International Journal of GEOMATE
(Geotechnique, Construction Materials and Environment)
ISSN: 2186-2982 (P), 2186-2990 (O), Japan

Vol. 31, Issue 145, September 2026, PP. 192-202; DOI: 10.21660/2026.145.g15387

CESIUM LEACHING UNDER SEVERE CONDITIONS FOR CEMENT / GEOPOLYMER SOLIDIFIED BODY OF CESIUM ADSORBED MORDENITE

*Takahito Yasukochi[1], Yasumasa Tojo[1], Kanako Toda[2], Kazuo Yamada[3] and Kazuto Endo[3]

[1] Graduate school of engineering, Hokkaido university, Japan; [2] Graduate school of engineering, University of Tokyo, Japan; [3] National Institute of Environmental Studies, Japan

*Corresponding Author, Received: 30 May 2025, Revised: 14 July 2026, Accepted: 16 July 2026

ABSTRACT: Following the accident at the Tokyo Electric Power Company's Fukushima Daiichi Nuclear Power Plant, decontamination was conducted, and approximately 140,000 m^3 of radioactive waste was generated. For the final disposal, it is essential to establish volume reduction and cesium (Cs) stabilization technology. Combustible waste was incinerated and melted to lower its volume, and soluble Cs became concentrated in the fly ash. Cs in the fly ash is soluble, and the Cs stabilization processes are needed, which could be done by Cs adsorbent like mordenite. This study explores Cs leaching behavior from the solidified body of Cs adsorbed mordenite. Solidified bodies with cement or geopolymer were prepared, and their Cs leaching characteristics were evaluated. In addition, changes in Cs leaching behavior due to freezing and thawing, and contact with seawater were evaluated as an estimated severe condition. As a result, Cs leaching was principally controlled by Cs desorption from the mordenite and Cs diffusion in the solidified bodies. The Cs leaching rate was not affected by freezing and thawing, but increased on immersion in seawater. While the type of binder (cement or geopolymer) affects the nature of surface precipitates formed, it has only a minor impact on the Cs leaching rate. The Cs leaching ratio was as low as below 0.5% even after 60 days of immersion in seawater, and the leached Cs concentrations were lower than the standard for environmental water. The results indicate that mordenite and its solidification were an appropriate means of final disposal.

Keywords: Cesium, Final disposal, Leaching test, Radioactively contaminated waste, Solidification

1. INTRODUCTION

The accident at the Japanese Tokyo Electric Power Company's Fukushima Daiichi Nuclear Power Plant generated waste contaminated with radioactive cesium (r-Cs) that was disposed of as follows. Waste of 8,000 Bq/kg or less was sent to conventionally controlled landfill [1]. Waste of 8,000–100,000 Bq/kg went to landfill after appropriate solidification [2]. Waste exceeding 100,000 Bq/kg is currently in temporary storage in Fukushima Prefecture, but is scheduled for out-of-prefecture final disposal by 2045 within 30 years after the start of storage [2].

The volume of contaminated waste, especially of combustible waste, can be reduced by thermal treatment. The waste is incinerated and then melted with the addition of calcium chloride ($CaCl_2$) to accelerate Cs volatilization [3]. The Cs-containing fly ash thus generated can be dispersed during landfill operations due to its fine-powder property, and its radioactivity exceeds 100,000 Bq/kg [4]. Prior to final disposal of the melting fly ash (MFA), it is important to immobilize the r-Cs, even though the landfill

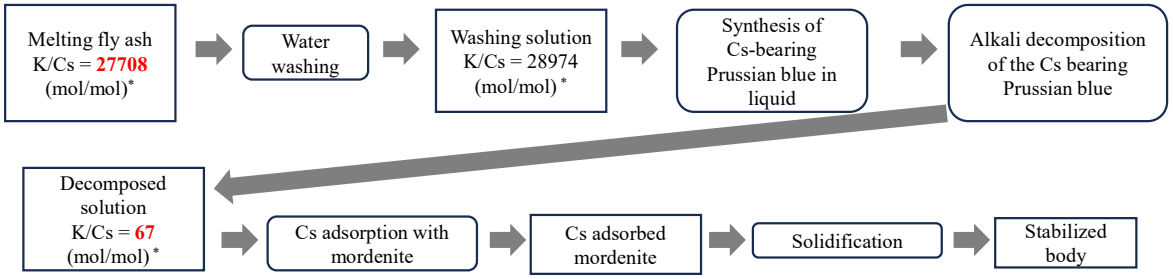

Fig. 1 Flowchart of r-Cs stabilization using mordenite.
*The K/Cs ratio was calculated from the report of a prior demonstration study [6].

structures are designed to prevent water inflow [5]. This is because disposal sites might be damaged by earthquakes or other events within the approximately 300-year period during which the Cs-137, with a half-life of 30.2 years, will remain radioactive. To minimize Cs leakage in the event of an accident, the Cs leaching rate from disposal bodies should be kept as low as possible within a reasonable limit.

Various methods have been developed for the immobilization of Cs and further reduction of the MFA volume [2]. Mordenite selectively absorbs Cs, but K is a competing cation for Cs adsorption. Even mordenite does not adsorb all Cs from fly ash washed solution with a K/Cs ratio close to 30,000 (Fig. 1) and the r-Cs concentration in waste-water remains above the discharge standard.

To reduce the K/Cs ratio, the following treatment is in estimation (Fig. 1). MFA is washed with water to transfer Cs to the solution, and Cs in the liquid phase is adsorbed and concentrated with Prussian blue (PB). The Cs-adsorbed PB is then decomposed and the r-Cs is re-transferred to the liquid phase, and then the r-Cs in solution is adsorbed onto mordenite [6, 7]. This reduces the K/Cs ratio to 67 from 27,708 (Fig. 1). The amount of K that competes with Cs for adsorption sites decreases, and almost all Cs in the solution is adsorbed by the mordenite. As a result, wastewater after the mordenite adsorption contains a few r-Cs.

Solidification using cement or a geopolymer (GP) is required because Cs-adsorbed mordenite is granular and may dispersed during transportation and landfill operations. Prior to final disposal, the Cs leaching rate and Cs leaching availability from the solidified body of the mordenite must be evaluated.

In this study, solidified bodies of Cs-adsorbed mordenite were prepared, and the Cs leaching behavior from them was evaluated under situations that are disadvantageous for Cs leaching prevention. In particular, the effects of immersion in seawater, which promotes Cs leaching from the ion exchanger mordenite, and freeze-thaw treatment, which can disrupt the pore structure of the solidified bodies, were evaluated.

