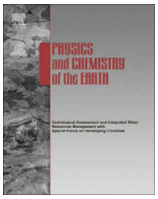
Physics and Chemistry of the Earth 33 (2008) 957–961

Contents lists available at ScienceDirect

Physics and Chemistry of the Earth

journal homepage: www.elsevier.com/locate/pce



Diffusion mechanism of sodium ions in compacted montmorillonite under different NaCl concentration

Tamotsu Kozaki [a,*], Jinhong Liu [a,b], Seichi Sato [a]

[a] *Division of Energy and Environmental Systems, Graduate School of Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo 060-8628, Japan*
[b] *Chinergy Company Ltd., B-916, Chuangxin Building, Tsinghua Science Park, Haidian District, Beijing 100084, China*

ARTICLE INFO

Article history:
Available online 7 June 2008

Keywords:
Bentonite
Montmorillonite
Self-diffusion
Sodium-22
Geological disposal
Radioactive waste

ABSTRACT

Compacted bentonite, the major mineral being montmorillonite, is a candidate buffer material for geological disposal of high-level radioactive waste. The diffusion behavior of radionuclides in the compacted montmorillonite is an important issue to be clarified for the safety assessment of geological disposal. In this study, one-dimensional, non-steady diffusion experiments using ^{22}Na at different diffusion temperatures and the measurement of the basal spacings by XRD were conducted for Na-montmorillonite saturated with NaCl solutions of different concentrations. Some basal spacings of the montmorillonite were found to decrease from 1.88 to 1.56 nm as the NaCl concentration increased from 0 to 0.1 M. The apparent self-diffusion coefficients at 298 K obtained in this study slightly increased as the NaCl concentration increased from 0 to 0.5 M, while the activation energies, calculated from the temperature dependences of the diffusion coefficients, were found to be 14, 22, and 17 kJ mol^{-1} at NaCl concentrations of 0, 0.1, and 0.5 M, respectively. These NaCl concentration dependences of the diffusion coefficients and their activation energies can be explained by assuming three independent diffusion processes (diffusion in pore water, on external surface of montmorillonite, and in interlayer of montmorillonite).

1. Introduction

Compacted bentonite is the most promising buffer material for geological disposal of high-level radioactive waste (Pusch and Yong, 2006). An important function of the compacted bentonite is to retard the transport of radionuclides from waste forms to the surrounding host rock after degradation of overpack. Due to the very low hydraulic conductivity of the bentonite, the radionuclide transport in the disposal system is considered to be mainly governed by diffusion. Therefore, it is essential to clarify the diffusion behavior of radionuclides in compacted bentonite under repository conditions – conditions in which relatively higher temperatures and groundwater with high ionic strength could be expected (JNC, 2000). However, the diffusion of radionuclides in compacted bentonite is regarded to be very complicated since it could be influenced by many parameters, such as the microstructures of the bentonite, the degree of compaction, the accessory minerals in the bentonite, pore water chemistry, and the types of exchangeable cations present.

Sodium, being a typical monovalent cation, is a suitable ion for modeling transport. It also plays an important role in the diffusion of radionuclides as an exchangeable cation of Na-bentonite. Many experimental results are available for Na$^+$ diffusion in compacted bentonite (Glaus et al., 2007; Kozaki et al., 1998, 2005; Liu et al., 2003; Molera and Eriksen, 2002; Muurinen et al., 1990; Van Loon et al., 2005a,b). In addition, several diffusion models (Bourg et al., 2006, 2007; Lehikoinen et al., 1998; Ochs et al., 2001) have been studied and computer simulations (Chang et al., 1995; Prayongphan et al., 2006) have been performed to explain the diffusion behavior of cations.

The activation energy for diffusion, which can be calculated from the temperature dependence of the diffusion coefficients, is an important parameter elucidating the diffusion process. However, to the best knowledge of present authors, there are no reports available on the study of the ionic strength dependence of the activation energy for Na$^+$ diffusion in compacted bentonite. In this study, therefore, the apparent self-diffusion coefficients of ^{22}Na$^+$ ions were determined under different temperatures and NaCl concentrations. This report examines the NaCl concentration dependence of activation energy for ^{22}Na$^+$ diffusion together with the microstructure of the water-saturated, compacted bentonite observed by the X-ray diffraction (XRD) method.

