EFFECT OF DRY DENSITY ON TECHNETIUM DIFFUSION IN COMPACTED BENTONITE

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Abstract : Bentonite is widely favored as a buffer material of HLW (high-level waste) repository. Diffusion tests were conducted to investigate the diffusion of technetium in compacted bentonite. The tests were under oxidizing condition and the dry densities of compacted bentonite were 1.4, 1.6, and 1.8 Mg/m^3. The values of measured apparent diffusion coefficients ranged from 3.46×10^{-11} m^2/s to 9.46×10^{-11} m^2/s, and they decreased with increasing the dry density. With no sorption on the bentonite, the diffusion of technetium was dependent on the pore structure of compacted bentonite, and it was also affected by anion exclusion between the technetium in the form of TcO_4^- and the bentonite particle with negative surface charge. The results obtained will be used for the safety assessment of a repository.

Key Words : compacted bentonite, diffusion coefficient, technetium

INTRODUCTION

A repository for high-level radioactive wastes will be constructed in the bedrock at a depth of several hundred meters below ground surface. The gap between the container and the wall of borehole drilled on the floors of emplacement rooms of the repository is filled with a buffer material. The present design concepts of the repository consider use of compacted bentonite as a buffer material.[1,2]

When a compacted bentonite is used for the buffer, it is installed to minimize the hydraulic conductivity and thus to control the transport of radionuclides by diffusion process. Understanding the characteristics of radionuclide diffusion therefore is essential in the assessment of radionuclide release through the buffer of a repository.

Technetium-99(Tc-99), one of major radionuclides in high-level wastes has a half-life of 2.11×10^5 yr and is known to be redox sensitive.[3,4] Under oxidizing conditions, it exists mostly in the form of $Tc(VII)O_4^-$ and, as a result, is little sorbed and diffuses rapidly in clays with a negative surface charge.[5,6] On the other hand, under reducing environments, it forms Tc(IV) compound which is more highly sorbed or is insoluble enough to limit the maximum concentration of technetium. For this reason, the diffusion of the technetium in the reducing conditions has been reported to be slower than that of the oxidizing ones.[7,8]

In the present study, in-diffusion tests are carried out to determine diffusion coefficients and to investigate the effect of dry density on the diffusion of technetium in compacted bentonite which is under consideration as a candidate buffer material for a HLW repository in Korea.

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DETERMINATION OF DIFFUSION COEFFICIENTS

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions. The mathematical description of the diffusion process in a homogeneous and isotropic medium such as free water is based on the Fick's I and II laws of diffusion which are expressed as follows, respectively :

$$\vec{F} = -D_o \nabla C \tag{1}$$

$$\frac{\partial C}{\partial t} = -\nabla \cdot \vec{F} = D_o \nabla^2 C \tag{2}$$

where $\vec{F}$ is the diffusive flux, C the concentration, D_o the diffusion coefficient in free water, and t the time.

However, the above Fick's I and II laws of diffusion are modified for applying them to a porous medium such as compacted bentonite, because there may be several diffusion pathways and physicochemical interactions between solid and liquid phases.[9] If the transport of a matter through compacted bentonite is controlled by diffusion, the equations (1) and (2) are described as

$$\vec{F_p} = -D_a \nabla \overline{C} \tag{3}$$

$$\frac{\partial \overline{C}}{\partial t} = -\nabla \cdot \vec{F_p} = D_a \nabla^2 \overline{C} \tag{4}$$

where $\vec{F_p}$ is the diffusive flux based on the cross sectional area of compacted bentonite, $\overline{C}$ the average concentration of a diffusant over the solid and liquid phases, D_a the apparent diffusion coefficient. In equations (3) and (4), D_a, which is not a molecular diffusion coefficient in free water but denotes an apparent diffusion coefficient in compacted bentonite, usually includes molecular diffusion, pore geometry, surface diffusion and physico-chemical processes (e.g., adsorption, ion-exchange, and precipitation).