The Cs leaching behavior from solidified Cs-adsorbed mordenite under disposal-relevant conditions has remained insufficiently characterized. This study therefore evaluates the practical Cs leaching rate under these disposal-relevant environments.

2. Research significance

For the safety design of the landfill for a solidified body of Cs-adsorbed mordenite (Fig. 1), it is essential to understand the Cs leaching behavior from the solidified body for landfill safety design. Although Cs leaching from them has been evaluated with the leaching tests in pure water [7], the influence of ionic solution immersion and Cs leachability from them has not yet been assessed. In this study, Cs leaching behavior under severe conditions from the stabilized body was evaluated to assess the Cs retention capability of the mordenite-based stabilized body in the actual landfill environment.

3. MATERIALS

Mordenite is known for its cation adsorption capacity [9]. Natural mordenite from Miyagi Prefecture (UniSelect UR3103Z, Ataka Asano Co. Ltd., Japan) served as the Cs adsorbent. The grain size was 1.9–2.3 mm.

3.1 Preparation of Cs adsorbed mordenite

The composition of the decomposed PB solution is adjusted based on the report of the on-site examination [8]. However, here, the concentration was 30-fold higher (Table 1). Although the on-site examination used a column-type adsorption test, Cs-loaded mordenite was prepared in this study by a simpler batch method. A 30-fold concentrated solution was employed to achieve a Cs uptake comparable to that obtained in the column test.

Cs-adsorbed mordenite was prepared as follows. Cs_2SO_4 (Fujifilm Wako Chemicals, Osaka, Japan), $Na_4[Fe(CN)_6]\cdot 10H_2O$ (Fujifilm Wako Chemicals, Osaka, Japan), and $K_4[Fe(CN)_6]\cdot 3H_2O$ (Fujifilm Wako Chemicals, Osaka, Japan) were dissolved in distilled water to the concentrations shown in Table 1.

The stable Cs-133 isotope was used because its leaching behavior is essentially identical to that of r-Cs [9]. The concentration of r-Cs in the contaminated MFA described above is approximately 150,000 Bq/kg [8]. Using the specific activity of Cs-137 as r-Cs (3.2×10^{12} Bq/g) [10], the Cs-137 concentration is approximately 1.14×10^{-9} mol/kg. In contrast, the

MFA contains stable Cs-133 at concentrations of

Table 1. Composition of decomposed Prussian blue solution

Component	Concentration (mmol/L)
Cs^+	0.0383
Na^+	0.461
K^+	2.56
SO_4^{2-}	0.0191
$Fe(CN)_6^{4-}$	0.756

the order of 10 mg/kg (7.52×10^{-5} mol/kg) [6]. Thus, the Cs-137 content is only about 10^{-4} of the stable Cs-133.

Before thermal treatment, the decontamination waste contains stable Cs-133 with a small amount of accident-derived radioactive Cs-137. While their initial chemical states may differ, both species are expected to form chemically equivalent phases during fly-ash collection. Consequently, no difference in leaching behavior is expected between stable Cs-133 and r-Cs in the MFA.

Mordenite was immersed in the simulated solution at a liquid-to-solid ratio of 5 mL/g and agitated at 200 rpm. After 30 min, the mordenite was removed, thoroughly washed with distilled water to eliminate non-adsorbed ions, and dried at 60℃. After adsorption, the immersing solution was sampled, filtered through a 0.45-µm membrane filter (A045A025A, Advantec, Japan) and the Cs concentration quantified via inductively coupled plasma mass spectrometry (ICP-MS) (ICP-MS-QQQ, Agilent Technology, USA).

The adsorbed cation levels were Cs 5.76 meq/kg and K 343 meq/kg, and the cation exchange capacity (CEC) of the mordenite was 349 meq/kg. After the adsorption, over 99% of the Cs in the initial solution was adsorbed onto the mordenite.

3.2 Solidification of Cs-adsorbed mordenite and freezing and thawing treatment

Cs-adsorbed mordenite was solidified using cement and GP. The amount of Cs-adsorbed mordenite added was set to the maximum level that still allowed the paste to maintain sufficient flowability for mixing and casting.

Cement (Portland blast-furnace slag blended cement type B, JIS R5211:2019, Taiheiyo Cement Corp., Japan) was mixed with water at a water-to-cement ratio of 0.6. Then, Cs-adsorbed mordenite was added to the cement paste to 40 wt%.

The GP was prepared by mixing 216.5 g of Na solution, 133 g of metakaolin (MK-11-SF-8, SOBUECLAY, Japan), and 150 g of Cs adsorbed mordenite. Na solution was prepared by mixing 24.7 g of NaOH (Wako guaranteed reagent, Fujifilm Wako Chemicals, Osaka, Japan), 105 g of sodium silicate solution (Wako reagent, Fujifilm Wako Chemicals, Osaka, Japan), and 86.8g of distilled water.

Metakaolin served as the primary aluminosilicate framework; the Si content was adjusted using sodium silicate, and NaOH was used to promote geopolymerization. The Na solution was prepared with a molar ratio of Na_2O: SiO_2: H_2O = 1: 1: 13, and metakaolin was then added so that the overall Na_2O: Al_2O_3 ratio became 1: 1. The mordenite content was set to the maximum amount that could be homogeneously dispersed within the paste.

Table 2. Leaching test conditions. DW: distilled water, SW: artificial sea water.
*Age at the start of the leaching test.

Solidification	Freezing and thawing	Solvent	Age* (days)
Cement	No	DW	72
	Yes	DW	79
	No	SWx1/10	72
	No	SW	88
Geopolymer	No	DW	79
	Yes	DW	72
	No	SWx1/10	79

The mixed paste was set in polytetrafluoroethylene (PTFE) tube molds 2 cm in diameter and 4 cm in height, and sealed with parafilm (PM-996, Bemis, USA). The specimens were cured at 30 °C in sealed plastic bags until day 9. At 9 days of curing, the solidified bodies had developed sufficient strength to avoid damage during demolding, and the early-stage hydration or geopolymerization reactions were considered to have stabilized.

When solidified bodies are disposed of in shallow subsurface environments in cold regions, they may be subjected to freeze–thaw cycles. Therefore, the effect of changes in pore structure caused by the freezing and thawing of pore water on the Cs leaching behavior was evaluated. Some specimens underwent freeze-thaw treatment in an incubator (MIR-554-PG, PHC, Japan) for 300 cycles of –10°C for 3 h and 20°C for 2 h.

