Proceedings of the 21st ICSMGE, Vienna, Austria, 14 – 19 June 2026. Pistrol, Adam & Schweiger (eds.)
Published by: ÖGG, Austrian Society for Geomechanics, Salzburg, Austria, ISBN 978-3-9503898-4-5
https://doi.org/10.53243/ICSMGE2026-2375

Cesium sorption of bentonite influenced by high concentrations of potassium and calcium in the leachate

Toru Inui, Sho Ogata
Department of Civil Engineering, The University of Osaka, Japan, inui@civil.eng.osaka-u.ac.jp

ABSTRACT: The 2011 accident of Fukushima-Daiichi nuclear power plant caused radioactive contamination of surface soil and waste by fall-out of radioactive chemicals such as ^{134}Cs and ^{137}Cs. For final disposal of fly ash generated by thermal treatment of burnable waste contaminated by radioactive Cs, installation of bentonite amended soil, which acts as a sorption layer against radioactive Cs, has been planned. However, the leachate from the Cs-enriched fly ash contained high concentrations of cations such potassium (K^+) and calcium (Ca^{2+}) ions, which have adverse effects on Cs sorption of the bentonite. In this study, a series of batch sorption tests was conducted for Na and Ca bentonites to assess the effects of high concentrations of K^+ and Ca^{2+} ions on their Cs sorption performance. When the synthetic leachate contained 1.0 mol/L-K^+ and 0.5 mol/L-Ca^{2+} ions, the distribution coefficients (K_d) for Cs decreased by approximately 70%, compared with the K_d value when no competing ions were present in the leachate. In addition, by applying the ion exchange theory, it was possible to roughly estimate the amount of Cs sorbed onto the Na bentonite influenced by concentrations of competing K^+ and Ca^{2+} ions, based on cation exchange capacity and Cs selectivity coefficients to K and Ca. Also, the testing results support that the ionic strength based on concentrations of K^+ and Ca^{2+} ions in the leachate becomes a good indicator for K_d values.

KEYWORDS: Cesium, bentonite, selective sorption, ion exchange theory.

1 INTRODUCTION

The 2011 accident at the Fukushima Daiichi Nuclear Power Plant resulted in the release of radioactive Cs into the environment, causing contamination of a wide area with radioactive chemicals. Combustible waste generated from the remediation works were incinerated, and the incineration residue is thermally treated (melted) for volume reduction at temporary ash treatment facilities in the interim storage facility. In the thermal volume reduction process, 3.2 to 4.6×10^5 m^3 of molten slag with low radioactivity concentrations and 4.6 to 7.0×10^4 m^3 of fly ash with high concentrations of radioactive cesium will be generated (Ministry of the Environment, Environmental Restoration and Material Cycles Bureau, 2025). Cs concentrations and leaching characteristics of the fly ash vary widely depending on the melting method. The Ministry of the Environment is now drafting treatment and disposal scenarios for the fly ash, because the Japanese law states that final disposal of the waste will be implemented outside the Fukushima prefecture after interim storage, while the molten slag with its radioactivity concentration lower than 8,000 Bq/kg is expected to be recycled in public construction works. Current treatment options for the fly ash include (a) cement stabilization/ solidification and (b) stabilization treatment such as calcination and vitrification of adsorbent material that has absorbed radioactive chemicals from the solution after the fly ash has been washed. In addition, detailed structures of the final disposal facility are still under design.

Considering the estimated concentration range of radioactive Cs of these wastes, disposal facilities equivalent to (a) near-surface pit disposal facilities for low-level radioactive waste under the Act on the Regulation of Nuclear Source Material, Nuclear Fuel Material and Reactors and (b) strictly-controlled disposal facilities under the Waste Disposal and Public Cleansing Act are suitable options (Inui 2022). In these disposal facilities, soil-bentonite mixture is expected to be installed as engineered barriers such as earthen covers and filling materials to prevent water from entering the waste and to retard migration of radioactive chemicals due to its low hydraulic conductivity and Cs sorption capacity (Figure 1). However, the leachate generated from these wastes may contain very high concentrations of cations and stable Cs in addition to radioactive Cs, and these ions are known to adversely affect the hydraulic barrier performance and Cs sorption capacity of the soil-bentonite mixture (Inui et al., 2016).

