

The concentration and pH dependent diffusion of ^{137}Cs in compacted bentonite by using capillary method

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Abstract

The ‘in-diffusion’ method was used to study the diffusion behavior of radionuclide ^{137}Cs in compacted bentonite using a capillary. The results (distribution coefficient, K_d , apparent and effective diffusion coefficients, D_a and D_e) derived from the capillary method are in good agreement with the literature data, and fit the Fick’s second law very well. The experiments were carried out at 3.3×10^{-3} and 3.3×10^{-5} mol/l cesium, pH 3–12, ionic strength 0.1 M NaClO_4 , and at room temperature. The results suggest that the diffusion of cesium in compacted bentonite is dependent on solution concentrations and pH values. In agreement with the literatures, the K_d values derived from the capillary experiments are in most cases lower than those derived from batch experiments: the K_d values are about one-half to one-third the values of those from batch experiments. The interlaminary space plays a very important role to the sorption, diffusion and transport of Cs^+ in compacted bentonite. The effective diffusion coefficient is higher than that of other nuclides in compacted bentonite, and the diffusion of cesium in compacted bentonite may be dominated by the surface diffusion.

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1. Introduction

After emplacement of high level radioactive waste in deep underground repository, the long-lived radionuclides may be leached from the waste and may subsequently be transported through the backfill materials, such as bentonite. Sorption of radionuclides onto the mineral surfaces and diffusion into the pores are important processes leading to the retardation of the transport

of radionuclides and other contaminants through the geosphere. Compacted bentonite has been considered as a good backfill material in the repositories of nuclear waste [1]. Bentonite’s prominent properties of high swelling and sealing ability and cation exchange capacity provide retardation for the transport of radionuclides from the waste form to the surrounding rocks in the repository. Migration of radionuclides through bentonite must be studied to estimate the potential hazard of the long-term radioactive waste disposals. Usually the sorption and diffusion of radionuclides on/through compacted bentonite are the important parameters for the performance assessment of radioactive wastes. The sorption

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behavior of radionuclides is often represented by the distribution coefficient, K_d , values derived from batch techniques. However, it is observed that these data can not be used unambiguously to predict the transport of radionuclides in compacted bentonite, because K_d values derived from batch experiments are usually higher than those obtained with compacted bentonite [1–4].

Radionuclides diffusion and its mechanisms in different compacted bentonite clays have been investigated during the last decades [5–9]. Kim et al. [9] studied the diffusion of Cs and Sr in compacted bentonite and indicated that it can not be concluded that the cation having a higher K_d value always migrates through the compacted bentonite slower than the cation having a lower K_d value. The diffusion of many radionuclides in compacted bentonite was studied and the results indicated that diffusion coefficients of radionuclides decrease with increasing bulk dry densities [1,10]. Kozaki et al. [6] studied the diffusion of Cs^+ in compacted bentonite and found that diffusion coefficients of Cs^+ was higher than those reported by Sato et al. [1]. Kozaki et al. [6] gave the reason that the difference was attributed to the difference in diffusion temperature and particle sizes of the bentonite. Kozaki et al. [8] also studied the effect of bentonite particle size on diffusion of Cs^+ in compacted bentonite and found that diffusion coefficient decreases with decreasing particle size. The effective diffusion coefficients of most radionuclides are similar to the apparent diffusion coefficient of HTO and in the range of 10^{-11} – 10^{-9} m^2/s . Ion exclusion effects are observed for I^- and Cl^- diffusion as D_e values lower than 10^{-11} m^2/s and surface diffusion effects are found for Cs^+ , Pa(III) and Sr^{2+} diffusion as D_e values higher than 10^{-9} m^2/s [10]. Most of the previous papers were mainly focused on the effect of temperature, particle size or the bentonite dry density on the diffusion of radionuclides in compacted bentonite. The study about the effect of pH and solution concentration on the diffusion of radionuclides in compacted bentonite is still very scarce [3,4,11].