4. METHODOLOGY

4.1 Leaching of solidified bodies

To evaluate the Cs leaching rate governed by diffusion within the solidified body, leaching tests were conducted according to the ANSI 16.1 method [11]. The cylindrical solidified specimens prepared by the methods described in Sections 3.1 and 3.2 were used. The treatment flow of the specimens is shown in Fig. 2. The solvent was replaced at predefined intervals and was agitated at 200 rpm. The solvent temperature was maintained at 25°C in a water bath. Solidified bodies were immersed in the solvent with a solid-to-liquid ratio of solvent volume (cm^3)/sample surface area (cm^2) = 10 (cm).

The solvent was sampled at the time of each replacement and filtered through a 0.45-µm membrane. The elemental composition was

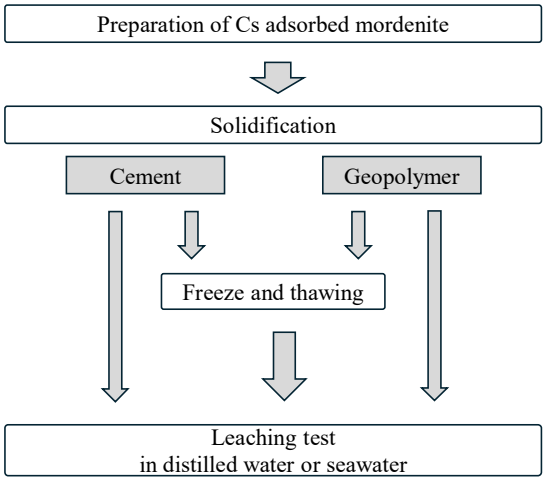

Fig. 2 Experimental procedure for the leaching tests.

measured via ICP-MS, and the amount of leached Cs at the time of each solvent replacement was calculated. The cumulative leached Cs was the sum of these values.

Table 2 shows the leaching test conditions. The solvent was changed after the first 6 h, then every other day until day 7, and thereafter at intervals of 1 week or longer. Seawater was prepared by dissolving artificial seawater powder (Instant Ocean, Aquarium Systems, USA) in distilled water to 35.0 or 3.5 g/L (SW x 1/10 in Table 2). The major elements in artificial seawater as measured via inductively coupled plasma optical emission spectroscopy **(**ICP-OES) (ICPE-9000, Shimadzu, Japan) were Na 9,600 mg/L, Mg 1,000 mg/L, Ca 331 mg/L, and K 247 mg/L. The pH was 8.2. The Cs-133 concentration in seawater can be assumed to be 0.3 µg/L [12]. It is sufficiently lower than the Cs concentration leached from the specimens and this seawater was acceptable for use in the leaching test.

4.2 XRD and SEM analysis

When solidified bodies were immersed in seawater, surface precipitation was evident. The precipitates were analyzed using X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive spectrometry (SEM-EDS). Specimens were prepared as follows. Cement- or GP- solidified bodies were immersed in distilled water or seawater for 28 days and then dried under vacuum (FDU-1200, Eyela, Japan). Cross-sectional slices were impregnated with epoxy resin and then polished. Carbon spattering prevented charge-up. Back-scattering electron (BSE) imaging and EDS employed a SEM (JSM-7200F, JEOL, Japan) operating at an accelerating voltage of 15 kV and a working distance of 9.6 mm. It should be noted that, in EDS analysis, the carbon content tends to be overestimated due to the carbon spattering.

Some precipitate was scraped off with a knife, ground in a mortar, and subjected to XRD (Smart Lab, Rigaku, Japan) using Cu-Kα1 radiation with a tube voltage of 45 kV, a tube current of 200 mA, a step size of 0.01° (2θ), and a scan rate of 4°/min.

5. RESULTS AND DISCUSSION

5.1 Cs leaching behavior from solidified Cs-adsorbed mordenite

Figure 3 shows the cumulative Cs leaching ratio from cement- and GP-solidified bodies. On immersion in DW, only 0.12–0.14% of all Cs leached within 133 days of immersion. Freezing and thawing did not significantly affect Cs leaching from either type of body.

Cs leaching increased when the solidified bodies were immersed in seawater. However, leaching from the cement-solidified body in seawater decreased remarkably after 7 days of immersion, but that from the GP-solidified body did not.

5.2 Difference in Cs leaching behavior between cement- and GP-solidified bodies.

It was previously reported that non-weathered cement paste has little cation adsorption capacity, and when soluble CsCl was solidified with cement, almost all of the Cs leached within several tens of days from a solidified body in the shape of a cylinder 2 cm in diameter and 4 cm in height [13, 14].

Cs leaching from cement solidified bodies proceeds as Cs desorbed into pore solution diffuses through the pores. Similar leaching through pores occurs from the GP-solidified bodies. On the other hand, GP possesses cation adsorption capacity due to its aluminosilicate framework [15], implying that Cs leaching should be slower than that from cement-solidified bodies. However, Fig. 3 reveals no significant difference in the Cs leaching rates between the cement- and GP-solidified bodies. This may be attributable to the low Cs adsorption selectivity of GP aluminosilicate. In Cs-adsorbed mordenite, over 90% of the adsorption sites are occupied by K. In GP-solidified bodies, Na that does not take part in geopolymerization likely remains dissolved in the pore solution. This triggers ion exchange between Na and K, increasing the K concentration of the pore solution. Desorbed K competes with Cs for the adsorption sites of GP; almost no Cs is adsorbed. Consequently, GP cation adsorption minimally delays Cs leaching.

5.3 Effect of seawater on Cs leaching and surface precipitation

The Cs leaching ratio was higher in seawater immersion than in distilled water immersion (Fig. 3). When a solidified body is immersed in seawater, the ion exchange equilibrium of the mordenite changes, and the Cs desorption ratio increases because the amounts of Na and K that serve as ion exchange cations for the Cs increase during the leaching test. The specific Cs leaching concentration is considered to be governed by the ion-exchange equilibrium of Cs with Na and K in seawater and in the pore solution of the solidified bodies.

Cs leaching from the cement-solidified body in seawater exhibited an inflection at 7 days of immersion, attributable to the precipitates. As shown in Fig. 4 (a), precipitates as thick as 10 µm formed on the surface of the cement-solidified body immersed in seawater. EDS and XRD revealed a calcite outer layer and a brucite interlayer (Table 3(a)). Cs diffusion may be suppressed by the dense layers of brucite and calcite, and Cs leaching therefore decreases.