In this study, a series of batch sorption tests was conducted on sodium (Na) and calcium (Ca) bentonites for solutions containing high concentrations of Ca^{2+} and K^+ ions to evaluate their effects on Cs sorption performance. Furthermore, assuming that Cs sorption by bentonite is dominated by ion exchange reaction, the predictability of Cs distribution coefficients, K_d, under conditions where Ca^{2+} and K ions coexist at certain concentrations was examined by applying ion exchange theory and comparing them with the K_d values obtained in the batch sorption tests.

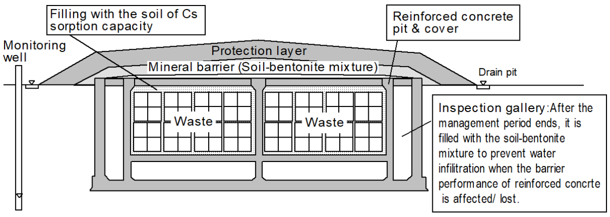

Figure 1. Schematic view of a final disposal facility for the residue from treatment of fly ash contaminated by radioactive Cs.

2 MATERIALS AND METHODS

2.1 *Bentonite*

Two types of bentonite were used in this study: Na-bentonite and Ca-bentonite, because it is well known that when Na-bentonite is exposed to the leachate containing high concentrations of Ca^{2+} ions, it changes the pore structure and increases hydraulic conductivity due to chemical alteration. One of the objectives of this study is to investigate the applicability of Ca-bentonite, which is less susceptible to chemical alteration than Na-bentonite, to the engineered barrier. Basic properties of two bentonites are presented in Table 1, including the exchangeable Na^+, Ca^{2+}, and Mg^{2+} ion contents based on JGS 0261, the free-swelling volume based on ASTM D 5890, and the methylene blue adsorption capacity based on JBAS-107-91.

To evaluate the effect of cations on the swelling performance of bentonite, the free swell volume was measured for Ca: 0.25 mol/L + K: 0.50 mol/L solution, Ca: 0.50 mol/L + K: 1.0 mol/L solution, Ca: 0.25 mol/L solution and K: 0.50 mol/L solution to investigate the sole and combined effects of Ca^{2+} and K^+ ions (Figure 2). When pure water was used as the solution, the swelling volumes were 14 mL/2 g for Na-bentonite and 7.5 mL/2 g for Ca-bentonite, indicating that Na-bentonite exhibited a higher swelling volume than Ca-bentonite. However, when Ca^{2+} and K^+ ions existed in the solution, the swelling volume of Na-bentonite decreased significantly and became comparable to that of Ca-bentonite. K^+ had a greater effect on the reduction in free swell volume than Ca^{2+} at an equal equivalent concentration.

Table 1. Bacic properties of the bentonite

Sample	Unit	Na-bentonite	Ca-bentonite
Exchangeable cation content		75.7	57.1
Na^+	cmol(+)/kg	55.5	12.0
Ca^{2+}		19.0	22.8
Mg^{2+}		1.2	22.3
Swelling	mL/2g	14.0	7.5
Methylene blue adsorption	mmol/100g	70	72

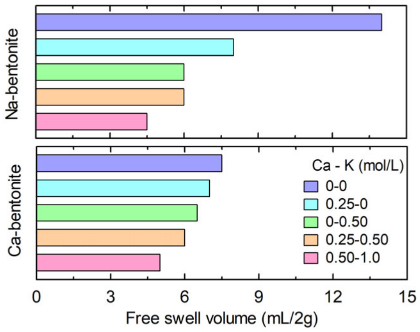

Figure 2. Free swell volumes of the bentonite for various solutions.

