Cesium sorption/desorption characteristics of sodium bentonite affected by major cations in leachate from MSW incinerator ash

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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. In disposal of soils and solid wastes containing low-levels of radioactive chemicals at existing MSW (municipal solid waste) landfills, installation of soil layers, such as excavated soils or bentonite amended soils, which act as sorption layers against radioactive cesium, has been planned. This manuscript addresses the results on a series of batch sorption/desorption tests to assess the effects of major cations in the leachate from MSW incinerator fly ash (MSWIFA) on the cesium sorption/desorption characteristics of sodium bentonite. The testing results indicated that major cations existing in the MSWIFA leachate such as sodium, potassium and calcium ions significantly reduced the cesium sorption capacity, and the higher concentrations led to the lower $K_d$ values, which were two orders lower than that for the distilled water when these cation concentration was higher than 10 meq/L. Particularly, calcium ion was most likely to inhibit the fixation of cesium rather than potassium and sodium ions, and the calcium ion concentration of the leachate was a good index to explain the adverse effect on the cesium sorption. Similarly, calcium and potassium ions most significantly promoted the desorption of cesium once fixed to the bentonite, more than 30% of which was desorbed when the leachate contained 10 meq/L of calcium or potassium ions.

Keywords: sodium bentonite, cesium, sorption, desorption, MSW incinerator fly ash

1. INTRODUCTION

One of the geoenvironmental issues caused by the 2011 off the Pacific coast of Tohoku Earthquake is the radioactive contamination of surface environment by fall-out of radioactive chemicals such as $^{134}$Cs and $^{137}$Cs, which was released by the accident at Fukushima Daiichi Nuclear Power Plant. Accordingly, MSW (municipal solid waste) incinerator ash containing the radioactive chemicals has been continuously generated. In case that it is contaminated with the concentrations lower than a certain criterion, it is allowed to be disposed of at existing MSW landfill sites. However, the cesium leaching behaviors are quite different between MSW bottom ash and fly ash, even though they may contain the similar concentration of radioactive cesium. While radioactive cesium in MSW bottom ash may be stable in terms of the leaching, most of cesium in fly ash will easily leach out (National Institute for Environmental Studies 2013). In addition, it should be noted that MSW landfills in Japan basically allow the rainfall infiltration into the waste layer to accelerate the biodegradation under semi-aerobic condition, as well as to wash out the soluble contaminants in the waste. Thus, when radioactively contaminated MSW fly ash is disposed of at the existing landfills, installation of soil layers which act as a hydraulic barrier and a sorption layer is considered to prevent the leakage of radioactive cesium as shown in Figure 1.

Fig. 1. Schematic view of disposal of radioactively contaminated MSW fly ash at existing landfills.

Natural soil or bentonite-amended soil is expected to be utilized as sorption layers, since they have both permeability and sorption capacity enough for sorption
layers. Many field monitoring data support that the mobility of cesium in subsurface is very limited due to high sorption capacities of soil particles (e.g. Kato et al. 2012). However, it is widely known that sorption performance of cations such as cesium is significantly affected by coexisting cations in the pore water. In this study, effects of typical cations which usually exist in the leachate of MSW incineration fly ash (MSWIFA), on the cesium sorption ability of sodium bentonite were examined. In addition, cesium once sorbed on/in soil particles might be desorbed while the leachate containing these cations continuously flows through the sorption layer due to cation exchange. Thus, a series of batch desorption tests is also conducted to assess how major cations in the leachate affect the desorption behavior of cesium sorbed on/in the sodium bentonite.

2 MATERIALS AND METHODS

2.1 Materials

Sodium bentonite (particle density: 2.88 Mg/m³, natural water content: 10%) used for the tests was obtained from a needle-punched geosynthetic clay liner (GCL) Bentofix® BFG 5000, and then sieved with a 75 μm-opening sieve. Solutions containing various types and concentrations of cations were prepared for the batch sorption/desorption tests. Firstly, solutions with sodium, potassium or calcium ion concentrations ranging from 0 to 500 mg/L were prepared by using the chloride chemicals. The simulated leachate from MSW incinerator fly ash (MSWIFA) was also prepared as follows. MSWIFA was collected in a certain incineration facility for municipal solid waste in Japan. The ash was mixed with distilled water in a ratio of 1 to 10 in mass basis. The solution was filtered by using a membrane filter with 0.2 μm opening. In addition, the solutions after diluting this leachate by 10 times and 100 times were used. Table 1 shows the chemical properties of these simulated leachate solutions.