This paper is an extension of the previous papers, where the diffusion of Eu(III) in compacted bentonite [4] and diffusion of $^{99}\text{TcO}_4^-$ [11] in compacted bentonite were studied. The experimental results showed that K_d values in compacted bentonite derived from capillary tests are more accurate to evaluate the diffusion or transport of radionuclides in compacted bentonite than those obtained from powdered bentonite in batch experiments. The sorption of radionuclides in compacted bentonite is dependent on the density of the compacted bentonite; the interlaminary space of compacted bentonite contributes significantly to the sorption, migration and diffusion of radionuclides in compacted bentonite. We also found that pH and radionuclide solution concentration affect the radionuclide diffusion in compacted bentonite significantly. This work mainly focused on the effect of solution concentration and pH on the diffusion

of $^{137}\text{Cs}^+$ in compacted bentonite. Herein the diffusion and sorption mechanism of $^{137}\text{Cs}^+$ in compacted bentonite is also discussed.

2. Experimental

2.1. Materials

All chemicals were purchased as analytical purity and used in the experiments without any purification. The bentonite MX-80 was provided by SUBATECH laboratory as a gift and used without any purification. The clay fraction amounts to $(82 \pm 3)\%$ of dry weight and consists of montmorillonite whose stoichiometric formula is $(\text{Si}_{3.96}\text{Al}_{0.04})(\text{Al}_{1.52}\text{Mg}_{0.26}\text{Fe}_{0.17}^{\text{III}})\text{Na}_{0.18}\text{Ca}_{0.11}\text{O}_{10}(\text{OH})_2$ [12]. The main mineral contents are quartz, feldspar, calcite (CaCO_3 , $(\text{Ca,Fe})\text{CO}_3$), siderite and pyrite. The water content of 8% was determined and taken into account in the calculation of the bentonite concentrations. The mineralogical and physical-chemical compositions of bentonite are listed in Table 1.

Reagent of $^{137}\text{CsCl}$ was purchased as solid phase and dissolved in 1 M HCl. The concentration of $^{137}\text{Cs}^+$ was measured by liquid scintillation counting using a Packard 3100 TR/AB liquid scintillation analyzer (Perkin–Elmer). The scintillation cocktail was UL TIMA Gold ABTM (Packard). The detailed experimental steps are illustrated in Fig. 1.

2.2. Experimental

All experiments were carried out at room temperature. The solutions were prepared with milli-Q water.

The length (L_0 , $L_0 = 3$ cm), mass (m_0) and volume (V_0) of the capillary were used to characterize the capillary. The volume was deduced from the inner diameter (0.120 cm) and the length of the capillary. When the capillary was filled with bentonite, it was placed in 50 ml of 0.1 M NaClO_4 solution. It generally took about three to four weeks for this step. In order to check that the

Table 1
Mineralogical and physico-chemical compositions of bentonite MX-80

Mineral	Weight content
Montmorillonite	80–84%
Quartz	6–7%
Feldspars	1.2%
Calcite	0.5–1.6%
Pyrite	0.6%
Plagioclases	3.4%
Phlogopite	2.5–4.3%
CEC	76 Meq/100 g

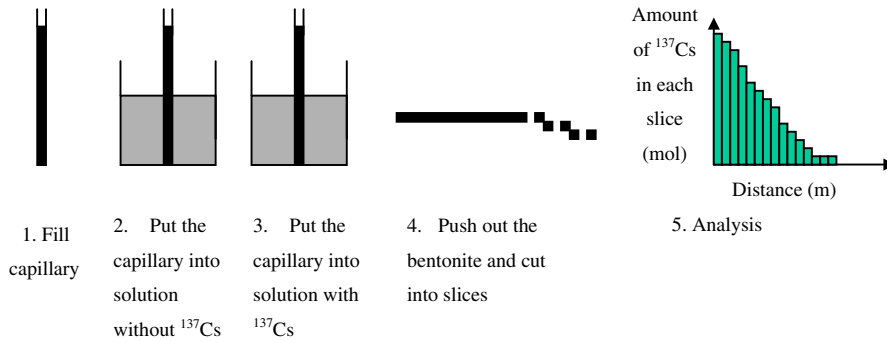


Fig. 1. The experimental procedure.

bentonite in the capillary was fully saturated with 0.1 M NaClO_4 after it was placed in the solution for 3 weeks, the bentonite in one capillary was pushed out and cut into 2 mm thick slices. The amount of Na^+ in each slice was measured by ICP-MS and the results indicated that the amount of Na^+ in each slice was equal within the analytical uncertainty. The ICP-MS measurements suggested that 3–4 weeks was enough for the bentonite in the capillary to be saturated with 0.1 M NaClO_4 .

