

# Hydraulic barrier performance of zeolite-amended clay liners against calcium chloride solution

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**ABSTRACT:** Barrier performance of the zeolite-amended bentonite liners, which were developed as an alternative to a bentonite sealing component of geosynthetic clay liners (GCLs) to contain radioactively contaminated municipal solid waste generated by the Fukushima nuclear disaster, was evaluated by performing a series of hydraulic conductivity tests. Effects of calcium ions in the permeant on hydraulic barrier and cesium (Cs) sorption performances were evaluated for two different types of liners; zeolite-bentonite mixture and zeolite-bentonite composite liners. The composite liners maintained lower hydraulic conductivity values than the zeolite-bentonite mixture and the single bentonite liners, due to calcium exchange by the zeolite in first wetting process. Cs sorption performance was greatly improved by the zeolite, regardless of the ways of zeolite amendment. It was proved that composite liners of the bentonite overlaid by the zeolite were more suitable for the interlayer of the GCLs for containment of radioactively contaminated waste.

*Keywords: bentonite, chemical compatibility, hydraulic conductivity, zeolite*

## 1 INTRODUCTION

Contamination of surface environment by fall-out of radioactive chemicals such as  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  was caused by the Fukushima nuclear disaster in 2011. In addition to soil and waste collected in remediation works, municipal solid waste (MSW) was also contaminated with radioactive cesium, which was concentrated in MSW incinerator ash (MSWIA) accordingly. MSWIA is allowed to be disposed of at existing MSW landfill sites or engineered containment facilities when radioactive concentrations of MSWIA are lower than 100,000 Bq/kg. Cs leaching behavior, which is a key factor of environmental impact, is quite different among soils, MSW bottom ash and fly ash. While radioactive cesium adhered to soils and MSW bottom ash are basically insoluble and stable, cesium in MSW fly ash are so soluble that 65 to 90% of Cs is easily released by (National Institute for Environmental Studies 2014). Existing MSW landfills in Japan allow rainfall infiltration into the waste layer to accelerate the waste degradation under semi-aerobic condition, as well as to wash out soluble contaminants in the waste. Thus, when radioactively contaminated MSW fly ash is disposed of in existing landfills, installation of soil layers which act as a hydraulic barrier and a sorption layer is necessary to prevent the leakage of radioactive cesium as shown in Figure 1.

Natural soil and bentonite-amended soil are expected to be utilized as sorption layers for Cs, since many previous studies support high affinity of Cs to fine soil particles (e.g. Kato et al. 2012, Shiozawa et al. 2011). Also, the authors have evaluated applicability of geosynthetic clay liners (GCLs) to the barrier layer for containment of radioactively polluted waste in existing MSW landfills (Inui, et al. 2016a). A thin interlayer of powder or granular bentonite in GCLs is expected to act as a sorption layer against radioactive cesium. However, potassium and calcium ions in the MSW leachate decreased the cesium sorption performance by a few orders at maximum. Thus, improvement of Cs sorption capacity is a critical issue to apply GCLs to containment of radioactively polluted waste.

In some previous studies, combined use of mineral filters with sodium bentonite as a sealing component in geosynthetics was attempted to improve sorption capacity against heavy metals and barrier per-

formance in saline environments (Frankovská et al. 2010, Janotka et al. 2002). Zeolite is known as a mineral which has a high affinity to Cs since micropore sizes of the zeolite minerals are very close to a typical hydrated ion size of Cs. The authors have evaluated cesium sorption performance of zeolite-amended GCLs by performing batch and column sorption tests, affected by high concentrations of sodium, potassium and calcium ions in MSWIA leachate (Inui et al. 2016b). Comparing with a conventional bentonite liner, zeolite amended GCLs maintained excellent cesium sorption performance even when 0.1 mol/L-calcium solution was permeated, while permeation of the waste leachate containing 0.11 mol/L- potassium ion allowed the release of Cs due to sorption competition. However, the effects of zeolite amendment on the hydraulic barrier performance of GCLs were complex and should be fully studied, since cation exchange properties of the zeolite influence cation concentrations of the permeants and hydraulic conductivity of sodium bentonite.