Experimentally the apparent diffusion coefficient of ions in compacted bentonite has been determined by several techniques: in-diffusion, through-diffusion, back-to-back diffusion, and reservoir-depletion method.[10] This study employs in-diffusion method, which consists of two layers of compacted bentonite and each layer is saturated with ion-spiked solution and ion-free water, respectively. The ions in the spiked compacted bentonite are allowed to diffuse across to the ion-free compacted bentonite. A schematic representation of the in-diffusion method is shown in Figure 1. If the layers of compacted bentonite are homogeneous and isotropic and the transport of ions occurs only to the x-direction, the equation (4) is expressed in the following simplified form.

$$\frac{\partial \overline{C}}{\partial t} = D_a \frac{\partial^2 \overline{C}}{\partial x^2} \tag{5}$$

The initial and boundary conditions are given to describe the experimental constraints of the in-diffusion method :

$$\overline{C}(x, 0) = \overline{C}_o, \qquad 0 < x < X_o \tag{6}$$

$$\overline{C}(x, 0) = 0, \qquad X_o < x < L \tag{7}$$

$$\frac{\partial \overline{C}(0, t)}{\partial x} = \frac{\partial \overline{C}(L, t)}{\partial x} = 0, \qquad 0 < t \tag{8}$$

Figure 1. Schematic representation of ion diffusion in the in-diffusion method.

where $\overline{C_o}$ is an initial ion concentration in the ion-spiked bentonite plug, X_o the location of interface between two bentonite plugs in the diffusion cell, and L the overall length of the diffusion cell. The solution of the equation (5) is given by Carslaw and Jaeger[11] as

$$\overline{C} / \overline{C_o} = \frac{x_o}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \exp\left(-\frac{D_a n^2 \pi^2}{L^2} t\right)$$
$$\cos\left(\frac{n\pi}{L} x\right) \sin\left(\frac{n\pi}{L} x_o\right) \quad (9)$$

subject to the initial and boundary conditions of the equations (6) to (8).

The apparent diffusion coefficient of ions in compacted bentonite are determined by fitting the experimental data with the above equation (9). The curve-fitting is made using Marquart's parameter estimation method based on an optimization theory.[12,13]

MATERIALS AND METHOD

Bentonite

The bentonite used is of the Ca-type. Its chemical composition is 56.8% SiO_2, 20.0% Al_2O_3, 6.0% Fe_2O_3, 2.6% CaO, 0.8% MgO, 0.9% K_2O, 1.3% Na_2O, 0.2% FeO, 1.3% SO_3, and 0.8% TiO_2. It has a cation exchange capacity of 57.6 meq/100 g, and the predominant exchangeable cation is Ca^{2+}. The bentonite contains montmorillonite (70%), feldspar (29%), and small amounts of quartz ($\sim 1\%$), as shown in Figure 2.[14] This bentonite was used for the diffusion tests after being air-dried and passed through No. 200 of ASTM (American Society for Testing and Materials).

Tracer and Solution

$NH_4{}^{99}TcO_4$ was used as radioactive tracer and a synthetic groundwater shown in Table 1 was used for preparing the experimental solution. The activity of the experimental solution was 9.94×10^{-1} Ci/m^3.
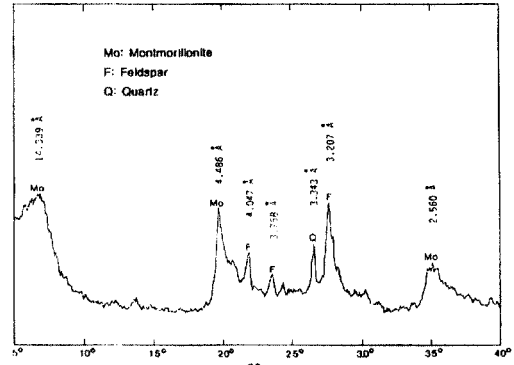

Figure 2. X-ray diffraction pattern of the Kyungju bentonite.

Table 1. Chemical composition of the synthetic groundwater used

Ion	Concentration (mg/L)
Na	57.00
SO_4	25.25
TIC	15.22
Si	7.20
Ca	7.40
K	0.70
F	7.65
Cl	16.80
NO_3	0.15
PO_4	0.50
Zn	0.01
Mn	0.01
Fe	0.01
Mg	0.70
Al	0.10
NO_2	0.10
pH (-)	8.06
Eh (mV)	405.9

In-diffusion Test

Figure 3 shows an experimental apparatus of in-diffusion test. A diffusion cell is made of two stainless steel cylinders with 30 mm of inner diameter and 30 mm of height. The dry densities of compacted bentonite are 1.4, 1.6, and 1.8 Mg/m^3.