Table 1 Chemical properties of the solutions used.

| Solutions          | Simulated leachate | 10 times dilution | 100 times dilution |
|--------------------|--------------------|-------------------|--------------------|
| pH                 | 12.4               | 11.4              | 9.3                |
| Electrical conductivity (mS/m) | 3.6×10³ | 4.6×10² | 5.3×10¹ |
| Al (mg/L)          | 1                  | N.D.              | N.D.               |
| Ca (mg/L)          | 5.3×10⁵            | 5.3×10⁴           | 5.4×10³            |
| Fe (mg/L)          | 1                  | N.D.              | N.D.               |
| K (mg/L)           | 3.5×10⁷            | 3.5×10⁶           | 3.5×10⁵            |
| Na (mg/L)          | 2.7×10⁷            | 2.7×10⁶           | 2.7×10⁵            |
| Pb (mg/L)          | 1                  | N.D.              | N.D.               |
| Zn (mg/L)          | 2                  | N.D.              | N.D.               |

2.2 Batch sorption test

Prior to the sorption test, cesium concentration of each solution listed in 2.1 was adjusted to 100 μg/L by using the standard cesium chloride solution. The tests were performed by mixing 0.05, 0.1, 0.2, 0.3 or 0.5 g of dried sodium bentonite with 100 mL of the solution in a 250 mL polyethylene bottle. The mixture was subjected to 24 hours of horizontal shaking on an incubator shaker at 150 rpm and under 20°C. After shaking, the mixture was centrifuged and then filtered using a 0.20 μm-opening filter. Concentrations of cesium were analyzed by a graphite furnace atomic absorption spectrophotometer. A sorption isotherm is described by calculating the amount of cesium sorbed with the equilibrium cesium concentration, and the distribution coefficient $K_d$ was determined from a slope of the sorption isotherm. Also, concentrations of major cations were analyzed through the inductively coupled plasma (ICP) analysis.

2.3 Batch desorption test

Sodium bentonite sample with its initial cesium concentration of 1.92 mg/g was prepared by mixing the sodium bentonite with the cesium solution of a designated concentration, curing it in three weeks and drying it. Desorbed amount was measured when the bentonite was mixed with the solutions with different $\text{Na}^+$, $\text{K}^+$ or $\text{Ca}^{2+}$ concentrations with approximately 500 mg/L in maximum, in the liquid to solid ratio of 200. The mixture was subjected to the horizontal shaking and the chemical analysis shown in 2.2 except that filtration was conducted by using both 0.20 μm-opening and 0.45μm-opening filters.

3 RESULTS AND DISCUSSION

3.1 Sorption behaviors in the MSWIA leachate

Figure 2 and Table 2 show the sorption isotherms and the $K_d$ values obtained, respectively, when the tests were performed for distilled water, and the three simulated leachate solutions shown in Table 1.

![Fig. 2. Sorption isotherms for the simulated leachate solutions and distilled water.](image-url)

Table 2. Distribution coefficients determined.

| Solutions          | $K_d$ (mL/g) | Coefficient for determination, $R^2$ |
|--------------------|-------------|-------------------------------------|
| Distilled water    | 1.0×10⁷     | 0.79                                |
| 100 times-diluted leachate | 1.1×10⁷     | 0.79                                |
| 10 times-diluted leachate  | 4.0×10⁷     | 0.97                                |
| Original leachate  | 8.0×10⁷     | 0.85                                |
$K_d$ values for the three simulated leachate were one to three orders of magnitude lower than $K_d$ for distilled water. Major differences between these solutions are concentrations of cations and pH values. According to Khan et al. (1994), cesium sorption capacity of a bentonite is pH-dependent and increased under the low-mid alkaline condition, while $K_d$ values are not increased if pH is higher than 9. Considering the pH values of these simulated leachate solutions (pH 9.3 to 12.4), pH value does not contribute a lot to the decreasing $K_d$ values. These observations indicate that existence of the cations in the simulated leachate is a main factor affecting the cesium sorption capacity.

Figure 3 shows concentration changes of cesium ion (Cs\(^+\)) and three cations after sorption test affected by the dose of bentonite for the 10 times-dilution leachate case. Potassium (K\(^+\)) and calcium (Ca\(^{2+}\)) ions as well as Cs ion were sorbed to the sodium bentonite according to the dose of bentonite. These concentration profiles clearly indicate that some coexisting cations in the simulated leachate were selectively sorbed to the bentonite and lowered the Cs sorption capacity.

3.2 Effects of major cations on Cs sorption behaviors

Figures 4 show the sorption isotherms for the solutions containing different concentrations of Na\(^+\), K\(^+\) and Ca\(^{2+}\), respectively. In the higher concentration cases, the isotherm slope becomes less steep; this trend suggests that the coexisting cations limited the Cs sorption by the sodium bentonite according to their concentrations. For example, the $K_d$ value for Na\(^+\) = 22 meq/L is 90% lower than that for the distilled water.