This paper presents the results of a series of hydraulic conductivity tests to assess the hydraulic barrier and cesium (Cs) sorption performances of two different zeolite-bentonite interlayers of zeolite-amended GCL; zeolite-bentonite mixture and zeolite-bentonite composite layer. Calcium chloride (CaCl<sub>2</sub>) solution was used as a permeant, since calcium is one of inorganic chemicals contained in MSWIA leachate with highest concentrations, and hydraulic conductivity of the sodium bentonite is very sensitive to divalent calcium ions (e.g. Katsumi et al. 2007). Based on the testing results, an optimum configuration of zeolite-bentonite sealing component of GCLs was discussed.

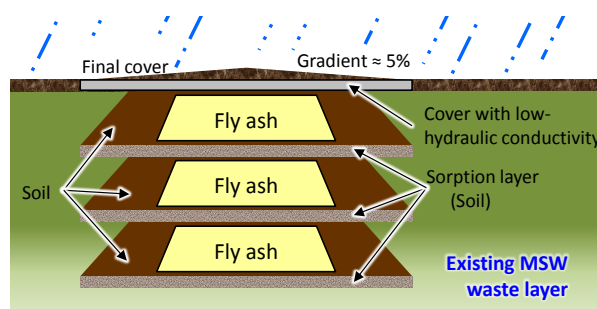


Figure 1. Schematic view of disposal of radioactively contaminated MSW fly ash in existing MSW landfills (modified from National Institute for Environmental Studies 2014).

## 2 MATERIALS AND METHODS

### 2.1 Materials

Sodium bentonite enclosed in a manufactured GCL, Bentofix<sup>®</sup> 5000 (NAUE Inc.), and powder zeolite mainly consisting of clinoptilolite were used in this study. Bentofix<sup>®</sup> 5000 is one of the GCLs widely used for waste containment, with 5000 g/m<sup>2</sup> sodium bentonite mass and 5 to 6 mm-thickness before hydration. Table 1 shows the basic properties of each material including the content of exchangeable cations and distribution coefficient for Cs determined by a conventional batch sorption test (Inui et al. 2016b).

Table 1. Basic properties of bentonite and zeolite samples.

Materials	Sodium bentonite	Zeolite powder
Particle density [Mg/m <sup>3</sup> ]	2.88	2.25
Distribution coefficient for cesium [mL/g]*	5.4 x 10 <sup>4</sup>	1.0 x 10 <sup>4</sup>
Exchangeable cations**		
Na [cmol(+)/kg]	70.4	18.1
K [cmol(+)/kg]	0.9	14.3
Ca [cmol(+)/kg]	23.7	20.6
Mg [cmol(+)/kg]	13.2	0.4

\*Data from Inui et al. (2016b), \*\*Determined by JGS 0261

### 2.2 Batch tests

Both of the zeolite and bentonite retain exchangeable cations as indicated in Table 1. When permeated with CaCl<sub>2</sub> solution in hydraulic conductivity tests, cation exchange by the zeolite influences cation composition of the permeant and hydraulic conductivity of the zeolite-bentonite interlayer.

To evaluate cation exchange properties against calcium ions, batch sorption tests were conducted by exposing dried zeolite to pure water and CaCl<sub>2</sub> solutions with equivalent Ca<sup>2+</sup> concentrations of 4.8 and

25 mmol(+)/L. 0.5 g and 2.0 g of dried zeolite was added to 100 mL of the solution. This means that the tests were conducted at two different solid-liquid ratios;  $L/S = 50$  and  $200$ . Then, the zeolite-solution mixture was shaken for 24 hours at 150 rpm in the horizontal direction. The solid-liquid separation was carried out by centrifugation at 3500 rpm for 30 minutes. After centrifugation, supernatant was filtered with a  $0.20 \mu\text{m}$ -opening syringe filter and the cation concentration was measured using an ICP-OES (Agilent, 700 Series). 2.0 g of dried sodium bentonite was tested in the same method. In addition, cation exchange properties against sodium ions were also evaluated since it is expected that certain concentrations of sodium ions are released from the sodium bentonite during permeation.