The in-diffusion tests are carried out under oxidizing conditions according to the following procedure. After being air-dried and weighed, the bentonite is mixed with a predetermined
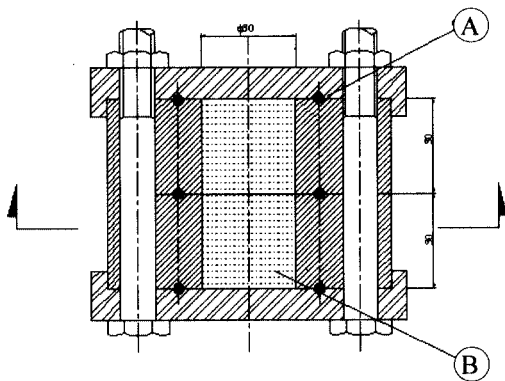
(A) O-ring, (B) Compacted bentonite

Figure 3. Experimental apparatus for the in-
diffusion test.

Figure 4. Distribution of Tc species in the
synthetic groundwater (at Eh = 405.9
mV).

amount of water or ^{99}Tc-spiked solution re-
quired to saturate the bentonite at a given dry
density. The mixture is kneaded for the uni-
form distribution of liquid phase in the
bentonite, and then is compacted in each
cylindrical cell to a given dry density using a
hydraulic press. The compacted bentonite is
left in a zip-bag for about 4 weeks for com-
plete saturation. When two compacted cylin-
ders are prepared, they are contacted and
combined firmly together with a restrain ram.
This experiment is conducted in a water bath
with a constant temperature of 25℃. After an
appropriate diffusion time, the cells are disas-
sembled and the bentonite plugs are extruded
being sliced by a predetermined thickness with
thin blade. The bentonite slices are divided into
two parts, one used to determine the water
content and the other used to analyze ^{99}Tc
activity. ^{99}Tc is extracted from the sliced
bentonite with 1×10^{-5} m^3 of 1 M HCl and
0.06 M NaBrO$_3$ for 3 days,[15] and its activity
is measured using liquid scintillation counter.
The measured values of activity are regarded
as an average value at the center of each slice.

RESULTS AND DISCUSSION

Tc Speciation and Its Interaction with Bentonite
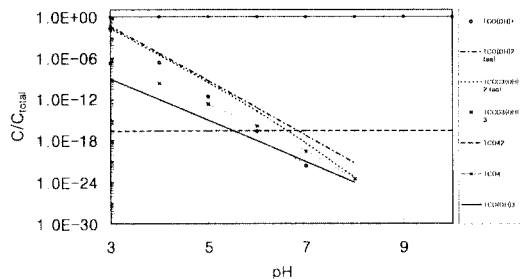
The speciation of technetium in the synthetic

groundwater was calculated using a chemical
equilibrium speciation program, PHREEQE.[16]
The results showed that the chemical state of
technetium was dependent upon the presence
of complexing ions as well as pH. The tech-
netium in the solution were present in the
following species: TcO$_4^-$, TcO(OH)$_2$(aq),
TcCO$_3$(OH)$_2$(aq), TcO(OH)$^+$, TcCO$_3$(OH)$_3^-$,
TcO(OH)$_3^-$, TcO$_4^{2-}$. Of these species, TcO$_4^-$ was
dominant all over the pH range (Refer to
Figure 4).

In order to see the sorption of technetium on
bentonite, batch tests were carried out for the
pH of 3 to 9 and the solution-to-bentonite ratio
of 5 to 15 m^3/Mg. There was very little or no
sorption of technetium on bentonite in given
experimental conditions. It is supposed to be
due to the fact that the technetium prevailed as
a anionic TcO$_4^-$, and thus it had no sorption on
the bentonite with negative surface charge. And
the sorption of technetium was not affected by
pH and solution-to-bentonite ratio.