In order to prevent the bentonite in the capillary from being released into the solution because of the swelling of the bentonite, the top and bottom of the capillary was closed with plastic film and only let a tiny hole. The loss of bentonite can be negligible during the equilibration step.

After the plastic film was removed, the capillary thus prepared was put into 15 ml 0.1 M NaClO_4 solution containing $^{137}\text{Cs}^+$ at a given concentration and pH value for a time t (74 days). It has been checked that the concentration of $^{137}\text{Cs}^+$ in the solution was constant during the diffusion time. Furthermore, it has been checked that there was no release of bentonite in the solution. The pH was controlled by adding 0.01 M HCl or NaOH during the experiments. After the diffusion time ($t = 74$ days), the capillary was removed from the solution and the bentonite was pushed out and cut into 2 mm thick slices. Each slice was then dissolved in 2 ml 1 M HNO_3 for 24 h. The amount of $^{137}\text{Cs}^+$ in each slice was measured to determine the diffusion profile $C = f(x)$, where x was the distance from the solution source.

The diffusion process of $^{137}\text{Cs}^+$ in the compacted bentonite is described as follows, according to Fick's second law:

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2}. \quad (1)$$

The solution to the diffusion equation for the initial and boundary conditions in this method has been given [13]

$$\frac{C}{C_0} = \text{erfc} \frac{x}{2\sqrt{D_a t}}, \quad (2)$$

where C is the amount of $^{137}\text{Cs}^+$ (mol) at a distance x from the solution–bentonite interface at time t . C_0 is the amount of $^{137}\text{Cs}^+$ (mol) at the interface between the bentonite and the bulk solution, and it was deduced from the experimental data by the fitting procedure in Eq. (2). D_a is the apparent diffusion coefficient (m^2/s), and $\text{erfc}()$ denotes the complementary error function and can usually be expressed as

$$\text{erfc}(z) = 1 - \frac{2}{\sqrt{\pi}} \int_0^z \exp(-x^2) dx. \quad (3)$$

The apparent diffusion coefficient (D_a) is commonly the most direct entity evaluated from the experiments when the diffusion profiles are observed. Diffusion phenomena of ions through compacted bentonite are difficult to analyze because several physical and chemical processes are included, such as ion exchange, physical and/or chemical adsorption, filtration and precipitation. The effective diffusion coefficient (D_e) is the entity that is the most invariant for the nuclides that do not have the surface diffusion or ion exclusion effects. The effective diffusion coefficient (D_e) is defined as

$$D_e = D_a(\theta + K_d\rho_b), \quad (4)$$

where θ is the porosity of the compacted bentonite (m^3/m^3) and ρ_b is the bentonite dry density (kg/m^3). Usually, the D_e values of different nuclides are similar to that of HTO and in the range of 10^{-11} – 10^{-9} m^2/s [10]. If the D_e value is higher than the average values, surface diffusion will be dominant on the diffusion of nuclide. On the contrary, if the D_e value is lower than the average value, ion exclusion will perhaps affect the diffusion of nuclide in the compacted bentonite.

3. Results and discussion

3.1. Diffusion profiles

Typical diffusion profiles for $^{137}\text{Cs}^+$ at different solution concentrations are given in Fig. 2. The solid line is

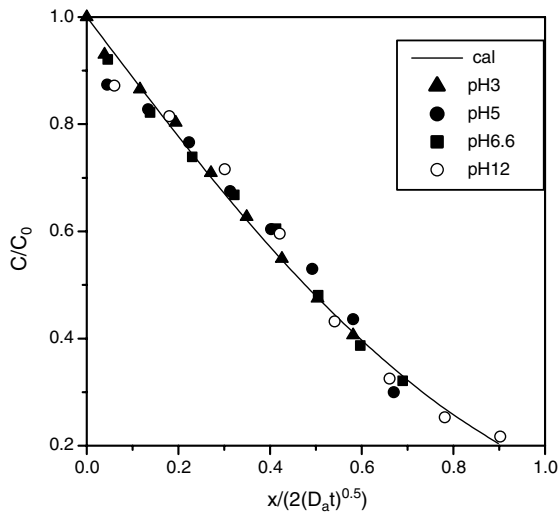


Fig. 2. Diffusion profiles of $^{137}\text{Cs}^+$ in compacted bentonite at $\rho_b = 1000 \pm 30 \text{ kg/m}^3$ and $\theta = 0.62 \pm 0.02$. The solid line is calculated from Eq. (2) with the parameters given in Table 2. $C(^{137}\text{Cs}^+) = 3.3 \times 10^{-5} \text{ mol/l}$.

the data fits from Eq. (2) for the solution concentration of $^{137}\text{Cs}^+$ $3.3 \times 10^{-5} \text{ mol/l}$. It was observed that for different pH values, the fits described the experimental data very well, suggesting the validity of this method.