### 2.3 Hydraulic conductivity test

Hydraulic conductivity tests were conducted to evaluate the hydraulic barrier performance of zeolite amended bentonite layers with two types of configurations (mixture and composite types) shown in Fig. 2. Table 2 summarizes the test cases of hydraulic conductivity tests. The total mass of zeolite-bentonite interlayer was 4 or 6  $\text{kg/m}^2$ , which is similar to the bentonite mass of typical GCLs (around  $5.00 \text{ kg/m}^2$ ). A mixture layer was prepared by mixing the bentonite and zeolite powders thoroughly before molding. A composite layer was prepared by molding a zeolite layer overlaid with a sodium bentonite layer separately. In both cases, a cylindrical specimen with 60 mm in diameter was molded by tapping compaction.

Using a flexible-wall permeameter according to ASTM D 5084, each specimen was saturated and permeated with the solution under a confining pressure of 30 kPa in upflow direction. Thus, the zeolite layer in a composite-type specimen was firstly permeated as shown in Fig. 2. The solution containing 0.1 mol/L (200 mmol(+)/L)- $\text{CaCl}_2$  and 1.0 mg/L-Cs was used. A falling head system was employed with a hydraulic head difference of 90 to 100 cm. Effluents were periodically collected to measure their pH, electrical conductivity, and concentrations of cesium and typical cations.

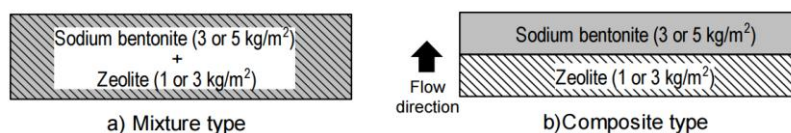


Figure 2. Configurations of zeolite-bentonite interlayers tested in this study.

Table 2. Test cases of hydraulic conductivity tests.

Case ID	Sodium bentonite mass ( $\text{kg/m}^2$ )	Zeolite mass ( $\text{kg/m}^2$ )	Type	Averaged void ratio after permeation
B3	3	-	Single	3.04
B5	5	-	Single	2.45
B5Z1_M	5	1	Mixture	2.42
B5Z1_C	5	1	Composite	2.22
B3Z3_M	3	3	Mixture	2.30
B3Z3_C	3	3	Composite	2.42
B3Z1_M	3	1	Mixture	2.58
B3Z1_C	3	1	Composite	2.51

## 3 RESULTS AND DISCUSSION

### 3.1 Cation exchange properties of zeolite and bentonite in batch tests

Figure 3 shows the batch test results of the zeolite and bentonite against calcium and sodium ions. For  $\text{CaCl}_2$  solution, calcium concentrations were decreased by the zeolite and bentonite. Instead, the bentonite released sodium and magnesium ions, and the zeolite released sodium and potassium ions by cation exchange, which is proved by the result for pure water that concentrations of cations released are negligible (Fig.3 (a)). These results indicate that the zeolite can attenuate calcium ions by exchange with sodium and potassium ions, and hydraulic barrier performance of the zeolite-bentonite interlayers permeated with  $\text{CaCl}_2$  solution may be influenced. However, the cation compositions at  $L/S = 50$  and  $200$  are similar.

Against  $\text{NaCl}$  solution (Fig.3 (d)), the zeolite attenuated sodium ions by 40% through cation exchange with calcium and potassium ions. This result indicates that calcium and potassium ions will be leached from the zeolite after leaching of sodium ions from the bentonite.