Figure 3 shows that the Cs leaching rate from the cement-solidified body during seawater immersion decreased sharply after day 7. This point coincides with the point at which the solvent exchange interval is changed from 1 to 7 days. This extension held the carbon dioxide content of the solvent at the dissolution equilibrium level for a longer period. Consequently, surface precipitation (Fig. 4(a)) may have progressed rapidly after this point. As Cs leaching increased linearly with the immersion time after precipitation, it is thought that the leaching rate was limited by dissolution of precipitates that contain Cs.

In contrast, for the GP-solidified body immersed in seawater, only partial precipitation was observed on the surface (Fig. 4 (b)). EDS (Table 3 (b)) and XRD revealed that this was calcite. The difference in the precipitated phases can be attributed to the difference in pore-solution pH between the cement and the geopolymer. The pore solution of the cement solidified body exhibits a higher pH, creating conditions favorable for brucite precipitation. As a result, the Cs leaching behavior for the cement-solidified body was strongly influenced by surface precipitation during seawater immersion more than for the GP-solidified body.

5.4 Cs leaching pathway of cement- and GP-solidified bodies of Cs-adsorbed mordenite

Granular mordenite (1.9–3.3 mm) was scattered in the solidified body of the Cs-adsorbed mordenite. Cs leaching would therefore be expected to proceed as shown in Fig. 5. Initially, the Cs in the mordenite is released to the pore solution via ion exchange with alkali metal ions in that solution, and then transferred by diffusion through the pores of the solidified body. Such Cs migration is considered to resemble chloride ion transport in concrete, which is governed by adsorption and diffusion within the cementitious microstructure [16].

Cement and GP each possess pores with diameters spanning from the nanometer to the millimeter scale [10]. The cement pore solution is

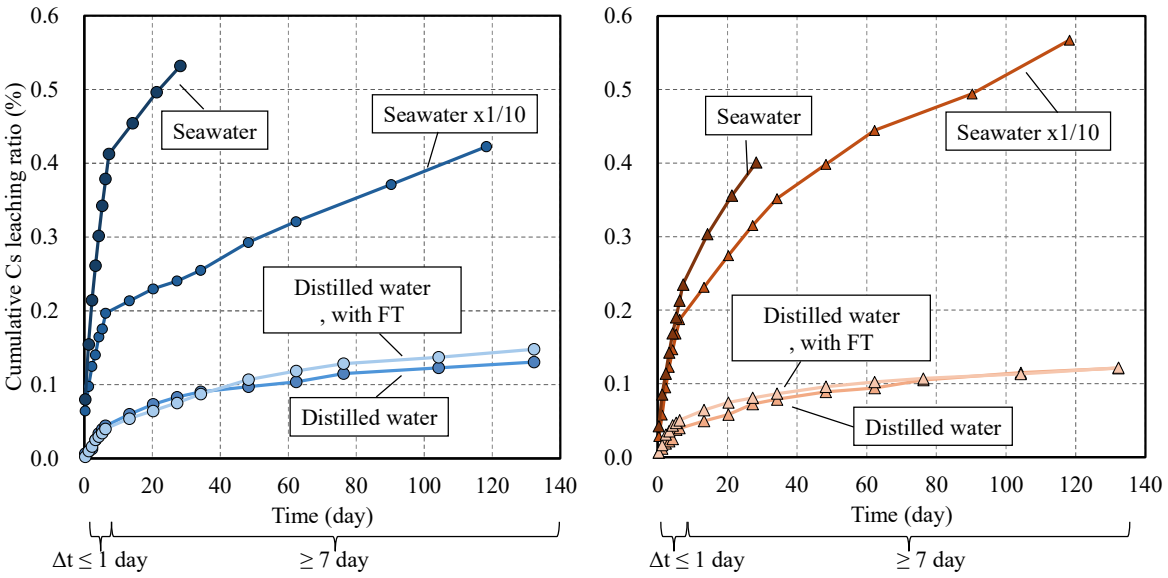

Fig. 3 Cumulative Cs leaching ratios from cement-solidified Cs-adsorbed mordenite (left) and GP-solidified mordenite (right). Δt: Solvent exchange times. FT: Freeze and thawing.

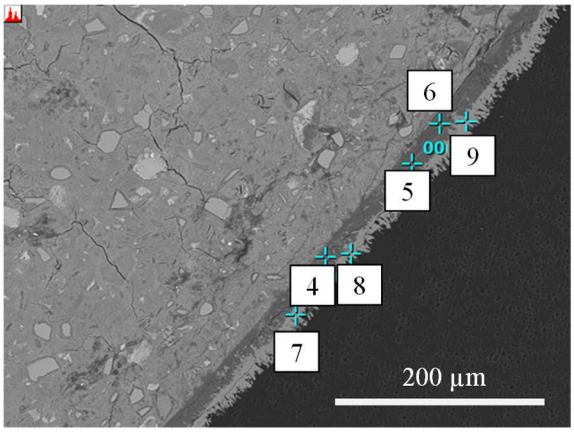

Fig. 4 (a) BSE image of a cross-section of a cement-solidified body immersed for 1 month in seawater.

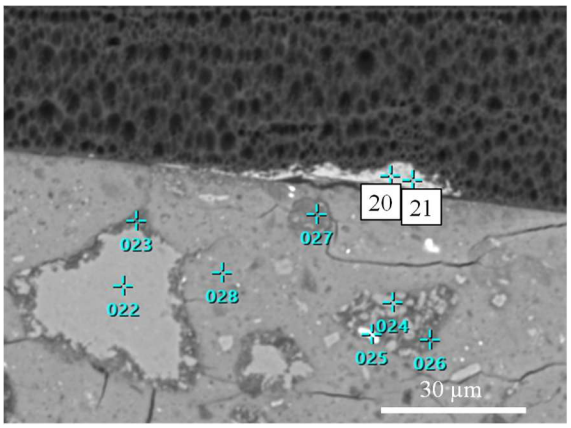

Fig. 4 (b) BSE image of a cross-section of a GP-solidified body immersed for 1 month in seawater

Table 3. (a). Elemental composition (mol%) as revealed by EDS at the points indicated in Fig. 4 (a).

Precipitate	Point	C	O	Mg	Ca
Inside	4, 5, 6	7.70	55.9	34.3	1.40
Outside	7, 8, 9	20.9	55.1	0.10	23.7

Table 3. (b) Elemental composition (mol%) as revealed by EDS at the points indicated in Fig. 4 (b).