3.2. Effect of solution concentration on the diffusion coefficient in the compacted bentonite

The apparent diffusion coefficients of $^{137}\text{Cs}^+$ derived from different solution concentrations at pH 6.6 with dry density of $1000 \pm 30 \text{ kg/m}^3$ are shown in Fig. 3. The D_a value increases slightly with increasing solution concentration. The D_a value of $^{137}\text{Cs}^+$ in compacted bentonite increases from 5.0×10^{-12} to $3.9 \times 10^{-11} \text{ m}^2/\text{s}$ when the solution concentration increases from $3.3 \times 10^{-8} \text{ mol/l}$ to $3.3 \times 10^{-2} \text{ mol/l}$. The diffusion of cesium in compacted bentonite is dependent on cesium solution concentration. The K_d , D_a and D_e values derived from the capillary experiments and the experimental conditions are listed in Table 2. Compared with the diffusion coefficients of $^{241}\text{Am(III)}$, $^{237}\text{Np(III)}$, Eu(III) , $^{129}\text{I}^-$, $^{99}\text{TcO}_4^-$, $^{36}\text{Cl}^-$ and HTO in compacted bentonite [1,3,6], the diffusion coefficient of $^{137}\text{Cs}^+$ in compacted bentonite is lower than that of $^{99}\text{TcO}_4^-$, $^{129}\text{I}^-$, $^{36}\text{Cl}^-$, HTO and higher than that of Eu(III) , $^{241}\text{Am(III)}$ and $^{237}\text{Np(III)}$. This suggests that the diffusion and transport of $^{137}\text{Cs}^+$ is slower than $^{99}\text{TcO}_4^-$, $^{129}\text{I}^-$, $^{36}\text{Cl}^-$, HTO and faster than Eu(III) , $^{241}\text{Am(III)}$ and $^{237}\text{Np(III)}$. Kozaki et al. [6,8] studied diffusion of Cs^+ in compacted bentonite and found that diffusion coefficient of Cs^+ in compacted bentonite decreases with increasing dry density and decreasing particle size. The

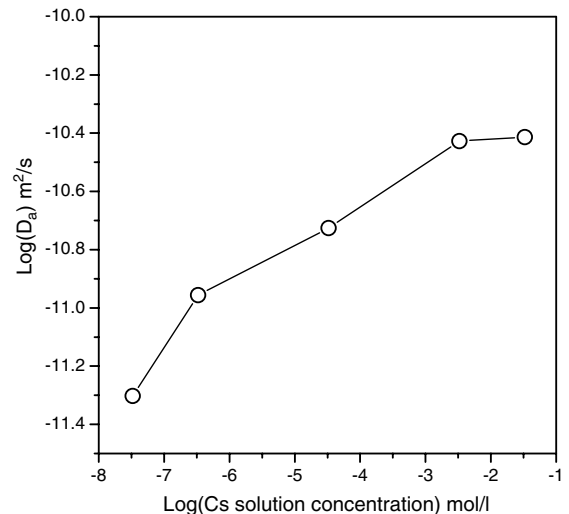


Fig. 3. D_a values derived from capillary test as a function of $^{137}\text{Cs}^+$ concentration. $\rho_b = 1000 \pm 30 \text{ kg/m}^3$, $\theta = 0.62 \pm 0.02$.

diffusion coefficient at dry density $1000 \pm 30 \text{ kg/m}^3$ is about $(1.0 \sim 1.5) \times 10^{-11} \text{ m}^2/\text{s}$ at particle diameters $<45 \mu\text{m}$ and $2.6 \times 10^{-11} \text{ m}^2/\text{s}$ at particle diameters $75\text{--}150 \mu\text{m}$. Kim et al. [9] studied diffusion of Cs^+ in compacted bentonite and got $D_a = 1.0 \times 10^{-11} \text{ m}^2/\text{s}$ at dry density of $1000 \pm 30 \text{ kg/m}^3$. The D_a values of Cs^+ diffusion in compacted bentonite at dry density of $1000 \pm 30 \text{ kg/m}^3$ are reported to be $4.0 \times 10^{-11} \text{ m}^2/\text{s}$ [1] and $1.3 \times 10^{-11} \text{ m}^2/\text{s}$ [14]. The $^{137}\text{Cs}^+$ diffusion coefficient in our experiment is quite close to those of the references. The results also indicate the validity of this fast and easy capillary method.

