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Transport number of sodium ions in water-saturated, compacted Na-montmorillonite

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ABSTRACT

Diffusion of radionuclides in bentonite buffer material has been studied by many researchers. The nuclides in a form of ion diffuse in the bentonite satisfying electro-neutrality. It is important to examine major charge carriers as a possible counter ion for understanding the diffusion behavior in the bentonite. In this study, transport numbers of Na⁺ ions, which are the major exchangeable cations in the sodium montmorillonite, which is the major mineral of bentonite, were experimentally determined as a function of dry density by a moving boundary method, using electromigration and electro-osmosis in the montmorillonite. The transport numbers were determined based on the electromigration of the Na⁺ ions, because the contribution of the electro-osmosis to the migration of the cations is considered to be negligible. The effect of pore water ionic strength in the montmorillonite on the transport number was also examined. It was found that the transport numbers did not depend on the dry density and were nearly equal to 1. Therefore, the Na⁺ ions behave as the predominant charge carrier in the montmorillonite. When salinity was increased up to 0.5 M, the transport numbers decreased down to 0.8. This suggests that the major part of the charge was carried by the Na⁺ ions but the contribution of other ions to the charge carrier increased gradually with increase of the ionic strength.

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1. Introduction

In the deep-geologic disposal of both high-level radioactive wastes and a part of transuranic (TRU) wastes, compacted bentonite is a promising material to be used as buffer material. Bentonite has high cation exchange capacity for radionuclides, and at the same time low hydraulic conductivity. This means that the hazardous nuclides are markedly retarded and do not migrate by advection but by diffusion. Therefore, this material is quite suitable for extremely long-term retardation of radionuclide migration toward surrounding host rocks. It is important to clarify the diffusion processes of radionuclides in detail as a part of the safety assessment of the geologic disposal.

Many researchers have reported diffusion coefficients of nuclides in water-saturated compacted bentonite. Migration processes of radionuclides by diffusion have been discussed (e.g. Neretnieks, 1985; Eriksen and Jansson, 1996; Oscarson, 1994). The diffusion in the buffer material occurs satisfying electro-neutrality. The water-saturated, compacted bentonite may have several kinds of ions, for instance, H⁺, OH⁻, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻, SO₄²⁻, etc. Therefore,

it is quite possible that the electro-neutrality is satisfied by the migration of these ions as counter ions. To understand the migration behavior of radionuclides in more detail, it is needed to examine the major counter ions in the compacted bentonite. However, there are quite few reports, in which the contribution of these counter ions was studied.

There are a few reports, in which the migration of ionic species in clay under an electric potential gradient is studied. Maes et al. (1999) studied the electrokinetic migration of sodium ions, strontium ions, iodine ions, and tritium which is in the form of HTO in Boom Clay. Dispersion coefficients and advection velocities for these species were reported. Using these values, they determined apparent diffusion coefficients of the several chemical species in the clay. In our previous work, Na⁺ ions were migrated under an electric potential gradient in montmorillonite (Higashihara et al., 2004). Electromigration of Na⁺ ions and electro-osmotic flow of pore water were studied. The results suggested that Na⁺ ions do not migrate in pore space but in interlayer spaces and/or possibly on outer-surfaces of the clay particle. This means that most of the Na⁺ ions are not subject to electro-osmotic flow in the montmorillonite, but to electromigration.

The purpose of the present work is to examine the contribution of Na⁺ ions as counter ions to the diffusion of radionuclides in

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water-saturated, compacted montmorillonite by proposing an experimental method to determine the transport number of the cations in the montmorillonite. Transport number is one of the basic electrochemical properties of materials, and suggests the contribution of counter ions to the migration of radionuclides. The transport number of Na^+ ions in the montmorillonite, t_{Na} is defined as a fraction of the charge carried by the Na^+ ions against the total charge carried by all kinds of ions. Some researchers discussed the contribution of protonic ions as the charge carrier in montmorillonite (Slade et al., 1987). However, in the disposal of radioactive wastes, it is important to understand properties of the water-saturated, compacted bentonite. The contribution of Na^+ ions in water-saturated montmorillonite, which is the major exchangeable cations, to the ionic conductivity is not clarified.

In this study, dry density and ionic strength dependence of the transport number of Na^+ ions is determined in water-saturated, compacted Na-montmorillonite, using a moving boundary method (Atkins, 1998). To determine the transport number of Na^+ , it is required that the contribution of the electro-osmotic flow to the migration of the ions is estimated. The contribution of the electro-osmotic flow under an electric potential gradient was examined; then, the transport numbers are obtained based on the experimental results.

2. Experimental and data analysis

To determine the transport number of Na^+ ions, two experiments were carried out. One was a migration experiment of Na^+ ions under an electric potential gradient. The migration of the Na^+ ions is traced, using $^{22}\text{Na}^+$ spiked as a thin layer. The layer of $^{22}\text{Na}^+$ represents a boundary moved under the potential gradient. The other experiment tracked the electro-osmotic flow of pore water using dissolved helium, which can be regarded as a non-sorbing tracer. The dissolved helium was migrated by the electro-osmotic flow. The contribution of electro-osmotic flow was examined using mechanical dispersion coefficients and dispersivity parameters.