Point	C	O	Ca
20, 21	26.5	53.3	19.6

highly ionic (principally Na and K) [17]. The GP pore solution contains Na ions arising via dissolution of unreacted NaOH in the GP paste. When the Cs is adsorbed by the mordenite, some Cs is then desorbed via ion exchange between Na and K in the pore solution and the Cs on the mordenite. As the mordenite selectively adsorbs the Cs, the desorption ratio remains low even in solvents of high ionic strength.

When the Cs-adsorbed mordenite described in the previous section, but not solidified, was immersed in artificial seawater at 35 g/L (Na 9,600 mg/L, Mg 1,000 mg/L) for 24 h, the liquid phase Cs concentration was about 116 µg/L, and the Cs desorption ratio was 0.73%. Although this solution did not accurately reproduce the pore solution of the solidified body, the low desorption ratio indicates that the minimal Cs leaching ratio from the solidified body was principally determined by the Cs desorption ratio of the Cs-adsorbed mordenite.

Cs desorbed into the pores solution moves through the pores via diffusion along a concentration gradient. Both cement and GP are porous, and Cs transfer is affected by the connectivity of the pores. On the outer surface of a solidified body, Cs leaches to the solvent via the concentration gradient between the pore solution and the solvent.

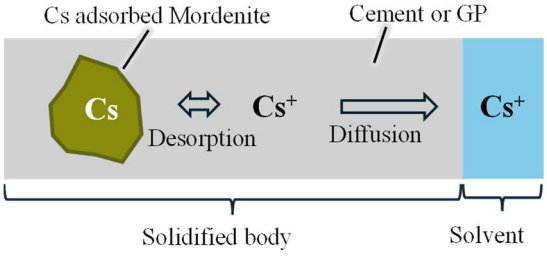

Fig. 5 Schematic diagram of the Cs leaching pathway from solidified Cs-adsorbed mordenite.

5.5 Apparent diffusion coefficients

When Cs leaching from a solidified body is controlled by the concentration gradient of the pore solution, leaching can be calculated as follows [18-21]. The Cs concentration in the solidified body is expressed by Eq. 1 of Fick's Second Law, assuming that the body is a semi-infinite medium [19].

$$\frac{C}{C_0} = \mathrm{erf}\left(\frac{x}{2\sqrt{D_a t}}\right) \quad (1)$$

where D_a is the apparent diffusion coefficient (m^2 /s), C is the Cs concentration in the solidified body (mg /m^3), and C_0 is the initial Cs concentration in the solidified body (mg/m^3). The leaching flux $J(t)$ (mg/(m^2·s)) at the surface of the body (x = 0) can be expressed as follows:

$$J(t) = -D_a \left.\frac{\partial C}{\partial x}\right|_{(x=0)} = C_0\sqrt{\frac{D_a}{\pi t}} \quad (2)$$

The leaching per unit area to a certain time (A (mg/m^2)), is obtained by integrating this flux with respect to time:

$$A = \int_0^t \mathrm{J(t)}\, dt = 2C_0\sqrt{\frac{D_a t}{\pi}} \quad (3)$$

The cumulative leaching ratio can be obtained by dividing the amount leached from the total surface

area to the target time by the initial content. If the surface area of the solidified body is S (m^2) and the volume V (m^3), then:

$$\text{Cumulative leaching ratio} = \frac{AS}{C_0 V} = 2\left(\frac{S}{V}\right)\sqrt{\frac{D_a t}{\pi}} \quad (4)$$

In the experiment, the amount of Cs leached at the n^{th} solvent replacement time was defined as A_n (mg), and the cumulative leaching amount was then $\sum A_n$ (mg). This was divided by the initial amount (A_0 (mg) = C_0V) to give the following relationship:

$$\frac{\Sigma A_n}{A_0} = 2\left(\frac{S}{V}\right)\sqrt{\frac{D_a t}{\pi}} \quad (5)$$

In other words, the cumulative leaching ratio is proportional to the square root of time. However, it should be noted that this calculation assumes that three-dimensional leaching within the specimen is equivalent to one-dimensional leaching through a semi-infinite solid. To obtain a more precise D_a, a one-dimensional leaching test that restricts the leaching direction to a single axis must be conducted in the future.

Figure 6 plots the cumulative leaching ratios against the square roots of immersion times. In all cases, the leaching ratio increased linearly up to 7 days of immersion (day$^{0.5}$ = 2.6), implying that Cs leaching was controlled by diffusion in the solid phase during this period.

The D_a values obtained from the slope of the regression line up to 7 days of immersion are listed in Table 4. For both the cement- and GP- solidified bodies, the D_a values of Cs were about 10^{-18} m^2/s in distilled water and 10^{-17} to 10^{-16} m^2/s in seawater. Freezing and thawing didn't affect the D_a.

Table 4. Apparent diffusion coefficient (D_a (m^2/s)) for each solidified Cs adsorbed mordenite. DW: Distilled water, SW: Artificial seawater

Solidification	Solvent	Freezing & thawing	D_a (m^2/s)
Cement	DW	No	4.1×10^{-18}
Cement	SWx1/10	No	6.3×10^{-17}
Cement	SW	No	3.3×10^{-16}
Cement	DW	Yes	3.5×10^{-18}
GP	DW	No	2.7×10^{-18}
GP	SWx1/10	No	9.8×10^{-17}
GP	SW	No	1.1×10^{-16}
GP	DW	Yes	3.1×10^{-18}

The D_a of Cs leaching from the cement-solidified body of Cs-adsorbed mordenite was 10^{-18} m^2/s, although the D_a from cement with soluble CsCl is reported to be about 10^{-12} m^2/s [13, 14]. The Cs D_a value for cement with soluble CsCl was six orders of magnitude greater than that for the cement-solidified body of Cs-adsorbed mordenite. This is principally attributable to Cs adsorption by mordenite. The difference in D_a between the cement solidified body of Cs adsorbed mordenite and cement containing soluble Cs is mainly due to Cs adsorption by the mordenite because there should be no significant difference in the connectivity of the pores in cement paste itself.

