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Migration of Cs⁺ through MX 80 bentonite under different ionic concentration

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Abstract - Compacted bentonite is a candidate buffer material for geological disposal of high-level radioactive waste. The diffusion behavior of radionuclides in the compacted bentonite is an important concern to be elucidated for the safety assessment of the geological disposal. In this study, one-dimensional, non-steady diffusion experiments using ¹³⁷Cs⁺ tracer were conducted for compacted bentonite saturated with distilled water or 0.5 M NaCl solution. An increase in the apparent diffusion coefficients was found in this study when the NaCl solution was used for the saturation of bentonite sample. The activation energies for the Cs⁺ diffusion, which were calculated from the temperature dependences of the diffusion coefficients, were significantly higher than that for Cs⁺ diffusion in free water, but no remarkable dependency of the activation energy on NaCl concentration was observed. Based on these experimental findings, diffusion mechanism of Cs⁺ in compacted bentonite is discussed in this study.

INTRODUCTION

For Geological disposal of high-level radioactive waste, compacted Na-bentonite containing montmorillonite as major mineral is considered as candidate buffer material that retard the transports of radionuclides from waste form to surrounding host rock. For the safety assessment of the geological disposal, the transport of radionuclides in the disposal system is an important issue to be studied. Due to the very low hydraulic conductivity of the bentonite, the radionuclide transports are considered to be mainly governed by diffusion. Therefore, it is essential to clarify the diffusion behavior of radionuclides in compacted bentonite under repository conditions in which relatively higher temperatures and groundwater with high ionic strength could be expected [1].

Cesium-135, which is present in nuclear wastes as a fission product, is an important radioisotope in the safely assessment of the geological disposal, because of its long half-life (2.3 Ma). Although extensive studies have been made for diffusivity of cesium ions in the compacted bentonite [2]-[6], diffusion mechanism of Cs⁺ ions in compacted bentonite has not been fully understood. Especially, to the best knowledge of present authors, there are few reports available for effect of the ionic strength on the activation energy for Cs⁺ diffusion in bentonite. In this study, therefore, apparent diffusion coefficients of ¹³⁷Cs⁺ in compacted bentonite were determined in laboratory experiments with different diffusion temperatures so as to discuss the diffusion process of Cs⁺ ions from the viewpoint of the activation energy.

EXPERIMENT

Bentonite used in this study was MX-80 that is a commercial product from a natural bentonite produced in Wyoming, USA. The montmorillonite content of this bentonite is approximately 80% [6]. The bentonite powder samples as received was compacted in an acrylic resin cell (20 mm diameter by 20 mm height) to obtain a dry density of 1.0 Mg m⁻³, and saturated with distilled water or 0.5 M NaCl solution for about 30 days. Diffusion experiments were conducted by applying a small amount of ¹³⁷Cs⁺ tracer solution to one end of the solution saturated sample. The spiked ends of the two bentonite samples were placed together as illustrated in Fig.1. The temperature of the bentonite samples was maintained to a set value within ± 0.1K between 288 to 323 K during whole period of time from the spike of the tracer to the end of the diffusion experiment. After a prescribed period of time for diffusion, the cell was disassembled and the bentonite specimen was sectioned into 0.5mm thickness as it was extruded from the cell in steps. The relative radioactivity of ¹³⁷Cs⁺ was measured in each slice with a well type NaI scintillation counter (Aloka Model, ARC-380). The detailed procedures for sample preparation and diffusion experiments are described elsewhere [7].

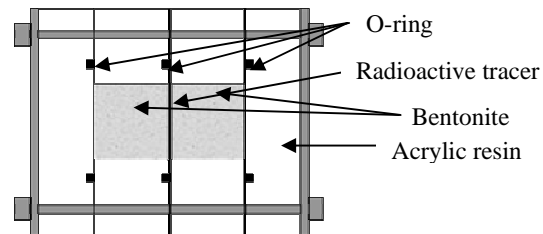


Fig. 1: Schematic of diffusion cell

RESULTS AND DISCUSSION

Assuming the tracer (i.e. ¹³⁷Cs⁺) to be an infinitely thin source, the concentration profile obtained in a diffusion experiment can be expressed by the following equation [8];

$$C(x,t) = \frac{M}{2\sqrt{\pi D_a t}} \exp\left(-\frac{x^2}{4D_a t}\right) \quad (1)$$

where D_a is the apparent diffusion coefficient of tracer in the compacted bentonite ($m^2 s^{-1}$), C is the concentration of the diffusing tracer ($counts m^{-3}$), t is the diffusion time(s), x is the distance from the bentonite surface on which tracer was spiked (m), and M is the amount of the deposited tracer source per unit area ($counts m^{-2}$). The apparent diffusion

coefficient was determined from a plot of $\log C(x)$ as a function of x^2 at the time t by least-squares fitting.