3.3. Effect of pH on the diffusion coefficient in compacted bentonite

The apparent diffusion coefficients (D_a) of $^{137}\text{Cs}^+$ in compacted bentonite as a function of pH at solution concentrations of 3.3×10^{-5} and $3.3 \times 10^{-3} \text{ mol/l}$ are shown in Fig. 4. The D_a value decreases very slightly with increasing pH values. At solution concentration of $4.3 \times 10^{-5} \text{ mol/l}$, the D_a value decreases from $2.6 \times 10^{-11} \text{ m}^2/\text{s}$ to about $1.1 \times 10^{-11} \text{ m}^2/\text{s}$ when pH increases from 3 to 12. At solution concentration of $4.3 \times 10^{-3} \text{ mol/l}$, the D_a value decreases from $4.3 \times 10^{-11} \text{ m}^2/\text{s}$ to about $1.8 \times 10^{-11} \text{ m}^2/\text{s}$ when pH increases from 3 to 12. The decrease of diffusion coefficient with increasing pH values indicates that the diffusion and migration of $^{137}\text{Cs}^+$ in compacted bentonite decreases with increasing pH values. To our knowledge, this is the first paper to report the effect of pH on the diffusion of $^{137}\text{Cs}^+$ in compacted bentonite. Oscarson et al. [2] studied the sorption of cesium on bentonite and concluded that cation exchange is the predominant mode for the sorption of

Table 2

The D_a and K_d values of $^{137}\text{Cs}^+$ in compacted bentonite at $\rho_b = 1000 \pm 30 \text{ kg/m}^3$ and $\theta = 0.62 \pm 0.02$

$^{137}\text{Cs}^+$ (mol/l)	pH	C_0 (mol)	D_a (m^2/s)	K_d^a (ml/g)	K_d^b (ml/g)	D_c (m^2/s)
3.3×10^{-8}	6.6	2.1×10^{-11}	5.0×10^{-12}	260	180	5.0×10^{-9}
3.3×10^{-7}		6.6×10^{-11}	1.1×10^{-11}	88	75	3.5×10^{-9}
3.3×10^{-5}		8.2×10^{-9}	1.9×10^{-11}	110	101	2.1×10^{-9}
3.3×10^{-3}		3.4×10^{-7}	3.7×10^{-11}	45	44	1.7×10^{-9}
3.3×10^{-2}		1.8×10^{-6}	3.9×10^{-11}	24	24	9.4×10^{-10}
3.3×10^{-5}	3	6.7×10^{-9}	2.6×10^{-11}	90	84	2.4×10^{-9}
	5	8.4×10^{-9}	2.0×10^{-11}	112	98	2.2×10^{-9}
	6.6	8.2×10^{-9}	1.9×10^{-11}	110	101	2.1×10^{-9}
	9	9.4×10^{-9}	1.7×10^{-11}	126	104	2.1×10^{-9}
	10	9.0×10^{-9}	1.5×10^{-11}	120	105	1.9×10^{-9}
	11	9.5×10^{-9}	1.3×10^{-11}	127	113	1.7×10^{-9}
	12	9.9×10^{-9}	1.1×10^{-11}	134	116	1.5×10^{-9}
3.3×10^{-3}	3	1.9×10^{-7}	4.3×10^{-11}	25	24	1.1×10^{-9}
	5	2.8×10^{-7}	4.0×10^{-11}	37	35	1.5×10^{-9}
	6.6	3.4×10^{-7}	3.7×10^{-11}	45	44	1.7×10^{-9}
	9	3.7×10^{-7}	3.1×10^{-11}	49	46	1.5×10^{-9}
	12	7.1×10^{-7}	1.8×10^{-11}	95	81	1.7×10^{-9}