2.2 *Batch sorption test*

To investigate the effect of high concentrations of cations on Cs sorption, batch sorption tests were conducted for the two bentonites using pure water, Ca: 0.25 mol/L+ K: 0.5 mol/L solution, and Ca: 0.5 mol/L + K: 1.0 mol/L solution, in which Cs (CsCl) dissolved at given initial concentrations. The initial concentrations of Cs were set at 1 mg/L, 10 mg/L, 100 mg/L, and 500 mg/L with a liquid to solid ratio of 250, and 1,250 mg/L, 1,500 mg/L, 1,750 mg/L, and 2,000 mg/L with a liquid-solid ratio of 500.

The solution was poured in a bottle with a predetermined amount of bentonite, shaken horizontally at a rate of 200 times/min for 24 hours, centrifuged at 5,000 rpm for 15 minutes for solid-liquid separation, and filtered through a 0.20 μm-opening syringe filter to obtain the test solution. Cs concentration in the test solution was measured using a graphite furnace atomic absorption spectrophotometer.

3 RESULTS AND DISCUSSION

3.1 *Testing results*

Figures 3 and 4 show the Cs sorption isotherms indicating the relationship between Cs equilibrium concentration (mg/L) and Cs sorbed (mg/kg) on the Na-bentonite and the Ca-bentonite, respectively. The distribution coefficient, K_d (L/kg), and its coefficient of determination, R^2, obtained by fitting the experimental results with Henry's sorption isotherm, are also presented in the figures.

K_d values in the absence of Ca^{2+} and K^+ ions, $K_{d,0\text{-}0}$, were 2.05×10^2 L/kg for the Na-bentonite and 2.31×10^2 L/kg for the Ca-bentonite. Cs sorption performances of the Na-bentonite and the Ca-bentonite degraded with increasing Ca^{2+} and K^+ concentrations in the solution. K_d values in the 0.50 mol-Ca^{2+}/L+ 1.0 mol-K^+/L solution were about 70% lower than that in the water. This was because Ca^{2+} and K^+ ions which compete with Cs sorption decreased the amounts of Cs sorbed. Figure 5 shows the distribution coefficients normalized by the $K_{d,0\text{-}0}$. Normalized K_d values of the Na- and Ca-bentonite were similar for both solutions. This observation supports that the effects of high concentrations of Ca^{2+} and K^+ ions on Cs sorption performance of both types of bentonites are comparable to each other.

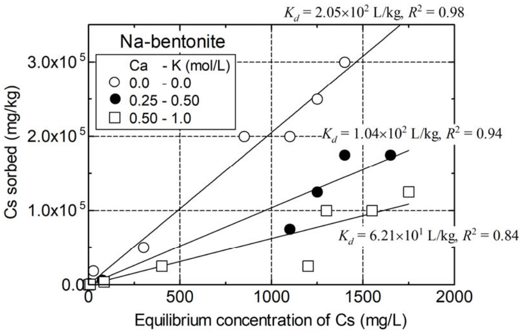

Figure 3. Sorption isotherms for the Na-bentonite.

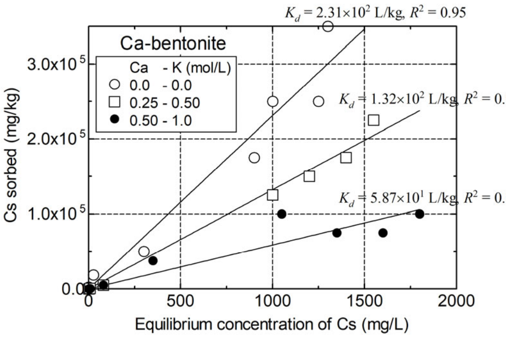

Figure 4. Sorption isotherms for the Ca-bentonite.