A typical concentration profile of ^{137}Cs in bentonite is shown in Fig. 2. The apparent diffusion coefficients at 298 K obtained for the bentonite saturated with distilled water were 1.5×10^{-11} and $1.6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. These values agree with those reported by other researchers [2],[3],[5], suggesting validity of the experimental procedures conducted in this study. On the other hand, the apparent diffusion coefficient was found to increase when the compacted bentonite was saturated with NaCl solution instead of distilled water. Molera and Eriksen (2002) reported similar increasing tendency of the apparent diffusion coefficient of Cs^+ at a dry density of 1.2 Mg m^{-3} as the NaCl concentration increased from 0.1 to 1.0 M, and attributed it to the decrease of K_d values with increasing ionic strength [4].

Fig. 3 shows the temperature dependences of the apparent diffusion coefficients of Cs^+ ions at different NaCl concentration. The activation energy for the diffusion of Cs^+ ions can be determined from the temperature dependence of the apparent diffusion coefficients at different NaCl concentration by using the following equation, i.e. Arrhenius law:

$$D_a = B \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where B is the constant (-), E_a is the activation energy for diffusion of $^{137}\text{Cs}^+$ in water saturated compacted bentonite (kJ mol^{-1}), R is the gas constant ($\text{J K}^{-1} \text{ mol}^{-1}$), T is the diffusion temperature (K). The activation energies for Cs^+ diffusion determined in the present study are 34.4 and 36.9 kJ mol^{-1} for the bentonite saturated with distilled water and NaCl, respectively. These values are significantly higher than the activation energy

for the diffusion of cesium ions in free water, 16.2 kJ mol^{-1} . According to the conventional diffusion model [5], Cs^+ ions in compacted bentonite are considered to diffuse in macro pores where is filled with free water. However, considering the higher activation energies obtained in this study, it is likely that Cs^+ ions in the compacted bentonite diffuse predominantly in other pathways (e.g. interlayers of montmorillonite aggregates) than the macro pore even at the high NaCl concentration in which larger macro pores are expected to be present due to the shrinkage of the interlayers [1].

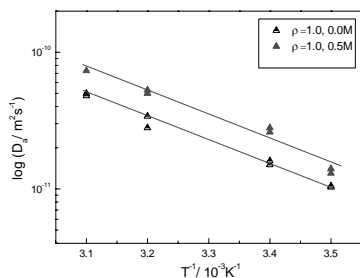


Fig. 2: Concentration profile of Cs^+ in Compacted Na-montmorillonite (dry density : 1.0 Mg m^{-3} , ionic strength 0.0 M, diffusion temperature: 298K, diffusion period: 265.5 h, D_a : $1.6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$)

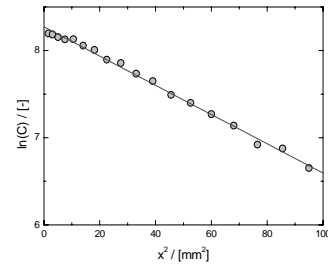


Fig. 3: Temperature dependences of the apparent diffusion coefficients of Cs^+ in compacted MX-80 at different ionic strength

CONCLUSION

The Migration behavior of $^{137}\text{Cs}^+$ in compacted bentonite clay was studied by diffusion experiments as a function of ionic strength and temperature. D_a values increased with increasing ionic strength by the change in sorption (K_d value decreases). The activation energy, E_a values are significantly higher than the value in free water even at the high NaCl concentration where large macro pores are considered to be present. These finding suggests that Cs^+ ions in the compacted bentonite diffuse predominantly in other pathways than the macro pore (e.g. interlayers of montmorillonite aggregates).

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