2. Experimental

The bentonite used in this study was homoionized Na-montmorillonite that was prepared from Kunipia-F (a product of Kunimine Industries Co. Ltd.) by three successive immersion of the bentonite in a fresh solution of 1 M NaCl. Excess NaCl salt was removed by

---

* Corresponding author. Tel.: +81 11 706 6687; fax: +81 11 706 6688.
E-mail address: kozaki@eng.hokudai.ac.jp (T. Kozaki).

1474-7065/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.pce.2008.05.007

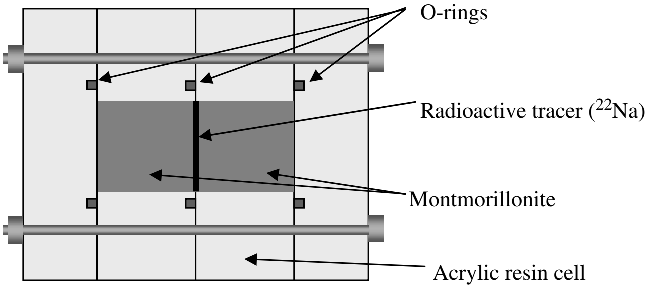


Fig. 1. Schematic of diffusion cell.

rinsing the bentonite with distilled water through a dialysis tube (Viskase Sales, UC36-32-100) until no Cl^- ions were detected with an $AgNO_3$ solution. The bentonite was dried in an oven at 378 K, mortared with a pestle, and then sieved to obtain a powder with aggregate sizes between 75 and 150 μm. The montmorillonite content and the cation exchange capacity (CEC) of the Na-montmorillonite as received were more than 98% (Ito et al., 1993) and 1.13 eq/kg-clay (Kozai et al., 1993), respectively.

The powdered Na-montmorillonite was compacted into 20 mm-diameter acrylic resin cells to obtain a dry density of 1.0 kg dm^{-3}. The cells were then saturated with NaCl solutions having NaCl concentrations from 0.01 to 0.5 M. The cell lengths were 20 mm for the diffusion experiments and 10 mm for the XRD measurements. The water content of the montmorillonite was 0.4 (gram of H_2O/gram of dry montmorillonite).

The basal spacing of the compacted bentonite in the solution-saturated state was determined from XRD profiles measured from 3 to 8° of 2θ using an X-ray diffraction apparatus (Rigaku RU-300) equipped with a copper cathode. Flat diffraction planes were obtained by sectioning the samples soon after they were removed from a water-saturation cell.

The apparent self-diffusion coefficients of $^{22}Na^+$ in the montmorillonite were determined by one-dimensional, non-steady diffusion experiments (so-called *back-to-back* diffusion method). In these diffusion experiments, a small amount of ^{22}NaCl radiotracer was applied to one end of a montmorillonite sample cell. Diffusion of the tracer was allowed to proceed by placing two montmorillonite specimens in contact as illustrated in Fig. 1. Five runs having temperatures of 288–323 K were made, but the temperature of each run was held constant. After a prescribed period of time for diffusion, each cell was disassembled and the montmorillonite specimens were sectioned into 0.5-mm-thick slices as the specimen was extruded progressively from the cell. The relative radioactivity of ^{22}Na was measured for each slice with a well-type NaI scintillation counter.

The apparent self-diffusion coefficients of $^{22}Na^+$ ions were obtained from the concentration profile measurements of the radiotracer in the montmorillonite samples. The activation energies (E_a) were determined from the temperature dependences of the apparent diffusion coefficients.

The detailed procedures of montmorillonite homoionization, compaction, water-saturation of the montmorillonite sample, XRD measurement, and the diffusion experiment are described elsewhere (Kozaki et al., 1998).

