 %). Electrophoretic tests are carried out at each concentration, and the amount of Cesium remaining in the soil is measured. According to the obtained results, the extraction and adsorption at each concentration are discussed.

As a test equipment, a simulated flexible container bag is prepared (see Photo. 1). First, a simulated contaminated soil is prepared. 114 g of standard sand and 6 g of vermiculite are mixed, and 36 mL of pure water is poured into the mixed sand in order to adjust the 30 % of moisture content. 1 mL of cesium chloride solution is added to the soil, and the test sample is cured for 168 hours. Next, the simulated soil is put into an acrylic container bag, a carbon rod to (15 mm of diameter, 40 mm of length) as an anode is placed perpendicularly to the center of the soil. In this stage, a 35  $\mu$ m opening bolting cloth is laid on the inside of the acrylic container bag, and then a simulated contaminated soil is put there so as to prevent mixing with zeolite and the test sample. In addition, 60 - 70 mL of potassium acetate solution, which is an electrolyte solution, is put into the acrylic container bag, and the simulated

contaminated soil is immersed in the electrolyte. An aluminum plate as a cathode is placed so as to surround the simulated contaminated soil, and 10 g of zeolite is installed between the bolting cloth and the aluminum plate. In the electrophoresis test, a constant current of 50 mA is applied for 48 hours with a voltage value of 40 V as an upper limit. In conducting electrophoretic tests, potassium acetate solution is sequentially put into the acrylic container bag to maintain the lowest possible voltage during the test. After energization, using potassium acetate solution as an extraction cleaning solution, the soil is stirred and washed by using a stirring device. Moreover, the concentration of cesium contained in the filtered and separated solution is analyzed by an atomic absorption spectrometer.

The extraction ratio is defined by the following equation (1).

$$\begin{aligned} & \text{Extraction ratio (\%)} \\ &= \frac{\text{Extracted amount (mg)}}{\text{Added amount (mg)}} \times 100 \end{aligned} \quad (1)$$

In order to ensure reproducibility, the average results obtained from the tests conducted three times are adopted as test results. The test conditions are summarized in Table 1.

### 4. RESULT OF ELECTROPHORESIS TEST

Fig. 3 shows the extraction rate of cesium under various concentrations of potassium acetate solution. The horizontal and vertical axes are the concentration of potassium acetate solution and the extraction ratio of cesium, respectively. The difference between the extraction rate of cesium with zeolite and that without zeolite is interpreted as the adsorption rate of cesium adsorbed on zeolite.

Table 1 Test conditions (In the case of using potassium acetate solution)

Mixed sand (sand + vermiculite)	120 g (114 g + 6 g)
Cs (cesium chloride)	1 mL
Pure water	36 mL (moisture content: 30 %)
Curing period	168 hours
Electrolyte and extraction solution	Potassium acetate 1.0 - 3.0 % (60 - 70 mL)
Adsorbent	Zeolite 10 g
Current value	50 mA (under 40 V)
Energizing time	48 hours



Photo. 1 A simulated flexible container bag (test equipment)

Fig. 3 suggests that the extraction ratio of cesium from the soil increases as the concentration of potassium acetate solution decreases. It is also found that the highest concentration of 3.0 % potassium acetate solution results in the lowest rate of cesium extraction from the soil. In the electrophoresis, due to the electrolysis reaction of water with the application of voltage, hydrogen ions and hydroxide ions are generated at an anode and a cathode, respectively as in [9]. Therefore, the solution near an anode and a cathode indicate acidity and basicity, respectively. In the case of the highest concentration of potassium acetate solution (3.0 %), the pH of the solution near an aluminum plate as a cathode indicates a high value (pH over 10). For aluminum, corrosion occurs at pH outside the range of 4 to 8. In the case of the high concentration of potassium acetate solution, it is considered that the electrophoresis is inhibited by the corrosion of an aluminum plate, and as a result, the extraction ratio of cesium decreases. Judging comprehensively from the extraction and adsorption ratios of cesium, it is found that potassium acetate has the highest performance for extraction and ion transport at the lowest concentration of 1.0 % of potassium acetate solution. The concentration of potassium acetate solution as the electrolyte becomes lower, as the voltage is increased. Then, the potassium acetate solution is sequentially put into the acrylic container bag from the viewpoint of ensuring the safety. A lot of potassium ions are required to extract cesium ions. It is considered that the potassium ions necessary for the extraction of cesium can be supplied more efficiently by sequentially adding a low concentration of potassium acetate solution as an extraction and electrolyte for the electrophoresis than by using a high concentration of potassium acetate solution.