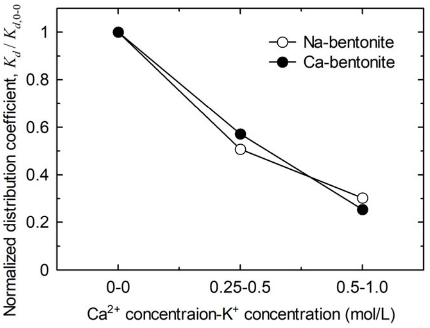

Figure 5. Relationship between Ca^{2+} and K^+ molar concentrations and normalized K_d values for Cs.

3.2 *Prediction of the effects of Ca^{2+} and K^+ ions on the Cs sorption*

In section 3.1, the K_d values for Cs in the presence of Ca^{2+} and K^+ ions at two different concentrations were experimentally determined. However, it is difficult to predict the actual concentrations of Ca^{2+} and K^+ ions in leachate in advance. Thus, in practice, it is desirable to predict the K_d values in the presence of these ions at arbitrary concentrations theoretically or empirically. In this section, based on the assumption that Cs sorption by the bentonite is dominated by ion exchange, ion exchange theory is applied to predict the K_d values for Cs in the presence of high concentrations of cations.

Bentonite is highly ion-exchangeable, and the exchange of cations contained in bentonite with Cs ions in the solution is the dominant Cs sorption mechanism. On the other hand, the presence of cations other than Cs ions in the solution inhibits the exchange of Cs ions, thereby the Cs sorption performance degrades. The degree to which this inhibition occurs can be predicted by determining the cation exchange capacity (CEC) of the bentonite and the selectivity coefficient for Cs ions relative to competing ions, according to the ion exchange theory (Yamada et al. 2023). The theoretical equations are outlined in the following section. In this study, the applicability of this prediction method based on the ion-exchange theory is examined by comparing the predicted sorption isotherms with those experimentally determined ad shown in Figures 3 and 4. In this manuscript, the applicability of the theory to the Na-bentonite is presented.

Also, to predict the K_d values influenced by coexisting cations more simply, the relationship between the ionic strength of the coexisting ions, I (mol/L) and the K_d values obtained in this study as well as in previous studies by the authors (Inui et al. 2016) is examined.

3.2.1 *Ion exchange theory and selectivity coefficients*

The following is a description of the ion exchange theory, applied to the sorption of Cs on Na-bentonite in this study. This is based on the theory applied to the adsorbents for dissolving Cs with high concentrations of cations (K^+, Na^+, Rb^+), developed by Yamada et al. (2023) and Tanaka et al. (2023). In this section, the theory is outlined, and these previous works can be referred to for the details.

Hereafter, the Na-bentonite is denoted by B. When K^+ ions and Cs^+ ions are exchanged in equilibrium, the Cs ion selectivity coefficient, $K_{Cs/K}$, for K^+ ions can be expressed by Equation (1).

$$K_{\mathrm{Cs/K}}=\frac{[\mathrm{B\text{-}Cs}][\mathrm{K}^+]}{[\mathrm{Cs}^+][\mathrm{B\text{-}K}]}=\frac{\left([\mathrm{Cs}]_0-[\mathrm{Cs}]\right)\left([\mathrm{K}]_0+[\mathrm{Cs}]_0-[\mathrm{Cs}]\right)}{[\mathrm{Cs}]\left\{\mathrm{CEC}-\left([\mathrm{Cs}]_0-[\mathrm{Cs}]\right)\right\}} \tag{1}$$

where CEC: cation exchange capacity of the bentonite (Eq/kg), [X]: molar concentration of X ions in solution at equilibrium (mol/L), $[X]_0$: initial molar concentration of X ions in solution (mol/L), [B-X]: X ion concentration in the bentonite (mol/kg). The distribution coefficient K_d (L/kg) can be expressed using the selection coefficient $K_{Cs/K}$ as follows.

$$K_{\mathrm{d}}=\frac{[\mathrm{B\text{-}Cs}]}{[\mathrm{Cs}^+]}=K_{\mathrm{Cs/K}}\frac{[\mathrm{B\text{-}K}]}{[\mathrm{K}^+]} \tag{2}$$

