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Effects of dry density and exchangeable cations on the diffusion process of sodium ions in compacted montmorillonite

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Abstract

As a part of the safety assessment of the geological disposal of high-level radioactive waste, the effects of dry density and exchangeable cations on the diffusion process of Na^+ ions in compacted bentonite were studied from the viewpoint of the activation energy for diffusion. The apparent self-diffusion coefficients of Na^+ ions in compacted Na-montmorillonite and in a Na- and Ca-montmorillonite mixture were determined by one-dimensional, non-steady diffusion experiments at different temperatures and dry densities. A unique change in activation energy as a function of dry density was found for the Na^+ ions in compacted Na-montmorillonite. The activation energy suddenly decreased from 18.1 to 14.1 kJ mol^{-1} as the dry density increased from 0.9 to 1.0 Mg m^{-3}, whereas it increased to 24.7 kJ mol^{-1} as the dry density increased to 1.8 Mg m^{-3}. Examination of the effect of exchangeable cations on the activation energies determined that the activation energies were almost constant, approximately 25 kJ mol^{-1}, for the montmorillonite specimens at a dry density of 1.8 Mg m^{-3}. However, three different activation energy values were obtained at a dry density of 1.0 Mg m^{-3}. These findings cannot be explained by the conventional diffusion model (the pore water diffusion model), which suggests that the predominant diffusion process alternates among pore water diffusion, interlayer diffusion, and external surface diffusion.

Keywords: Activation energy; Diffusion; Sodium; Sodium montmorillonite; High-level radioactive waste; Geological disposal; Bentonite; Calcium montmorillonite

1. Introduction

Diffusion behavior of radionuclides in compacted bentonite is of great interest in the safety assessment of the geological disposal of high-level radioactive waste, since compacted bentonite is a candidate buffer material that can retard the transport of radionuclides from the waste form to surrounding rock in a repository (JNC, 2000; SKB, 1983; NAGRA, 1994).

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Many reports are available regarding the diffusivity of radionuclides in compacted bentonite. From the results of the experiments using radiotracers, diffusion behavior of radionuclides is regarded to be a complicated processes that could be affected by many parameters, such as the microstructures of bentonite, the degree of compaction, the accessory minerals in bentonite, pore water chemistry, and the types of exchangeable cations present. In the diffusion model, pore water diffusion (the diffusion of radionuclides in the aqueous phase in pores of the compacted bentonite) has been assumed to govern the total diffusivity of radionuclides in compacted bentonite (Sato et al., 1992; Oscarson, 1994). However, some researchers have included the effects of surface diffusion (the diffusion of radionuclides on clay surfaces) because there are discrepancies in the diffusion coefficients between experimental and predicted values when using the pore water diffusion model (Muurinen et al., 1989; Berry and Bond, 1992). The controversy about the model has continued because the diffusion behavior of radionuclides in compacted bentonite has not been fully understood.

Electrical conductivity measurement is one of approaches to study the diffusion behavior. However, it was pointed out that the charge carrier for the conduction in compacted Na-bentonite is protonic rather than sodium ions (Nakazawa et al., 1999). This means that this method cannot evaluate the diffusion behavior of radionuclides without the information of the transport numbers of radionuclides in compacted bentonite. The structure and micro dynamics of adsorbed water, which is closely related to the diffusion behavior of radionuclides, were discussed on the basis of the experimental results obtained by X-ray diffraction, NMR, IR, and quasi elastic neutron scattering methods (Poinsignon, 1997). In addition, microscopic motions of specific ions in compacted bentonite were simulated by molecular dynamics (MD) method, whereas the relation between the microscopic and the macroscopic motions of ions has been under development (Ichikawa et al., 1999). Therefore, it is still necessary to carry out the diffusion experiments using radiotracers, which can provide the information of the macroscopic motions.

For the clarification of the diffusion process, the activation energy for diffusion of radionuclides in compacted bentonite is an important parameter, which can be obtained in the diffusion experiments using radiotracers. Activation energies at specific dry densities of clay have been reported; 21 kJ mol^{-1} for tritium and 10 kJ mol^{-1} for chloride ions (Relyea et al., 1986), between 10 and 22 kJ mol^{-1} for cesium ions (Tsukamoto and Ohe, 1989), 17.5 kJ mol^{-1} for chloride ions (Robin et al., 1987), and 17.8 kJ mol^{-1} for iodine ions (Oscarson et al., 1992). In addition, the dry density dependencies of the activation energy for apparent diffusion coefficients have been reported for Na^+ ions (Kozaki et al., 1998a), Cs^+ ions (Kozaki et al., 1996), Sr^{2+} ions (Kozaki et al., 1997), Cl^- ions (Kozaki et al., 1998b, 2001a), and Ca^{2+} ions (Kozaki et al., 2001b) in Na-montmorillonite (the major clay mineral of bentonite). On the other hand, the effect of exchangeable cations on the diffusion behavior of cesium ions in a Na- and Ca-montmorillonite mixture has been studied from the viewpoint of activation energy (Kozaki et al., 1999a). These studies suggested that the predominant diffusion process changes with the increase in dry density of clay and the type of exchangeable cations present.

In this study, the diffusion behavior of sodium ions was examined. This behavior is closely related to the diffusion behaviors of the other radionuclides since Na^+ ions are major exchangeable cations of Na-type montmorillonite. The activation energy for the apparent self-diffusion of sodium ions was determined in loosely compacted Na-montmorillonite and in compacted Na- and Ca-montmorillonite mixtures with different equivalent ionic fractions of calcium ions. The effects of the dry density including the lower dry density region (loosely compacted montmorillonite) and of Ca^{2+} ions on activation energy for the diffusion of sodium ions in compacted montmorillonite were studied.

2. Experimental

The montmorillonite used in this study is Kunipia-F, a product of the Kunimine Industries Co. Ltd. Homoionized Na-montmorillonite was as described in the previous papers (Kozaki et al., 1997, 1998a); ten grams of Kunipia-F was added to 1 dm^3 of 1 M NaCl solution and agitated for 24 h. The montmorillonite suspension was allowed to settle for another 24 h. The supernatant was then exchanged with fresh