5.6 Estimation of maximum Cs leaching ratios through ion-exchange calculations

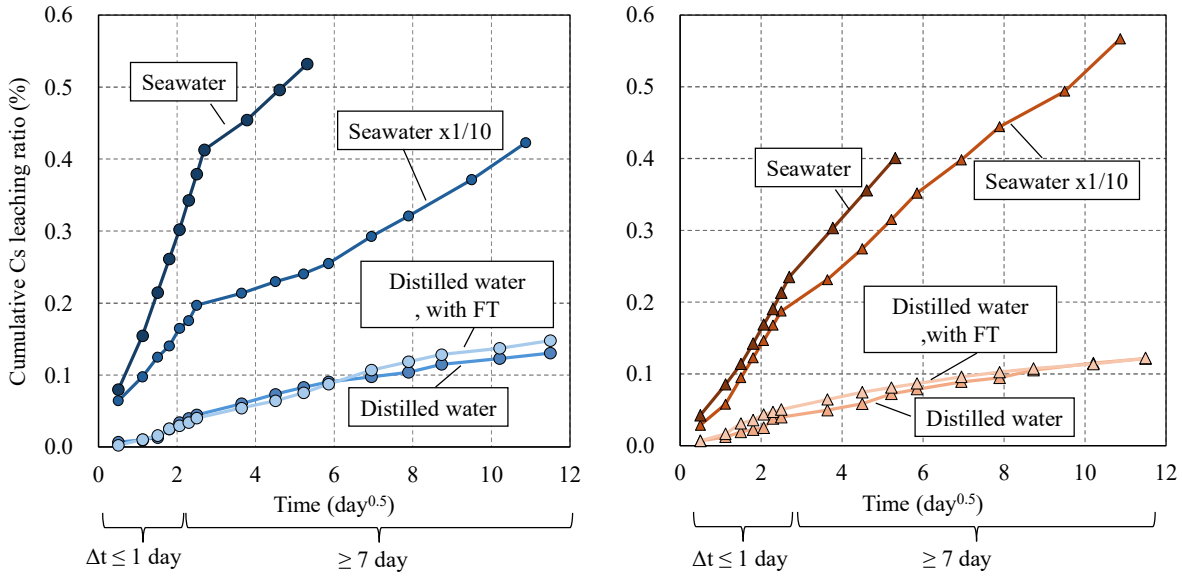

Fig. 6 Cumulative Cs leaching ratio from a solidified body of Cs-adsorbed mordenite vs. the square root of the immersion time (left: cement-solidified body, right: GP-solidified body). Δt: solvent exchange times. FT: Freeze and thawing.

The leaching test alone cannot adequately evaluate the long-term behavior of Cs-137 (half-life: 30.2 years), which retains its radioactivity over extended periods. Therefore, ion-exchange equilibrium calculations were performed to estimate the long-term maximum Cs leaching ratio. By comparing the experimental Cs leaching behavior with the results of the ion-exchange equilibrium calculations, the potential for Cs leaching from the solidified bodies containing ion-exchange material like mordenite was assessed.

Ion exchange theory [23, 24] was used to obtain the maximum Cs leaching ratios from solidified bodies. Cs leaching from an ion exchange material such as mordenite is determined by the ion exchange equilibrium with K. Some K and Na from the cement within solidified bodies serve as counter cations (A) at the sites of Cs adsorption on mordenite. During seawater immersion, K is also present in the solvent. The Cs adsorption amount (Cs leaching ratio) at equilibrium in the leaching test can be calculated as the ion exchange between adsorbed Cs and A in the system, regarding the ion exchange selectivity factor $K_{Cs/A}$ described below. This Cs leaching ratio is the theoretical maximum leaching amount, disregarding diffusion-rate. Rate-limiting diffusion through the pores of the solidified bodies discussed in the previous section is ignored.

First, consider the ion exchange reaction of Cs^+ competing with cation A^+ at ion exchange site X- in mordenite. The reaction where A^+ from X-A, thus adsorbed A^+, exchanges with Cs^+ in solution can be expressed by the following equation:

$$Cs^+ + X\text{-}A \overset{k_{Cs}k_A}{\rightleftarrows} A^+ + X\text{-}Cs \quad (6)$$

where k_{Cs} is the adsorption reaction rate of Cs^+ and k_A is the rate of the reverse reaction.

The ratio of the Cs^+ adsorption rate to that of the reverse reaction is defined as the ion selectivity coefficient $K_{Cs/A}$ for Cs relative to A.

$$K_{Cs/A} \equiv \frac{k_{Cs}}{k_A} \quad (7)$$

The Cs^+ adsorption rate k_{Cs} is proportional to $[Cs^+]$ [X-A], and the rate k_A of the reverse reaction is proportional to $[A^+]$[X-Cs]. Therefore, the time-dependent change in Cs adsorption on the ion exchange site ($\frac{\partial[X\text{-}Cs]}{\partial t}$) can be expressed as follows:

$$\frac{\partial[X\text{-}Cs]}{\partial t} = k_{Cs}[Cs^+][X\text{-}A] - k_A[A^+][X\text{-}Cs] \quad (8)$$

At adsorption equilibrium, the time derivative of Cs adsorption ($\frac{\partial[X\text{-}Cs]}{\partial t}$) becomes zero:

$$\frac{k_{Cs}}{k_A} = \frac{[X\text{-}Cs]}{[Cs^+]}\frac{[A^+]}{[X\text{-}A]} \quad (9)$$

Thus:

$$K_{\frac{Cs}{A}} \equiv \frac{k_{Cs}}{k_A} = \frac{[X\text{-}Cs]}{[Cs^+]}\frac{[A^+]}{[X\text{-}A]} \quad (10)$$

Here, for cations Cs^+ and A^+ in solution, equation (11) is derived from the law of conservation of mass. (x) represents the molar amount (quantity, not concentration) in solution. $(x)_0$ is the initial molar amount. The amount of Cs in solution after desorption equilibrium is the sum of the initial Cs^+ level and the decrease in the amount of A^+ in solution attributable to the ion exchange reaction:

$$(Cs^+) = (Cs^+)_0 + [(A^+)_0 - (A^+)] \quad (11)$$

In the same manner, using the mass balance between cations adsorbed onto mordenite and cations released into the liquid phase before and after Cs desorption delivers equations 12 and 13:

$$(X\text{-}Cs) = (X\text{-}Cs)_0 + [(Cs^+)_0 - (Cs^+)] \quad (12)$$
$$(X\text{-}A) = (X\text{-}A)_0 - [(Cs^+)_0 - (Cs^+)] \quad (13)$$

Here, the four unknowns at equilibrium ($[Cs^+]$, $[K^+]$, [X-Cs], and [X-A]) can be obtained by solving equations (10), (11), (12), and (13). Given the ion selectivity factor $K_{Cs/K}$, the initial concentrations of Cs and A in solution ($[Cs^+]_0$, $[K^+]_0$) and the initial concentrations of Cs and A at the ion exchange site ($[X\text{-}Cs]_0$, $[X\text{-}A]_0$), the Cs concentration at ion exchange equilibrium and the Cs leaching ratio can be determined.