From Equation (2), it can be understood that the K_d value for Cs is affected by the concentration of coexisting K^+ ion. If $K_{Cs/K}$ can be determined, the K_d value can be estimated for variable concentrations of K^+ ions in the solution with a certain liquid to solid ratio. Similarly, $K_{Cs/Ca}$ can be determined by Equation (3)

$$K_{\mathrm{Cs/Ca}}=\frac{[\mathrm{B\text{-}Cs}]^2[\mathrm{Ca}^{2+}]}{[\mathrm{Cs}^+]^2[\mathrm{B\text{-}Ca}]} \tag{3}$$

Cs equilibrium sorption amount and K_d values influenced by the concentrations of K^+ and Ca^{2+} ions can be estimated using the CEC of bentonite and selectivity coefficients.

3.2.2 *Evaluation of selection coefficients by sorption tests on two-component systems*

Batch sorption tests were conducted on a two-component system of Cs^++K^+ and Cs^++Ca^{2+} to determine the selectivity coefficients, $K_{Cs/K}$ and $K_{Cs/Ca}$. Two levels of concentrations of Ca^{2+} and K^+ ions were set at 0.50 (Eq/L) and 1.0 (Eq/L). The initial concentrations of Cs were set to 10 mg/L, 100 mg/L, 500 mg/L, and 1000 mg/L. Other experimental procedures were similar to those described in Section 2.2. By applying the selectivity coefficients obtained in this experiment to the ion exchange theory described in 3.2.1, the equilibrium Cs sorbed amount and K_d values for the three-component Cs + Ca + K system were predicted and compared with the measured K_d values obtained in the experiments of the three-component system described in Section 3.1.

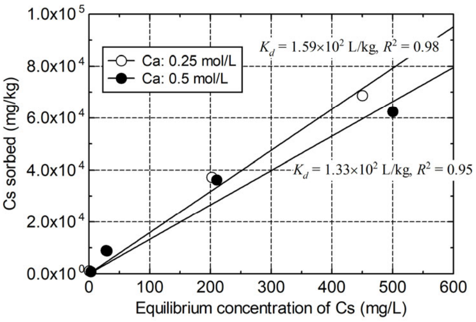

Figure 6. Sorption isotherms in $Cs^+ + Ca^{2+}$ system.

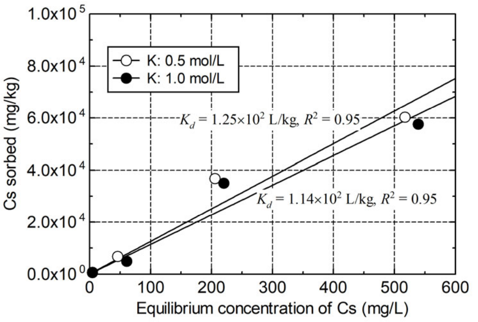

Figure 7. Sorption isotherms in $Cs^+ + K^+$ system.

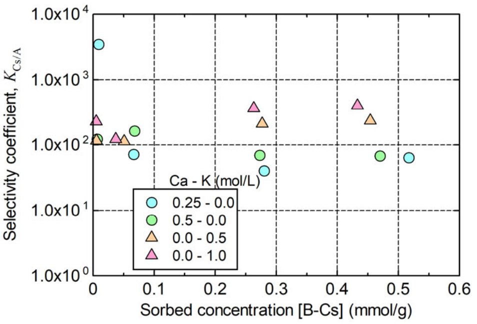

Figure 8. $K_{Cs/A}$ values under various conditions for the Na-bentonite.