Tc Diffusion in Compacted Bentonite

The in-diffusion test premises complete satu-
ration in the bentonite plug. To identify this
premise, the moisture contents were measured
from each sliced bentonite, which was deter-
mined gravimetrically by drying them at 110℃
for 2 days. Figure 5 is a typical example of the
distributions of moisture content (ω / ω_s) in the
bentonite plugs, and it is for the bentonite plug
with the density of 1.4 Mg/m^3. As shown in
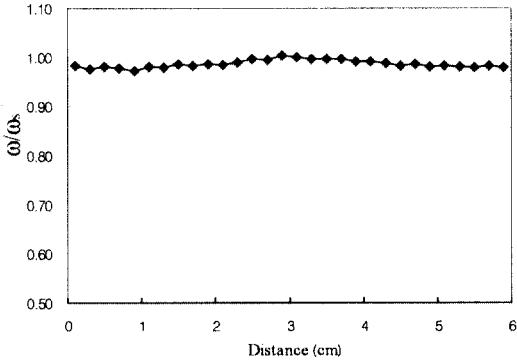the figure, the moisture content in the bentonite

Figure 5. Moisture content distribution in the bentonite plug with the dry density of 1.4 Mg/m^3 (ω_s is a moisture content at saturation).

plug is more than 97% of the moisture content at saturation state. This indicates that the bentonite plug was in nearly full saturation during the diffusion experiment.

The concentration profiles of technetium obtained from diffusion tests were plotted in the relative concentration $\overline{C}/\overline{C}_o$ versus x for their curve-fitting with the theoretical values of equation (9). The $\overline{C}_o$ which is an initial concentration in the radionuclide-spiked bentonite plug, was obtained from the following mass balance:

$$\overline{C}_o = (\sum_{i=1}^{n_t} \overline{C}_i g_i)/(\sum_{i=1}^{n_t} g_i) \qquad (10)$$

where n_t is the total number of slices obtained from the two bentonite plugs, n_o the number of slices in the radionuclide-spiked bentonite plug, $\overline{C}_i$ the concentration of the radionuclide in the ith slice, and g_i the mass of sample in the ith slice. Robin et al. presented that the $\overline{C}_o$ value obtained in this manner was very close to that measured directly on the bentonite plug saturated with radionuclide-containing solution.[17]

Figsure 6(a), (b), (c) are the concentration profiles of technetium in the compacted bentonites with the dry densities of 1.4, 1.6, 1.8 Mg/m^3, respectively. They revealed all roughly smooth profile in shape except some fluctua-
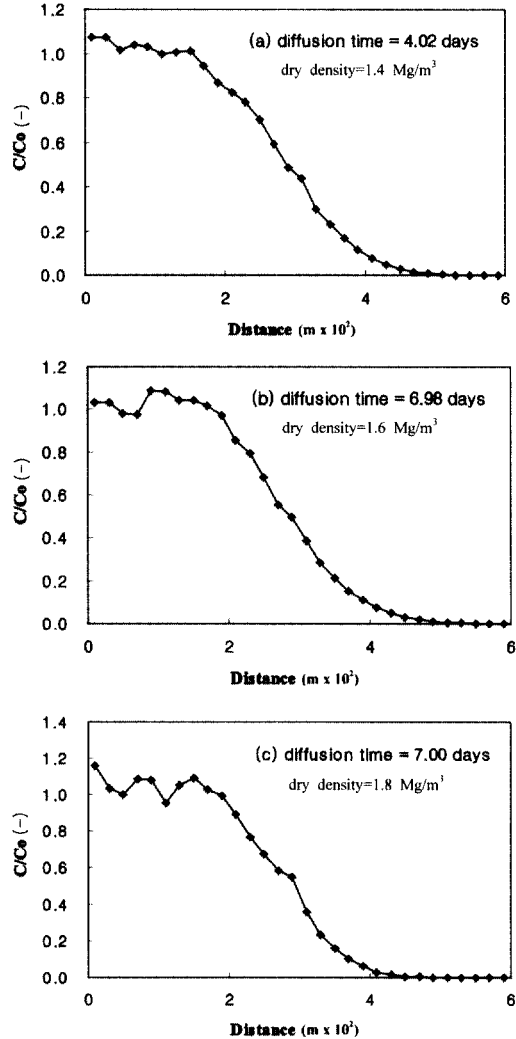