Based on previous reports [24], the ion exchange selectivity of mordenite was assumed to be around $K_{Cs/K} = 20$. The desorption Cs concentration $[Cs^+]$ was then calculated to determine the Cs leaching ratio at desorption equilibrium.

The countercation that primarily exchanges with Cs adsorbed onto mordenite in the cement-solidified body is considered as K. The cement pore water contains K^+ and Na^+ originating from the cement. Although the pore solution composition was not chemically analyzed, the maximum amounts of K and Na that could exchange with Cs cannot exceed the total contents of the cement. The Na content of cement is approximately one-third that of K. Furthermore, the ion exchange selectivity of mordenite is in the order Cs > K > Na [8]. Based on these points, it can be assumed that Cs leaching from cement-solidified bodies is mainly determined via ion exchange with K^+.

Within the leaching test system of this study for cement-solidified bodies, the K that can exchange with Cs is limited to, first, K in the cement pore solution and, second, K in the solvent in the case of seawater immersion. Table 5 shows that the K content of cement material is 0.382 wt%. If all of this K leaches to the solvent, 0.988 mmol of K^+ would be present in the leaching test bottle (Table 6). The Cs leaching concentrations at ion exchange equilibrium were calculated at $K_{Cs/K}$ = 20, $[Cs^+]_0$ = 0 mmol, $(X\text{-}Cs)_0$ = 1.15 mmol/kg, and $(X\text{-}K)_0$ = 918 mmol/kg. The initial (X-Cs) and (X-K) values were determined using the adsorption mass balance during preparation of the Cs-adsorbed mordenite.

Table 6 shows the desorbed Cs ratios at ion exchange equilibrium, calculated from the solutions of Eq. 10‑13 and the total K content of the system. During leaching in distilled water, no K is supplied on solvent exchange, and the cumulative Cs leaching ratio (Fig. 3) would therefore be expected to remain below 0.27% long term. During seawater immersion, K in the solvent and the overall amount of K in the system increase on solvent exchange, indicating that the maximum Cs leaching ratio can be increased by solvent exchange. This indicates that while the Cs leaching ratio will approach 100% when exposed to an infinite volume of seawater, it can be suppressed to 1% or less under the liquid-to-solid ratio used in this study. Compared to the result of the leaching test, the measured Cs leaching ratio (Fig. 3) was lower than 0.32% for seawater x1/10 and 0.81% for seawater x1. In all solvents, the measured Cs leaching ratios (Fig. 3) were less than the maximum ratios, implying that Cs leaching from the solidified bodies was limited by diffusion within the solidified bodies.

It should be noted that the above calculations assume that all of the K in the cement was in solution. However, this was not the case. The true maximum leaching ratios would therefore be expected to be lower than the values in Table 6. The maximum Cs leaching ratios presented here are conservative.

Based on these results, the low Cs leaching ratio from Cs-adsorbed mordenite solidified bodies revealed in Fig. 3 can be primarily attributed to the ion-exchange selectivity of mordenite, and the leaching rate is further reduced by diffusion within the solidified bodies.

The above calculations quantitatively demonstrate the Cs capture capacity of solidified Cs-adsorbed mordenite bodies. Furthermore, the maximum Cs leaching ratio, which assumes ion exchange equilibrium between Cs and K, can easily be calculated using the ion exchange equations. Based on this, it is possible to predict the maximum Cs leaching ratio and concentration upon contact with liquids of various compositions under diverse accident scenarios.

Some challenges remain regarding the calculation of the maximum Cs leaching ratios from GP-solidified bodies. It may be that some Na in the GP dissolves and is then ion-exchanged with Cs and K in the mordenite. If this is the case, a three-component ion exchange calculation involving the Cs, K, and Na in the Cs-adsorbed mordenite is required. This should be investigated further.

Table 5. Composition of major elements in the blast furnace slag cement (wt%) measured by X-ray fluorescense (ZSX Primus IV, Rigaku, Japan).

K	Na	Mg	Al	Ca	Si	S
0.382	0.133	1.54	4.37	40.5	10.0	1.38

Table 6. The amount of K in the leaching test systems and the available Cs leaching ratio for cement-solidified bodies.
DW: distilled water, SW: seawater

Solvent	DW	SW x1/10	SW
The amount of K in the leaching test system (mmol)	0.988	1.19	2.97
Available Cs leaching ratio	0.27%	0.32%	0.81%

6. CONCLUSIONS

This study investigated the cesium leaching behavior of cement- and geopolymer-solidified bodies containing Cs-adsorbed mordenite. The leaching process consisted of two sequential steps: (1) Cs desorption from mordenite and (2) diffusion through the pore structure of the solidified bodies. Owing to the strong Cs selectivity of mordenite, the overall Cs leaching ratio remained extremely low.

The apparent diffusion coefficients (D_a) of the solidified bodies were on the order of 10^{-18}–10^{-16} m^2/s, indicating highly restricted Cs mobility. Freeze–thaw cycling between −10°C and 20°C for 300 cycles produced no measurable change in leaching behavior. In contrast, seawater immersion enhanced Cs desorption through ion-exchange effects, resulting in leaching amounts approximately four times higher than those in distilled water.

Even under seawater immersions, the Cs leaching ratio remained approximately 0.5% after 30 days for a cylindrical specimen with a diameter of 2 cm and a height of 4 cm. This leaching ratio reflects diffusion-limited transport, and larger specimens exhibit even slower increases in Cs leaching ratio owing to their reduced surface-area-to-volume ratio, indicating enhanced long-term retention for full-scale solidified bodies.

These findings demonstrate that the combination of mordenite's strong Cs adsorption selectivity and diffusion-limited transport within the solidified matrix effectively suppresses Cs release, even under severe environmental conditions. Therefore, solidification of Cs-adsorbed mordenite using cement or geopolymer is a robust and reliable method for long-term Cs immobilization in final disposal applications.

In actual disposal facilities, the parameter to be monitored is assumed to be the r-Cs concentration in the generated leachate. To estimate the r-Cs concentration in leachate, it is necessary to perform calculations that incorporate the leaching-rate data obtained in this study together with additional parameters such as water migration velocity and r-Cs adsorption in the barrier system.