3. Results and discussion

3.1. Basal spacings of montmorillonite

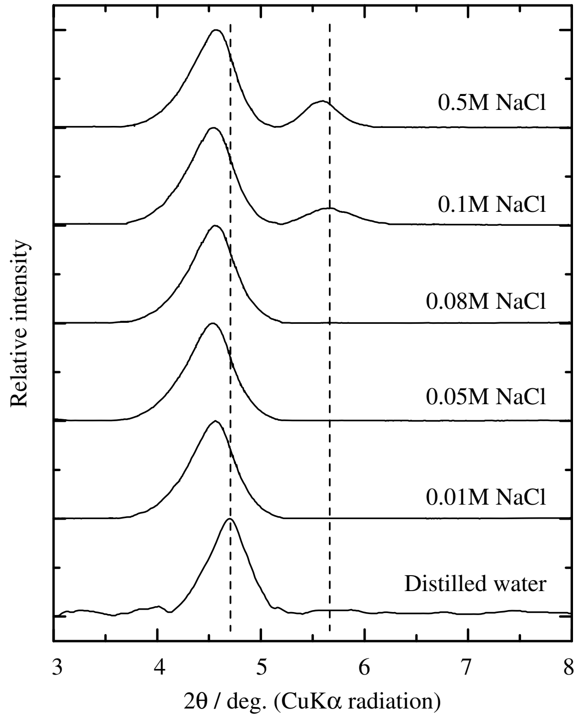


Fig. 2. XRD profiles of the compacted Na-montmorillonite with a dry density of 1.0 kg dm^{-3} saturated with NaCl solutions of different concentrations. Dotted lines correspond to a basal spacing of 1.88 nm (left line) and of 1.56 nm (right line).

Fig. 2 shows XRD profiles of the compacted Na-montmorillonite saturated with NaCl solutions of different concentrations. At the 1.0 kg dm^{-3} dry density studied here, 1.88 nm basal spacings were observed in all specimens exposed for all NaCl concentrations, while weak 1.56 nm basal spacing peaks were found in the specimens having NaCl concentrations of 0.1 and 0.5 M. In a previous study for compacted Na-montmorillonite saturated with distilled water at different dry densities (Kozaki et al., 1998), basal spacings of 1.88 nm at dry densities from 1.0 to 1.5 kg dm^{-3} and of 1.56 nm at dry densities from 1.4 to 1.8 kg dm^{-3} were observed, whereas neither of the diffraction peaks were obtained at dry densities below 1.0 kg dm^{-3}. The basal spacings of 1.88 and 1.56 nm correspond to a three-water-layer hydrate state and a two-water-layer hydrate state, respectively, of the interlayer (interlamellar) spaces of montmorillonite (Watanabe and Sato, 1988). It should be noted

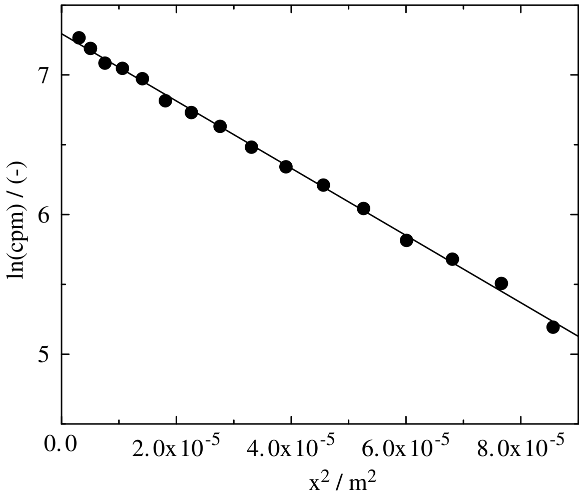


Fig. 3. Concentration profile of $^{22}Na^+$ in compacted Na-montmorillonite (dry density: 1.0 kg dm^{-3}, NaCl concentration: 0.2 M, diffusion temperature: 298 K, diffusion period: 23.6 h, Da: 1.2×10^{-10} m^2 s^{-1}).