Figures 6 and 7 shows the Cs sorption isotherms in a two-component system of Cs+Ca and Cs+K, respectively. Henry's sorption isotherm was employed to fit the testing results and determine the K_d values. Figure 8 shows the Cs selectivity coefficients, $K_{Cs/A}$, of the Na-bentonite, obtained from the results of the two-component batch sorption tests. From Figure 6, K_d values decreased with increasing concentration of Ca^{2+} or K^+ ion. The influence of K^+ ions on K_d values was slightly larger than that of Ca^{2+} ions with an equal equivalent concentration. Figure 8 shows that $K_{Cs/K}$ values range from 1.1×10^2 to 4.0×10^2 with an average of 2.2×10^2 for the range of K^+/Cs^+ in this experiment, and $K_{Cs/Ca}$ values range from 6.3×10^1 to 1.6×10^2, except the case where the Cs^+ concentration is very low, with an average of 8.6×10^1. $K_{Cs/A}$ values remain almost constant expect when the initial Cs^+ concentrations are very low. This observation is consistent with the results of the previous studies on the adsorbents such as zeolite (Tanaka et al. 2023, Yamada et al. 2023).

3.2.3 *Discussion*

Figures 9 present the sorption isotherms based on the predicted amounts of Cs sorbed on the Na-bentonite in the three-component system (Ca^{2+}: 0.25 mol/L+ K^+: 0.5 mol/L and Ca^{2+}: 0.5 mol/L+ K^+: 1.0 mol/L, respectively) by using the average $K_{Cs/A}$ values and the CEC of the Na-bentonite of 70 cmol(+)/kg, along with the Henry's sorption isotherms experimentally determined in Figure 3 under the equivalent conditions. The K_d

value defined as the slopes of the predicted sorption isotherms are also presented in the figures.

Although the predicted and measured K_d values are of the same order of magnitude, the predicted K_d values are lower by approximately 50% than the measured K_d values. This is partially because the activity of Ca^{2+} and K^+ ions is restricted under the condition where both cations coexist in high concentrations, but the activity change caused by the high ionic strength is not considered in this study. However, the K_d values can be roughly predicted by the ion exchange theory even in the presence of multiple cations, provided that the $K_{Cs/A}$ for each cation are obtained. In order to verify the applicability of the ion exchange theory in more detail, it is necessary to confirm the reproducibility of the theory at various concentrations of cations which compete with Cs sorption.

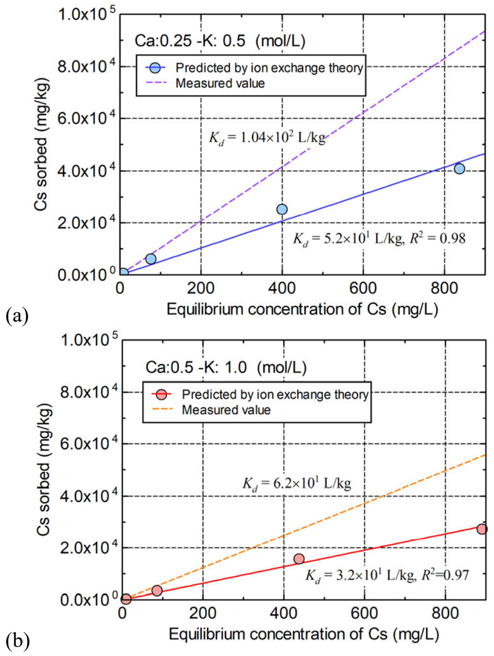

Figure 9. Comparison of predicted and measured isotherms: (a) Ca: 0.25 mol/L + K: 0.5 mol/L, (b) Ca: 0.5 mol/L + K: 1.0 mol/L.

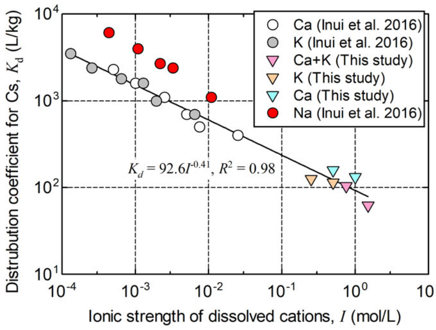

Figure 10. Relationship between the ionic strength and the measured K_d values of the Na-bentonite

Figure 10 shows the measured K_d values of the Na-bentonite for Cs in the presence of cations that inhibit Cs sorption obtained in this study and in previous studies by the authors (Inui et al. 2016), with the ionic strength of the coexisting ions, I (mol/L). Note that the Na-bentonite used in this study has properties slightly different from the Na-bentonite used in the previous study. In the previous study, K_d values under the conditions when Ca^{2+} and K^+ ions were present at relatively low concentrations. The relationship between I and K_d values could be expressed as a linear relationship by taking both logarithms, and the K_d values determined in this study for the high concentration region are consistent with the results extrapolated from the low concentration region. Therefore, it is possible to estimate the K_d values influenced by Ca^{2+} and K^+ ions from the ionic strength.