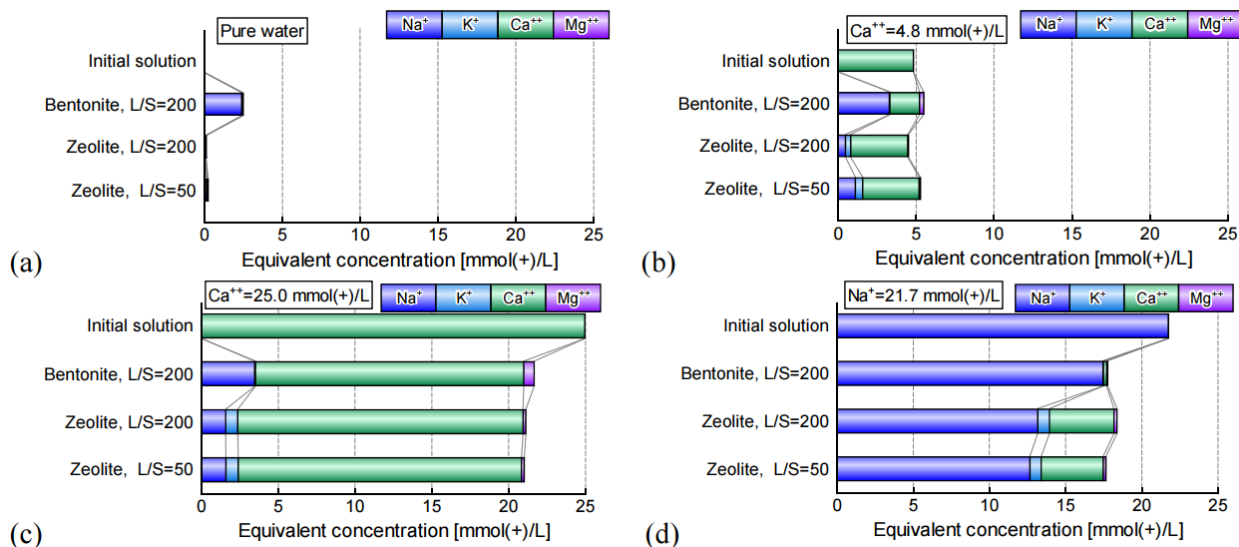


Figure 3. Cation compositions before and after the batch tests for (a) pure water, (b) 4.8 mmol(+)/L CaCl<sub>2</sub> solution, (c) 25.0 mmol(+)/L CaCl<sub>2</sub> solution, and (d) 21.7 mmol(+)/L NaCl solution. (d) Magnesium ion