Figure 5 shows the relationships between the cation concentrations (equivalent concentration basis) and the $K_d$ values obtained. Overall, the lower $K_d$ values were obtained for a certain cation concentration in the order of Ca\(^{2+}\), K\(^+\), Na\(^+\). This means that calcium ion was most likely to prevent the sodium bentonite from sorbing Cs ion rather than potassium and sodium. This order corresponds well to the general preference of cation exchange equilibria in soil; highly charged cations (Ca\(^{2+}\)) tend to be held more preferentially than cations with less charge (Na\(^+\) < K\(^+\)) and secondly, cations with a small hydrated radius (Na\(^+\) < K\(^+\)) are less likely to be removed from the exchange complex. It can be concluded that the combined influence of these two criteria is important for the adverse effect of the coexisting cations on the Cs sorption ability.
values for these leachate cases were similar to those for the cases with the equivalent Ca\(^{2+}\) concentration, even though these leachates contain considerable concentrations of Na\(^+\) and Ca\(^{2+}\) as shown in Table 1. This result support the effect of Ca ion on Cs sorption is dominant even when other influential cations exist, since the cation with a higher valence and larger ionic radius are more likely to be held by the bentonite.

3.3 Desorption characteristics affected by the coexisting cations

Figure 6 shows the Cs desorption ratio, which is defined by a ratio of the amount of desorbed Cs to the initial Cs content, affected by the filter opening size as well as the K\(^+\) concentration. For the lower K\(^+\) concentration region, the larger desorption ratio was observed when using a 0.45 \(\mu\)m opening filter, since more fine bentonite particles sorbing Cs, which was counted as desorbed fraction, passed through the 0.45 \(\mu\)m opening filter. In contrast, for the higher concentration region, the desorption ratio was not affected by the filter opening size since fine particles easily flocculated and they were trapped in the filter regardless of the opening size.

![Fig. 6. Effect of the filter opening size on the Cs desorption ratio.](image1)

Figure 7 shows the Cs desorption ratio affected by the initial cation concentration (Filter opening size: 0.20 \(\mu\)m).

![Fig. 7. Cs desorption ratio affected by the initial cation concentration (Filter opening size: 0.20 \(\mu\)m).](image2)

Figure 7 shows the Cs desorption ratio affected by the initial cation concentration in equivalent concentration basis. The higher desorption ratios were given by a certain concentration of cation in the order of Ca\(^{2+}\), K\(^+\), Na\(^+\), although the difference between Ca\(^{2+}\) and K\(^+\) was minor. This order is consistent with the order for the effect on the Cs sorption reported in 3.2. Thus, it can be considered that the combined influence of charge and hydrated radius of the coexisting ion is similarly dominant for the Cs desorption characteristics.

However, these desorption behaviors was confirmed only in the equilibrium condition through the batch test, and not verified yet in in situ “flow through” condition, where re-sorption of desorbed Cs is expected. Further study is necessary to verify the possibility of leakage of Cs triggered by the cations dissolved in the MSWIFA leachate.

4 CONCLUSIONS

Effects of sodium, potassium and calcium ions, which usually exist in the MSWIFA leachate, on the Cs sorption/desorption behaviors of the sodium bentonite were assessed by performing a series of batch tests. The conclusions derived are summarized as follows.

1) Major cations existing in the MSWIFA leachate such as sodium, potassium and calcium ions significantly lowered the cesium sorption capacity of sodium bentonite. The distribution coefficients when these cations dissolved in the solution at the concentration of 500 mg/L were two orders lower than that determined in the distilled water.

2) Calcium ion was most likely to prevent the sodium bentonite from sorbing Cs rather than an equivalent concentration of potassium and sodium ions due to the combined effects of ion valence and hydration radius. In addition, calcium concentration became a good index to estimate the effect on the cesium sorption even when other influential cations exist.

3) Calcium and potassium ions rather than sodium ion significantly promoted desorption of cesium once fixed to the bentonite. This order is consistent with the order for the disturbance of cesium sorption by these cations.

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REFERENCES

1) Kato, H., Onda, Y., and Teramage, M. (2012): Depth distribution of \(^{137}\)Cs, \(^{134}\)Cs, and \(^{131}\)I in soil profile after Fukushima Dai-ichi Nuclear Power Plant Accident, *Journal of Environmental Radioactivity*, 111, 59-64.

2) Khan, S.A., Raiz-ur-Rehman, and Khan, M.A. (1994): Sorption of cesium on bentonite, *Waste Management*, 14(7), 629-642.

3) National Institute for Environmental Studies (2013): *Technical Report on Proper Waste Treatment and Disposal Considering the Fate and Transport of Radionuclide*, 3rd Edition, http://www.env.go.jp/jishin/attach/haikihyouka_kentokai/10-mat_3.pdf (browse on March 6, 2014), in Japanese.