4 CONCLUSIONS

Cs sorption performance of both Na- and Ca-bentonite for the leachate containing high concentrations of Ca^{2+} and K^+ ions was evaluated by batch sorption tests, which is important for the safety assessment of the final disposal facilities for fly ash from thermal volume reduction treatment of the radioactively contaminated waste generated by the decontamination work of the Fukushima Daiichi Nuclear Power Plant accident.

Distribution coefficients for Cs, K_d, decreased with increasing concentrations of Ca^{2+} and K^+ ions, and that the K_d value decreased by about 70% in the presence of 0.50 mol-Ca^{2+}/L and 1.0 mol-K^+/L, compared with that in the absence of competing cations. Application of the ion-exchange theory to the Cs sorption in the presence of Ca^{2+} and K^+ ions was attempted. The amounts of Cs sorbed are roughly predicted by the theory but underestimated by 50% based on the selectivity coefficients for each ion and the CEC of the bentonite. On the other hand, the ionic strength of competing cations can be a good indicator of the K_d values. In the future, the combined effects of ions other than Ca^{2+} and K^+ ions that inhibit Cs sorption need to be identified, and the Cs distribution coefficient of soil-bentonite mixture needs to be evaluated to clarify the applicability of soil-bentonite mixture for containment of the radioactively contaminated fly ash.

5 ACKNOWLEDGEMENTS

This research was supported by the Environment Research and Technology Development Fund (JPMEERF22S20900) of the Environmental Restoration and Conservation Agency provided by Ministry of the Environment of Japan. The authors would like to acknowledge Dr. Kazuo Yamada (National Institute for Environmental Studies, Japan), Dr. Tomohiro Kato (Kyoto University) and Mr. Tomoya Mitsuhashi (former graduate student, The University of Osaka) for their invaluable guidance and cooperation in performing and analyzing the sorption tests.

6 REFERENCES

Inui,T. 2022. Technical challenges for design of final disposal of residues from treatment of radioactively contaminated soils and wastes caused by the Fukushima Daiichi Nuclear Power Station accident, *Material Cycles and Waste Management Research*, 33(6), 467-476 (in Japanese).

Inui, T., Katsumi, T., and Takai, A. 2016. Cesium sorption/desorption characteristics of sodium bentonite affected by major cations in leachate from MSW incinerator ash, *Japanese Geotechnical Society Special Publication*, 2(53), 1841-1844.

Ministry of the Environment, Environmental Restoration and Material Cycles Bureau. 2025. Options for final disposal outside the prefecture (Draft), Document 3 for 10th meeting of Working Group for Investigating Technology for Volume Reduction of Removed Soil at Interim Storage Facilities, https://josen.env.go.jp/chukanchozou/facility/effort/investigative_commission/volume_reduction_technology_250207.html (Access on March 1, 2025) (in Japanese).

Tanaka, Y., Yamada, K., and Endo, K. 2023. Evaluation of Cs adsorption performance of certain natural mordenite type zeolite with ion exchange theory, *Proc. 15th Symp. on Environmental Geotechnics*, Japanese Geotechnical Society, 423-427.

Yamada, K., Ichikawa, T., Endo, K., and Osaka, M. 2023. A case study of performance evaluation of adsorbent for Cs enrichment from radioactive fly ash washing solution, *Journal of the Society for Remediation of Radioactive Contamination in the Environment*, 11(1), 3-13 (in Japanese).