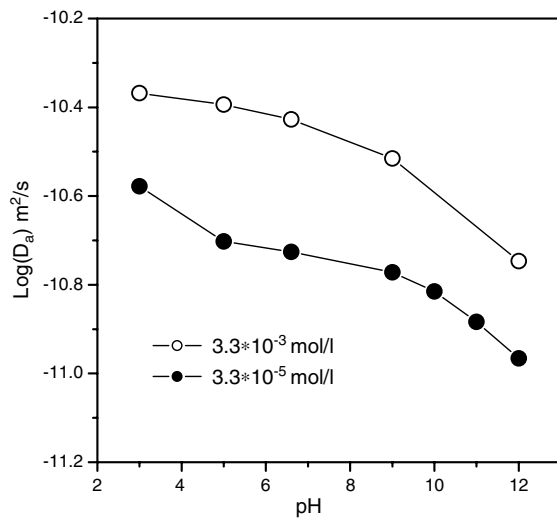
^a K_d values are calculated from C_0 which derived from Eq. (2).^b K_d values are calculated from the amount of $^{137}\text{Cs}^+$ in the first slice.

Fig. 4. D_a values derived from capillary test as a function of pH. $\rho_b = 1000 \pm 30 \text{ kg/m}^3$, $\theta = 0.62 \pm 0.02$. Solid points: $C(^{137}\text{Cs}^+) = 3.3 \times 10^{-5} \text{ mol/l}$, open points: $C(^{137}\text{Cs}^+) = 3.3 \times 10^{-3} \text{ mol/l}$.

cesium on bentonite. The cation exchange is characterized by a strong dependency on background electrolyte concentration, a weak dependency on pH and linear sorption isotherm [15]. From the sorption property of cesium on bentonite, the diffusion of cesium in compacted bentonite should be weakly dependent on pH values. Our results of cesium diffusion in compacted bentonite are a little different from the conclusion of

batch experiments. The difference between the capillary test and batch experiments may be attributed to the content of interlaminary space of the compacted bentonite. The effect of pH on the distribution coefficient of cesium in compacted bentonite will be discussed in the following part.

3.4. Effect of solution concentration and pH on the distribution coefficient in compacted bentonite

The distribution coefficients in compacted bentonite from the capillary experiments are listed in Table 2. No significantly high concentrations of $^{137}\text{Cs}^+$ were found near the source. This means that no precipitation of $^{137}\text{Cs}^+$ occurred on the surface of the compacted bentonite. The K_d values in the compacted bentonite were deduced from the amount of $^{137}\text{Cs}^+$ at the interface between the bentonite and the bulk solution, C_0 , which was derived from Eq. (2), and the amount of $^{137}\text{Cs}^+$ in the first slice of compacted bentonite, C_{slice1} , which was derived from liquid scintillation analyzer

$$K_d(\text{cal}) = \frac{C_S}{C_L} = \frac{(C_0 - V_{\text{slice1}} \cdot \theta \cdot C_L)/(\rho \cdot V_{\text{slice1}})}{C_L} \quad (5)$$

and

$$K_d(\text{slice1}) = \frac{C_S}{C_L} = \frac{(C_{\text{slice1}} - V_{\text{slice1}} \cdot \theta \cdot C_L)/(\rho \cdot V_{\text{slice1}})}{C_L}, \quad (6)$$

where C_S is $^{137}\text{Cs}^+$ concentration in the solid (mol/g), C_L is the concentration in solution (mol/l), C_0 is the amount in the interface deduced from Eq. (2) (mol), C_{slice1} is the

amount in the first slice of bentonite measured by liquid scintillation analyzer (mol), V_{slice1} is the volume of the first slice (m^3), ρ is the bulk density (g/m^3) and θ is the porosity of the compacted bentonite (m^3/m^3). Both K_d values are listed in Table 2. It is clear that there is little difference between the two K_d values; the results suggest the validity of the experimental method and calculation.

From Table 2, it is clear that the distribution coefficient is dependent on $^{137}\text{Cs}^+$ concentration. The K_d values in compacted bentonite from capillary experiments decrease with increasing cesium concentration. The strong dependence of distribution coefficient of Cs^+ sorption on solution concentration is consistent with the diffusion coefficient of Cs^+ diffusion in the compacted bentonite. The diffusion coefficient decreases with increasing solution concentration. The results are consistent with the results of Cs^+ sorption on bentonite at different solution concentrations [16]. At low concentration the sorption is mainly dominated by chemisorption and surface complexation, while at high concentration the sorption is mainly influenced by cation exchange and surface complexation. This is the reason why the distribution coefficient decreases with increasing solution concentrations. The sorption and diffusion of Eu and Tc in compacted bentonite was studied and the results indicate that K_d values measured with compacted bentonite are about one-half to one-third the value of those with batch tests [3,4,11]. The difference was attributed to the fact that cation cannot enter the small and occluded pores and thus it could not access the entire volume, or all the sorption sites, of the compacted bentonite.