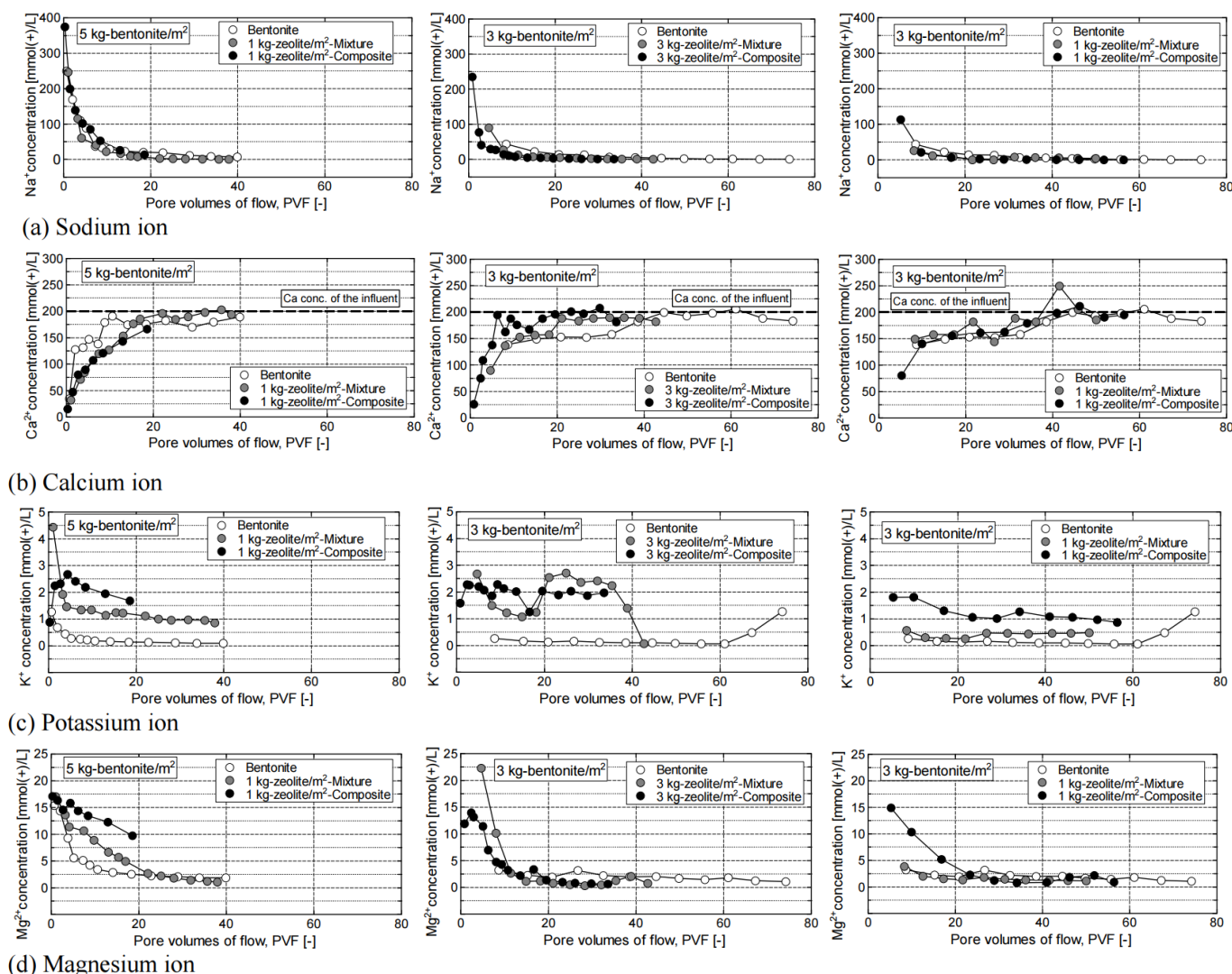


Figure 4. Cation concentrations of the effluents collected in hydraulic conductivity tests: 5 kg-bentonite/m<sup>2</sup> + 1 kg-zeolite/m<sup>2</sup> cases (left), 3 kg-bentonite/m<sup>2</sup> + 3 kg-zeolite/m<sup>2</sup> cases (center), and 3 kg-bentonite/m<sup>2</sup> + 1 kg-zeolite/m<sup>2</sup> cases (right).

### 3.2 Cation exchange behaviors in hydraulic conductivity tests

Figures 4 show Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> concentrations with the cumulative effluent volume in pore volumes of flow (PVF) in hydraulic conductivity tests. Na<sup>+</sup> concentrations were correlated to the bentonite

mass, and the higher Na<sup>+</sup> concentrations were observed for 5 kg-bentonite/m<sup>2</sup> cases. However, in the cases where the zeolite was mixed with or underlay the bentonite, Na<sup>+</sup> concentrations were lower compared with the bentonite cases, when PVF was larger than 10.

Ca<sup>2+</sup> concentrations remained lower than the influent concentration until PVF reached around 20. This indicates that Ca<sup>2+</sup> ions in the influent were exchanged with other cations retained by the bentonite and zeolite. However, as indicated in Fig. 3(d), Ca ions were also released from the zeolite by exchange with sodium ions, which were leached from the bentonite. Thus, 3 kg-zeolite cases gave higher concentrations than 1 kg-zeolite cases after the permeation started. Regarding potassium ions, K<sup>+</sup> concentrations were higher in the cases in which the zeolite was amended. Potassium ions are possibly released from the zeolite when Ca<sup>2+</sup> solutions are permeated as indicated in the batch test results (Fig. 3(c)). While, Mg<sup>2+</sup> concentrations increased in the cases of 5 kg-bentonite/m<sup>2</sup>. Magnesium ions retained by the bentonite are probably exchanged and released by the permeation of CaCl<sub>2</sub> solution, as also indicated in Fig. 3(c).