7. ACKNOWLEDGEMENTS

This research was supported by the Environmental Research and Technology Development Fund (No. JPMEERF22S20910) of the Ministry of the Environment of Japan, and JST SPRING (No. JPMJSP2119).

8. REFERENCES

1. Endo K., Comprehensive management of environmental accident-derived radioactive contaminated waste (in Japanese). Journal of Atomic Energy Society of Japan, atomoΣ, Vol. 59, 2017, pp. 439–441. https://doi.org/10.3327/jaesjb.59.8_439
2 Ministry of Environment Japan, Basic Concept of Interim Storage Facilities which is Necessary to Deal with Environmental Contamination by Radioactive Substances Caused by the Accident at TEPCO's Fukushima Daiichi Nuclear Power Station (in Japanese), 2011. https://www.env.go.jp/content/900483920.pdf. Accessed 25 Feb 2024
3. Mori H., Expectations and challenges for establishment of volume reduction system for radioactive decontaminated soil; Seeking technical consistency from temporal storage to final disposal (in Japanese). Journal of SRCCE, Vol. 4, pp. 47–60, 2016.
4. Kuramochi S., Thermal volume reduction technologies for radioactively contaminated waste in the interim storage facility: Current status and future prospects (in Japanese). Journal of Material Cycles and Waste Management, Vol. 30, pp. 31–38, 2019. https://doi.org/10.3985/mcwmr.30.31
5. Inui T., 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 (in Japanese). Journal of Material Cycles and Waste Management, Vol. 33, pp. 467–476, 2022. https://doi.org/10.3985/mcwmr.33.467
6. Ichikawa S., Nishizaki Y., Takano T., Kumagai N., Technology for Removing Radioactive Cs from Incineration Fly Ash (in Japanese). Hitz Technical Report, Vol. 77, pp. 14–19, 2016.
7. Japan Environmental Safety Corporation, Individual Test Results and valuation details: Report for web (appendix 2). https://www.jesconet.co.jp/interim/page_00043.html. Accessed 4 Nov 2024
8. M. Barrer R., Klinowski J., Ion exchange in mordenite. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, Vol. 70, pp. 2362–2367, 1974. https://doi.org/10.1039/F19747002362
9. Ikegami M., Takase Y., Kometani T., Yoneda M., Shimada Y., Matsui Y., Fukutani S., Elution characteristics of Cs and Sr in heat-treated soil (in Japanese). Japanese Journal of JSCE G, Vol. 70, No. 7, pp. 203-208, 2014. https://doi.org/10.2208/jscejer.70.III_203
10. Cs-137 (Caesium-137) Radiation Safety Data. Ionactive. https://ionactive.co.uk/resource-hub/guidance/cs-137-caesium-137-radiation-safety-data Accessed 24 Nov 2025
11. Park L. G., Measurement of the Leachability of Solidified Low Level Radioactive Wastes by a Short-Term Test Procedure, An American Nuclear Society Standard, 2019
12. Nozaki Y., Trace elements in seawater: average concentrations and vertical distribution in the north pacific (in Japanese). Geochemistry, Vol. 26, pp. 25–39, 1992. https://doi.org/10.14934/chikyukagaku.26.25
13. Kojima Y., Tojo Y., Hwang I-H., Matsuo T., Toda K., Cs leaching characteristics from cement/geopolymer solidified Cs containing fly ash, Proceedings of the 13th SRRCE, 2024
14. Yasukochi T., Yamada K., Arai H., Tojo Y., Ichikawa T., Endo K., Study on cement solidification method of melting fly ash, Proceedings of the 13th SRRCE, 2023
15. Niu X., Elakneswaran Y., Islam C. R., Provis J. L., Sato T., Adsorption behavior of simulant radionuclide cations and anions in metakaolin-based geopolymer. Journal of Hazardous Materials, Vol. 429, pp. 128373, 2022. https://doi.org/10.1016/j.jhazmat.2022.128373

16. Sri M. A., Kemal P., Eko C. I., Chloride diffusion rate in loaded fly ash concrete using steady-state migration test. International Journal of GEOMATE, Vol. 29, No. 135, pp. 50-57, 2025. https://doi.org/10.21660/2025.135.5100
17. Andersson K., Allard B., Bengtsson M., Magnusson B., Chemical composition of cement pore solutions. Cement and Concrete Research, Vol. 19, pp. 327–332, 1989. https://doi.org/10.1016/0008-8846(89)90022-7
18. Terashima Y., Iwai S., Inoue Y., Fukui M., Study on the elution of radionuclides from solidified wastes. Japanese Journal of Health Physics, Vol. 5, pp. 13–23, 1970. https://doi.org/10.5453/jhps.5.13
19. Abdel Rahman R. O., Zaki A. A,. El-Kamash A. M., Modeling the long-term leaching behavior of 137Cs, 60Co, and 152,154Eu radionuclides from cement–clay matrices. Journal of Hazardous Materials, Vol. pp. 145, 372–380, 2007. https://doi.org/10.1016/j.jhazmat.2006.11.030
20. Abdel Rahman R. O., Zaki A. A., Comparative study of leaching conceptual models: Cs leaching from different ILW cement based matrices. Chemical Engineering Journal, Vol. 173, pp. 722–736, 2011. https://doi.org/10.1016/j.cej.2011.08.038
21. El-Kamash A. M., El-Dakroury A. M., Aly H. F., Leaching kinetics of 137Cs and 60Co radionuclides fixed in cement and cement-based materials. Cement and Concrete Research, Vol. 32, pp. 1797–1803, 2002. https://doi.org/10.1016/S0008-8846(02)00868-2
22. Papadokostaki K. G., Savidou A., Study of leaching mechanisms of cesium ions incorporated in Ordinary Portland Cement. Journal of Hazardous Materials, Vol. 171, pp. 1024–1031, 2009. https://doi.org/10.1016/j.jhazmat.2009.06.118
23. Tanaka Y., Yamada K., Endo K., Feasibility of ion exchange theory in radioactive Cs adsorbent for accumulation of decontaminated waste (in Japanese). Proceedings of the 34th Material Cycles and Waste Management, Vol. 34, pp. 549, 2024. https://doi.org/10.14912/jsmcwm.34.0_549
24. Ichikawa T., TOPICS: Volume reduction of radioactive contaminated waste using ferrocyanide transition metals as Cs adsorbents (in Japanese). Japanese Society of Radiation Chemistry, Vol. 105, pp. 29–35, 2018. https://doi.org/10.32157/jsrc.105.0_29