Fig. 5 shows the distribution coefficients of $^{137}\text{Cs}^+$ derived from different pH values at concentrations of 3.3×10^{-5} and 3.3×10^{-3} mol/l, respectively. At concentration of 3.3×10^{-5} mol/l, the distribution coefficient increases very slowly from 90 ml/g (pH = 3) to 134 ml/g (pH = 12) with increasing pH values. At concentration of 3.3×10^{-3} mol/l, K_d value increases from 25 ml/g (pH = 3) to 49 ml/g (pH = 9) and then increases quickly to 95 ml/g at pH 12. The sorption of cesium on compacted bentonite is weakly dependent on pH values although K_d value increases slowly with increasing pH values. At high pH values the sorption of cesium on bentonite may be dominated by surface complexation and cation exchange [15], and thus the distribution coefficient is higher at high pH values than those at low pH values. As a comparison the sorption data of cesium on powdered bentonite in batch experiments are given, the K_d values of Cs sorption are 105 ml/g ($C_{\text{Cs}} = 7 \times 10^{-4}$ mol/l), 140 ml/g ($C_{\text{Cs}} = 3.2 \times 10^{-5}$ mol/l) and 240 ml/g ($C_{\text{Cs}} = 7 \times 10^{-8}$ mol/l), respectively, at pH 7.7 and in 0.1 M NaClO_4 solution [16]. The K_d values in compacted bentonite are much lower than those in powdered bentonite from batch experiments. The interlaminary space contributes significantly to cesium sorption and diffusion in compacted bentonite.

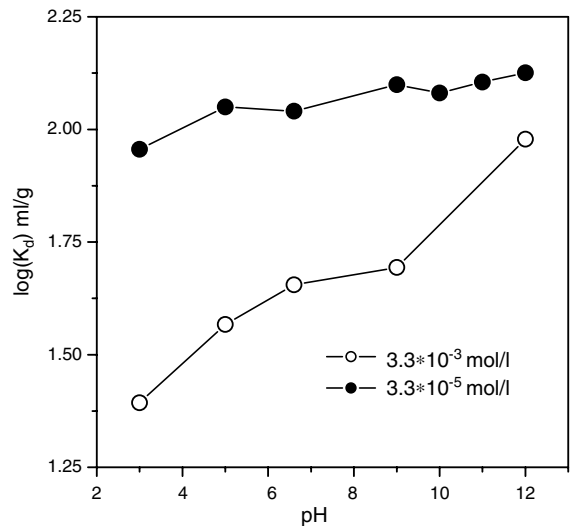


Fig. 5. K_d values derived from capillary test as a function of pH. $\rho_b = 1000 \pm 30 \text{ kg}/\text{m}^3$, $\theta = 0.62 \pm 0.02$. Solid points: $C(^{137}\text{Cs}^+) = 3.3 \times 10^{-5} \text{ mol}/\text{l}$, open points: $C(^{137}\text{Cs}^+) = 3.3 \times 10^{-3} \text{ mol}/\text{l}$. K_d values are calculated from Eqs. (2) and (5).

3.5. Comparison of effective diffusion coefficient

The effective diffusion coefficients (D_e) were calculated from Eq. (4) with the K_d values calculated from Eq. (2) given in Table 2 and are shown in Fig. 6 as a function of pH and in Fig. 7 as a function of solution concentration. The D_e values are independent of pH