### 3.3 Hydraulic conductivity of zeolite-bentonite interlayers

Figures 5 show hydraulic conductivity (*k*) values of zeolite-bentonite layers with PVF. Note that the bentonite was not hydrated prior to the permeation and the zeolite-bentonite layer was permeated by 200 mmol(+)L-CaCl<sub>2</sub> solution under the confining pressure of 30 kPa.

For the case of 5 kg-bentonite/m<sup>2</sup> (Case B5 in Table 2), which is equivalent with the bentonite mass of conventional GCLs, the *k* values were 1 to 2 x 10<sup>-9</sup> m/s. Comparing with the *k* values of the single 3 kg-bentonite/m<sup>2</sup> layer (Case B3), the average *k* of the B3 was higher by one to two orders of magnitude than that of the B5 because of a larger void ratio of the B3 after permeation, as shown in Table 2. This is probably because the hydraulic conductivity tests were conducted for the zeolite-bentonite mixture, instead of the GCL itself confined with needle-punching and the specimen swelled significantly.

For the cases in which the zeolite was amended, the low *k* values were reasonably obtained for 5 kg-bentonite/m<sup>2</sup> cases, and the composite-type layers showed the lower *k* values than the mixture type and the single bentonite layers, regardless of the bentonite mass. Mixing of the zeolite decreased the bentonite content in a unit volume, resulting in the higher *k* values in the mixed type. In the composite type, calcium ions in the permeant were partially absorbed or exchanged into monovalent sodium and potassium ions (see Fig. 3(c)) before the permeant reached the bentonite. Accordingly, the first wetting effects by the CaCl<sub>2</sub> solution was attenuated by the zeolite. As indicated in Figs.4 (b) and (d), although the use of zeolite increased divalent calcium and magnesium concentrations in the effluents, *k* values of the composite type was not adversely affected. From these observations, the composite use of zeolite is more preferable than the mixture use of zeolite from the viewpoint of hydraulic barrier performance.

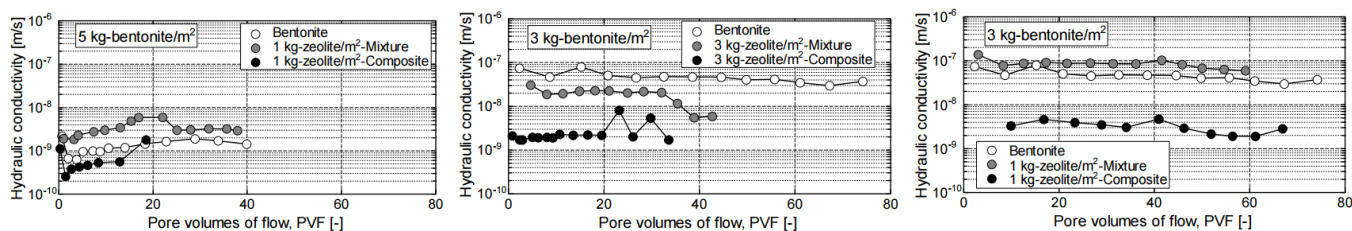


Figure 5. Hydraulic conductivity values of zeolite-bentonite layers with pore volumes of flow: 5 kg-bentonite/m<sup>2</sup> cases (left), 3 kg-bentonite/m<sup>2</sup>+3 kg-zeolite/m<sup>2</sup> cases (center), and 3 kg-bentonite/m<sup>2</sup> +1 kg-zeolite/m<sup>2</sup> cases (right).

### 3.4 Cesium sorption behavior

Figures 6 show the Cs<sup>+</sup> concentrations of the effluent with PVF. Cs<sup>+</sup> concentrations were obviously reduced by the use of zeolite in both mixture and composite types. The zeolite-amended specimens showed the concentrations of approximately < 0.01 mg/L throughout the test period.