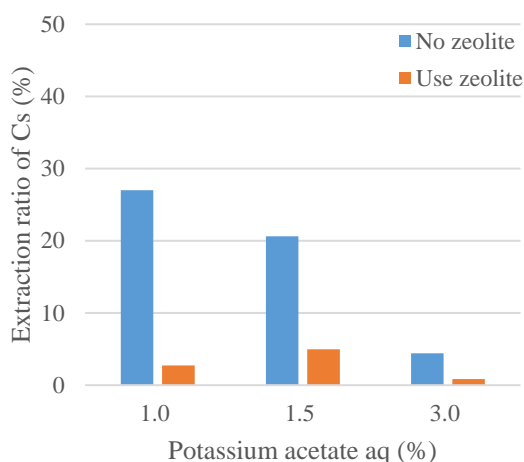


Fig. 3 The extraction ratio of cesium by potassium acetate solution

Incidentally, it is generally known ammonium acetate has a higher extraction capacity than potassium acetate in order to extract cesium fixed to clay minerals. For the reason, in regard to the extraction from the soil and the adsorption on zeolite, the result of the electrophoresis test utilizing ammonium acetate as extraction solutions and electrolytes is compared to that utilized potassium acetate as extraction solutions and electrolytes. Fig. 4 shows the extraction ratio cesium under various concentrations of ammonium acetate solution. Fig. 4 shows The horizontal and vertical axes are the concentration of ammonium acetate solution, and the extraction ratio of cesium. As with Fig. 3, the difference between the extraction rate of cesium with zeolite and that without zeolite is interpreted as the adsorption rate of cesium adsorbed on zeolite.

In the electrophoretic test using ammonium acetate solution as an extraction and electrolyte solution, not only a bolting cloth but also a filter paper is laid on the inside of an acrylic container bag to prevent mixing of zeolite and the specimen. Then, the simulated contaminated soil is put into the acrylic container bag. Except this condition, all the conditions for the electrophoretic test using ammonium acetate solution as an extraction and electrolyte solution are the same as those for the electrophoretic test using potassium acetate solution as an extraction and electrolyte solution. The test conditions are summarized in Table 2.

As compared to Fig. 3 with Fig. 4, whether or not filter paper is used, it is indicated that the adsorption ratio of cesium by a potassium acetate solution is more than that by an ammonium acetate solution in the lowest concentration of the electrolyte and extraction solution (1.0 %). Ammonium and potassium acetate solution show neutrality and weakly basicity, respectively. When the pH falls below the zero charge point, it is

Table 2 Test conditions (In the case of using ammonium acetate solution)

Mixed sand (sand + vermiculite)	120 g (114 g + 6 g)
Cs (cesium chloride)	1 mL
Pure water	36 mL (moisture content: 30 %)
Curing period	168 hours
Electrolyte and extraction solution	Ammonium acetate 1.0 – 4.5 % (60 - 70 mL)
Adsorbent	Zeolite 10 g
Current value	50 mA (under 40 V)
Energizing time	48 hours

possible that the electroosmotic flow reverses due to the changes of the surface electric charge of the soil from a negative charge to a positive one as in [10]. It is considered that the flow of cesium ions to a cathode is inhibited by the back run of the electroosmotic flow because the pH of the ammonium acetate solution is less than that of the potassium acetate solution. It seems that the pH of an electrolyte and extraction solutions affects the extraction ratio of cesium.

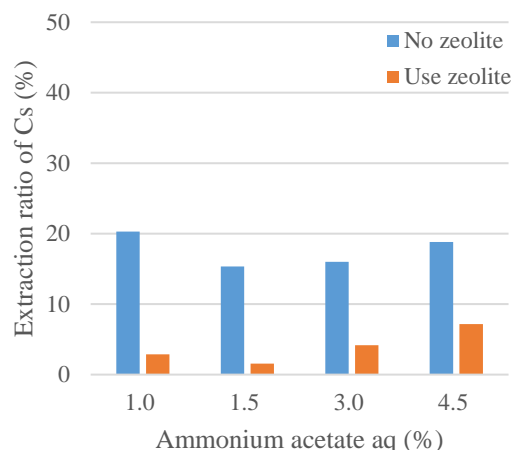


Fig. 4 The extraction ratio of cesium by ammonium acetate solution

## 5. CONCLUSION

9 years have passed since a large amount of radioactive materials were diffused due to the accident at the Fukushima Daiichi Nuclear Power Station of Tokyo Electric Power Company. At present, the decontamination work by stripping of the topsoil soil has almost been completed. However, a large amount of the contaminated soil containing the radioactive cesium remains to be stored in the temporary storage place. Considering the agendas of transportation to an intermediate storage facility and disposal in an incineration facility, it is desirable to reuse materials that can be used as construction materials instead of bringing all contaminated soil in an intermediate storage facility into an incineration facility. It is desirable to remove only radioactive cesium efficiently in the flexible container bag in order to reduce the dose of contaminated soil in a flexible container bag stored in a temporary storage place by decontamination below 8000 Bq/kg.

As one of the methods which efficiently realize the removal of only the radioactive cesium, the technique using the electrophoresis is employed. Adsorption to zeolite is inhibited by the presence of ammonium ion when an electrophoretic test is conducted using ammonium acetate as an

electrolyte and extract solution and zeolite as an adsorbent. Therefore, the electrophoretic tests are conducted by changing the electrolyte and extract solution from ammonium acetate to potassium acetate.

In this study, it is demonstrated that cesium can be removed efficiently by the low concentration of the potassium acetate solution in electrophoresis. It is necessary to clarify the relationship between the pH of the contaminated soil and the extraction ratio of cesium in the future.

## 6. ACKNOWLEDGMENTS

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