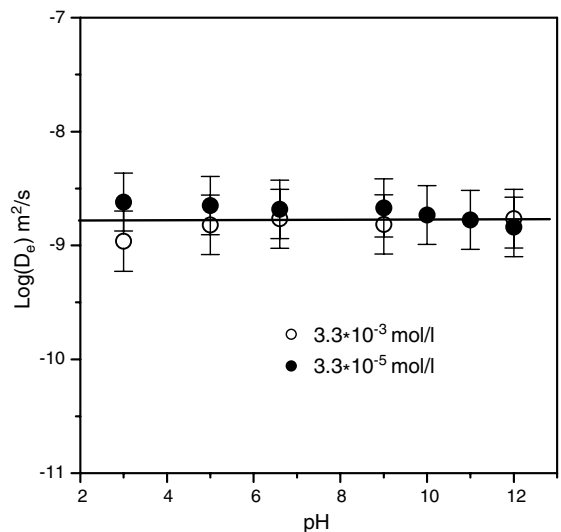


Fig. 6. D_e values derived from capillary test as a function of pH. $\rho_b = 1000 \pm 30 \text{ kg}/\text{m}^3$, $\theta = 0.62 \pm 0.02$. Solid points: $C(^{137}\text{Cs}^+) = 3.3 \times 10^{-5} \text{ mol}/\text{l}$, open points: $C(^{137}\text{Cs}^+) = 3.3 \times 10^{-3} \text{ mol}/\text{l}$.

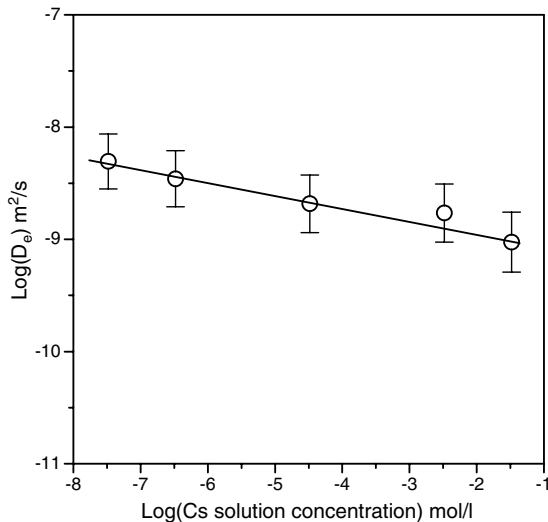


Fig. 7. D_e values derived from capillary test as a function of $^{137}\text{Cs}^+$ concentration. pH = 6.6, $\rho_b = 1000 \pm 30 \text{ kg/m}^3$, $\theta = 0.62 \pm 0.02$.

values and a little decrease with increasing solution concentration. The D_e value decreases from 5.0×10^{-9} to $9.4 \times 10^{-10} \text{ m}^2/\text{s}$ when cesium concentration increases from $3.3 \times 10^{-8} \text{ mol/l}$ to $3.3 \times 10^{-2} \text{ mol/l}$. Although apparent diffusion coefficient (D_a) increases with increasing solution concentration, the distribution coefficient (K_d) decreases quickly with increasing solution concentration, and thus the result is that D_e value of Cs decreases with increasing solution concentration. Considering the properties of D_e value of nuclide diffusion in compacted bentonite, D_e is the entity that is the most invariant to radionuclides that do not have the surface diffusion or ion exclusion effects. The decrease in the D_e values of Cs diffusion with increasing solution concentration indicates that the diffusion mechanisms of Cs in compacted bentonite at low and high solution concentrations are different. The results need further investigation. In comparison with the values of HTO in compacted bentonite [10], the D_e values of $^{137}\text{Cs}^+$ is higher than that of HTO and most nuclides, which suggests that the diffusion of $^{137}\text{Cs}^+$ in compacted bentonite is mainly dominated by surface diffusion.

4. Conclusion

The results from the capillary method show that it is a fast and easy method to study the diffusion of radionuclides in compacted bentonite. The method allows us to study the effect of pH and solution concentration of radionuclides on the diffusion of radionuclides in compacted bentonite simultaneously. Cesium moves faster in compacted bentonite comparing to most of other

radionuclides (such as Ni, Eu, U, Np, Pu, Am, Cm, Sm, Zr) [1,10,14]. A comparison of effective diffusion coefficient with those of HTO shows that surface diffusion dominates the diffusion of Cs^+ in compacted bentonite. The diffusion of Cs^+ in compacted bentonite decreases slightly with increasing pH values and also increases slightly with increasing Cs^+ solution concentration. The K_d values are dependent on the solution concentration and increase very weakly with increasing pH values. The K_d values derived from capillary tests are in most cases lower than those derived from batch experiments, and the difference between the two K_d values is a strong function of the dry density. Our results suggest that the interlaminary space of compacted bentonite contributes significantly to radionuclide diffusion and migration in compacted bentonite.

It is necessary to note that the ratio of surface between bentonite and capillary to volume of bentonite is very large and this may give significant effects on the experimental results. This effect will be studied further.

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