2.1. Sample material and experimental setup

Kunipia-F powder, which is a product of Kunimine industries Co. Ltd., was used for montmorillonite specimens. The major mineral component of Kunipia-F is Na-montmorillonite. To determine the amount of exchangeable cations, those ions were extracted using a 0.1 M NH_4Cl solution. The amounts of the ions were determined using a plasma emission spectrometer (SHIMADZU ICPS-7500). Obtained values were 1.19 equiv./kg for Na^+ ions and 0.167 equiv./kg for Ca^{2+} ions, respectively.

The compacted montmorillonite specimens were prepared in the following procedure. The Na-montmorillonite powder, which was heated in an oven for removing adsorbed water at 378 K, was weighed and compacted in an acrylic resin cell, 20 mm in diameter and 20 mm in height. The columns were saturated with 0.1 M NaClO_4 solution. The dry densities of the clay column were 1.2, 1.4, and $1.6 \times 10^3 \text{ kg m}^{-3}$. Solutions of different ionic strengths, 0.2, and 0.5 M, in addition to 0.1 M were prepared to examine effect of ionic strength on the transport number. Three montmorillonite columns with dry density of $1.0 \times 10^3 \text{ kg m}^{-3}$ were in contact with the 0.1, 0.2, 0.5 M solutions and were let to expand. In addition, for measuring the electro-osmotic flow, a part of these columns were saturated with dissolved helium. These methods of saturation were described in our previous paper (Higashihara et al., 2004).

NaCl solution with ^{22}Na tracers purchased from the Japan Radioisotope Association, were spiked on the montmorillonite

specimens as a thin layer source with 20 mm in diameter. The ^{22}Na tracers were migrated under an electric potential gradient. The helium-saturated column and the helium-free column were contacted like a diffusion couple. The montmorillonite specimens, which consist of helium-saturated and helium-free columns were polarized. The details of the experimental setup were also described in our previous work (Higashihara et al., 2004).

Polarization was carried out for 4.0 h. The applied constant current, I , and the electric potential gradient, E , were $3.0 \times 10^{-2} \text{ A}$ and $3.9 \times 10^2 \text{ V m}^{-1}$, respectively. In the region where migration of $^{22}\text{Na}^+$ and helium occurred by electromigration and electro-osmosis, the potential gradient was kept constant during the polarization by choosing the position in the montmorillonite specimen where pH was unchanged because of constant current polarization (Higashihara et al., 2004). Temperature was kept at 298 K using a water bath. After the polarization, to determine the concentration profiles of dissolved helium and $^{22}\text{Na}^+$, each montmorillonite specimen was sectioned into 1.0 mm-thick wafers. The amount of helium in each wafer was measured using a quadrupole gas analyzer (ANELVA AQA-100 MPX). The radioactivity in the wafers was measured with a well-type NaI(Tl) scintillation counter (Aloka ARC-380).

2.2. Data analysis

The migration in the water-saturated montmorillonite under an electric potential gradient is expressed by the one dimensional advection–dispersion type equation:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - U_i^a \frac{\partial C_i}{\partial x} \quad (1)$$

where, C_i , D_i , and U_i^a are concentration, hydraulic dispersion coefficient, and velocity of species i in the compacted montmorillonite, respectively. The variable x indicates the distance in the montmorillonite columns from the origin, which is spiked plane for ^{22}Na or a contact plane between two kinds of pellets with and without helium. The variable t is the time of polarization. The initial and boundary conditions for ^{22}Na can be given as:

$$\begin{aligned} C_{\text{Na}}(x, 0) &= M\delta(x) \\ C_{\text{Na}}(\pm\infty, t) &= 0, \quad t \geq 0 \end{aligned} \quad (2)$$

$\delta(x)$ is the Dirac delta function and M is the injected amount of ^{22}Na . The montmorillonite specimens in the x -direction are sufficiently longer than the moving distance of $^{22}\text{Na}^+$ ions. So, the length of the clay is regarded to be infinite. For dissolved helium, these equivalent conditions are:

$$\begin{aligned} C_{\text{He}}(x, 0) &= C_{\text{He},0}(1 - H(x)) \\ C_{\text{He}}(+\infty, t) &= 0, \quad C_{\text{He}}(-\infty, t) = C_{\text{He},0}, \quad t \geq 0, \end{aligned} \quad (3)$$

where, $C_{\text{He},0}$ is initial concentration of helium in the helium-saturated montmorillonite column and $H(x)$ is the Heaviside function.

The solution of Eq. (1) based on the conditions (2) and (3) can be described as follows (Hemond and Fechner-Levy, 2000; Ogata, 1970).

$$C_{\text{Na}} = \frac{M}{2\sqrt{\pi D_{\text{Na}} t}} \exp \left\{ -\frac{(x - U_{\text{Na}}^a t)^2}{4D_{\text{Na}} t} \right\} \quad (4)$$

$$C_{\text{He}} = \frac{C_{\text{He},0}}{2} \operatorname{erfc} \left(\frac{x - U_{\text{He}}^a t}{2\sqrt{D_{\text{He}} t}} \right) \quad (5)$$

The obtained concentration profiles for $^{22}\text{Na}^+$ and helium were analyzed using least-square-fit curves based on Eqs. (4) and (5), respectively. The values of D_{Na} , U_{Na}^a , D_{He} , and U_{He}^a were determined by fitting with the Eqs. (4) and (5). The hydraulic dispersion coefficient is expressed as follows (Maes et al., 1999), using an apparent diffu-

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