Figure 7 shows the Cs<sup>+</sup> concentrations only for the zeolite-amended cases with an enlarged vertical axis. Overall, the composite-types gave the relatively lower Cs<sup>+</sup> concentrations regardless of the zeolite mass, although Cs sorption capacity was not exhausted in all the cases. Considering that hydraulic conductivity values shown in Figures 5, the longer retention period was achieved in the composite-types and the sorption of Cs was accordingly promoted. In addition, Cs sorption by the zeolite was significantly prevented by presence of potassium ions in the permeant (Inui et al. 2016b). However, considering that the K<sup>+</sup> concentrations in the effluent of the composite-types were very low and only slightly higher than those of the mixture-types, it can be considered that the effects of potassium ions were not significant in these cases.

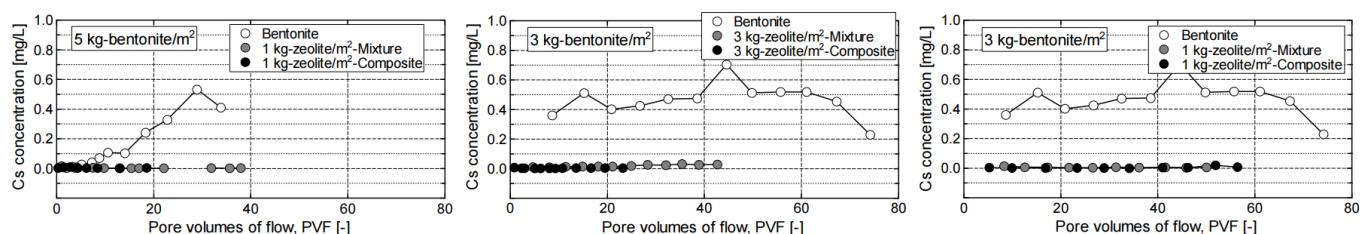


Figure 6. Cesium concentrations of the effluents collected in hydraulic conductivity tests: 5 kg-bentonite/m<sup>2</sup> + 1 kg-zeolite/m<sup>2</sup> cases (left), 3 kg-bentonite/m<sup>2</sup>+3 kg-zeolite/m<sup>2</sup> cases (center), and 3 kg-bentonite/m<sup>2</sup>+1 kg-zeolite/m<sup>2</sup> cases (right).

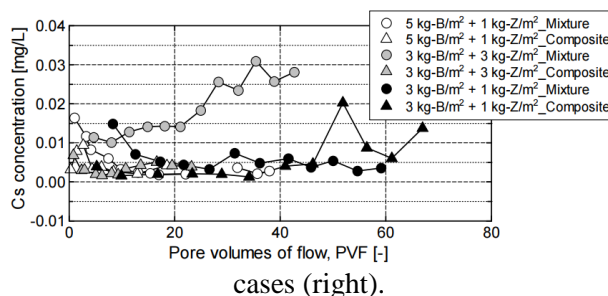


Figure 7. Cesium concentrations of the effluents from the zeolite-amended specimens.

#### 4 SUMMARY

Barrier performance of the zeolite-amended bentonite liner, which is developed as an alternative to a bentonite sealing component of GCLs to contain radioactively contaminated municipal solid waste, was evaluated when permeated with calcium chloride solution. The zeolite-bentonite composite liner maintained a better hydraulic barrier performance than the zeolite-bentonite mixture and the single bentonite layer, since calcium exchange by the zeolite attenuated the first wetting effects by calcium ions on the bentonite. The composite-type liner had hydraulic conductivity values equivalent to those of the bentonite, regardless of the bentonite and zeolite mass. From these observations, it can be concluded that the composite-type zeolite-bentonite liner can be used as an interlayer of the GCLs for containment of radioactively contaminated waste, with the low hydraulic conductivity and improved Cs sorption capacity.

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