Figure 6. Concentration profiles of technetium in compacted bentonites.

tion in the spiked bentonite. In these figures, the technetium diffused more than 2 cm into the unspiked bentonite plug for only 7 days. The apparent diffusion coefficients, D_a, were estimated to be 9.46×10^{-11} m^2/s for the dry density of 1.4 Mg/m^3, 4.53×10^{-11} m^2/s for the dry density of 1.6 Mg/m^3, and 3.46×10^{-11} m^2/s for the dry density of 1.8 Mg/m^3 (Table 2).

The D_a values decreased with the increase of the dry density of compacted bentonite as shown in Figure 7. This seems to be attributed to the change of the pore structure, no sorption of pertechnetate (TcO_4^-) on bentonite taken into

Table 2. Diffusion coefficients of technetium
and tritium and formation factor of
compacted bentonite

Ion	Dry density (Mg/m^3)	$D_a \ (= D_p)$ (m^2/s)	f $(-)$
Technetium	1.4	9.46×10^{-11}	0.064
"	1.6	4.53×10^{-11}	0.031
"	1.8	3.46×10^{-11}	0.023
Tritium*	1.4	3.43×10^{-10}	0.141
"	1.6	2.22×10^{-10}	0.091
"	1.8	1.73×10^{-10}	0.071

account. That is, the negative effect of the pore structure on the technetium diffusion, with the dry density increasing, gets more and more significant and thus the D_a decreases. Table 2 indicates that the formation factors of compacted bentonites calculated by the following equation (11) applicable to the non-sorbing radionuclides,[18] may explain this phenomena.

$$D_a \ = \ D_p \ = \ D_o f \qquad (11)$$

where D_p is the diffusion coefficient in pore water of compacted bentonite, D_o the diffusion coefficient in free water (1.48×10^{-9} m^2/s for the TcO$_4^{-}$[19] and 2.44×10^{-9} m^2/s for the tritium[20]), and f the formation factor expressed as a function of tortuosity and constrictivity. As listed in Table 1, the formation factor of compacted bentonite for technetium decreased with increasing the dry density. Table 1 also shows that the smaller values of formation factor were obtained for the technetium as compared with those of the tritium at the same dry densities. These smaller values can be explained by the effect of 'anion exclusion'.[21,22] That is, the pertechnetate as a anion is repelled by electrostatic force from bentonite particle surface with negative charge[23] and thus the pathway available for the diffusion of pertechnetate comes to be more limited than tritium with neutral charge. It follows from this that the diffusion of technetium depends upon the anion exclusion as well as the change in the pore structure of compacted bentonite.
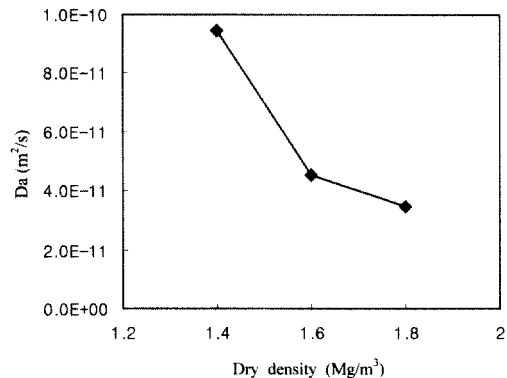

Figure 7. Apparent diffusion coefficients of technetium as a function of dry density.

CONCLUSIONS

Under the oxidizing conditions, the technetium existed as TcO$_4^{-}$ and had no sorption on the bentonite. It was concluded from the in-diffusion tests that the apparent diffusion coefficients of technetium ranged from 3.46×10^{-11} to 9.46×10^{-11} m^2/s when the dry densities of compacted bentonite were in the range of 1.4 to 1.8 Mg/m^3, and they decreased with increasing the dry density. The decrease in D_a with an increase in the dry density was affected by the pore structure of compacted bentonite and the anion exclusion of TcO$_4^{-}$ from the bentonite particle with negative surface charge.

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