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Applied Clay Science 29 (2005) 267–281

Applied CLAY Science

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Effects of the orientation of smectite particles and ionic strength on diffusion and activation enthalpies of I^- and Cs^+ ions in compacted smectite

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Received 5 August 2004; received in revised form 24 January 2005; accepted 2 February 2005
Available online 7 April 2005

Abstract

The apparent diffusion coefficients (D_a) for I^- and Cs^+ ions in compacted Na-smectite which is a major constituent clay mineral of bentonite were studied as a function of smectite's dry density (0.9–1.4 Mg/m^3), ionic strength ([NaCl]=0.01, 0.51 M), temperature (22–60 °C) and diffusion direction to the orientated direction of smectite particles. The Na-smectite was prepared by ion-exchanging with Na^+ ions a Na-bentonite, Kunipia-F®, of which smectite content is over 99 wt.%. The D_a-values for both ions showed a tendency to be higher in the parallel direction than in the perpendicular direction to the orientated direction of smectite particles at a low-ionic strength of [NaCl]=0.01 M. The D_a-values for I^- ions showed different trends depending on diffusion direction and dry density at a high-ionic strength of [NaCl]=0.51 M. Namely, although the D_a-values for I^- ions showed a tendency to be higher in the parallel direction than in the perpendicular direction to the orientated direction of smectite particles at a high-dry density of 1.4 Mg/m^3, these showed a reciprocal tendency at dry densities of 0.9–1.0 Mg/m^3. The D_a-values for Cs^+ ions uniformly increased with an increase of ionic strength in both diffusion directions. Considering electrostatic effect from smectite surface and the change in tortuosity on dry density, ionic strength and diffusion direction to the orientated direction of smectite particles, I^- ions are considered to mainly diffuse in interstitial pores. While, Cs^+ ions can diffuse in both interlayer and interstitial pores, and the D_a-values are considered to have elevated by competing with Na^+ ions. The activation enthalpies (ΔE_a) for I^- ions, slightly higher (ΔE_a=19.8–20.0 kJ/mol) than that of the diffusion coefficient in free water (D^o) for I^- ions (ΔE_a=17.36 kJ/mol) at a low-ionic strength of [NaCl]=0.01 M, decreased with an increase of ionic strength, became of similar level to that of the D^o at a high-ionic strength of [NaCl]=0.51 M, increased with an increase of dry density. On the contrary, the ΔE_a-values for Cs^+ ions, clearly higher (ΔE_a=25.6–28.4 kJ/mol) than that of the D^o for Cs^+ ions (ΔE_a=16.47 kJ/mol) even in low-dry density over the ionic strength, increased with an increase of dry density. The ΔE_a-values for Cs^+ ions are considered to be due to the decrease in the activity of porewater in addition to the effect of ion exchange enthalpy between Cs^+ and Na^+ ions in smectite.

Keywords: Geological disposal; Bentonite; Diffusion; Cesium; Iodine; Activation enthalpy

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doi:10.1016/j.clay.2005.02.003

1. Introduction

Spent fuel is produced from a nuclear power plant and is recovered useful Pu and U in reprocessing facilities. The remaining liquid waste, which includes fission products, actinide elements and activated products of the corrosion products, and has a quite high radioactivity, is called a high-level radioactive waste (HLW). The liquid waste is solidified in a stable glass matrix (vitrification) in stainless steel containers (canisters). A variety of research and development have been promoted so far assuming that these vitrified wastes are stored for cooling and radioactive decay for 30–50 years in surface facilities and will be disposed of in a deep underground deeper than 300 m in depth (geological disposal). Fig. 1 shows a design example of the multi-barrier system in HLW geological disposal (e.g., JNC, 2000a). The multi-barrier system consists of vitrified waste form (canister), overpack (metal container to encapsulate the canister), the bentonite buffer and the host rock. The use of a compacted Na-bentonite is considered as the bentonite buffer. After vitrified wastes have been disposed of in a deep underground, radionuclides immobilized in the glass matrix will begin to leach by contacting groundwater, and subsequently will migrate in the bentonite buffer surrounding the waste glass by diffusion because of its low hydraulic conductivity.

In the safety assessment of the geological disposal for HLW in Japan, a role as a barrier function of the bentonite buffer composing the multi-barrier system is quite important, and a lot of related studies have been therefore reported up to date (e.g., Sato et al., 1992). Particularly, since the diffusion properties of radionuclides leached from vitrified wastes in compacted bentonite directly affect the release rate of radionuclides from the compacted bentonite to the geosphere, it is regarded as one of the important characteristics in the safety assessment.

It is well known from conventional studies that the retardation of radionuclides in the diffusion process in compacted bentonite is affected by various physical and chemical properties such as porosity, bentonite's dry density (Sato et al., 1992, 1993, 1995; Sato, 1998), the sorption properties of radionuclides, the kind of exchangeable cations in the interlayer of smectite (Kozaki et al., 1999), porewater chemistry (Muurinen et al., 1985), microstructure, additives to bentonite (e.g., silica sand) (Sato, 2001), initial bentonite grain size (Nakajima et al., 1998; Sato,

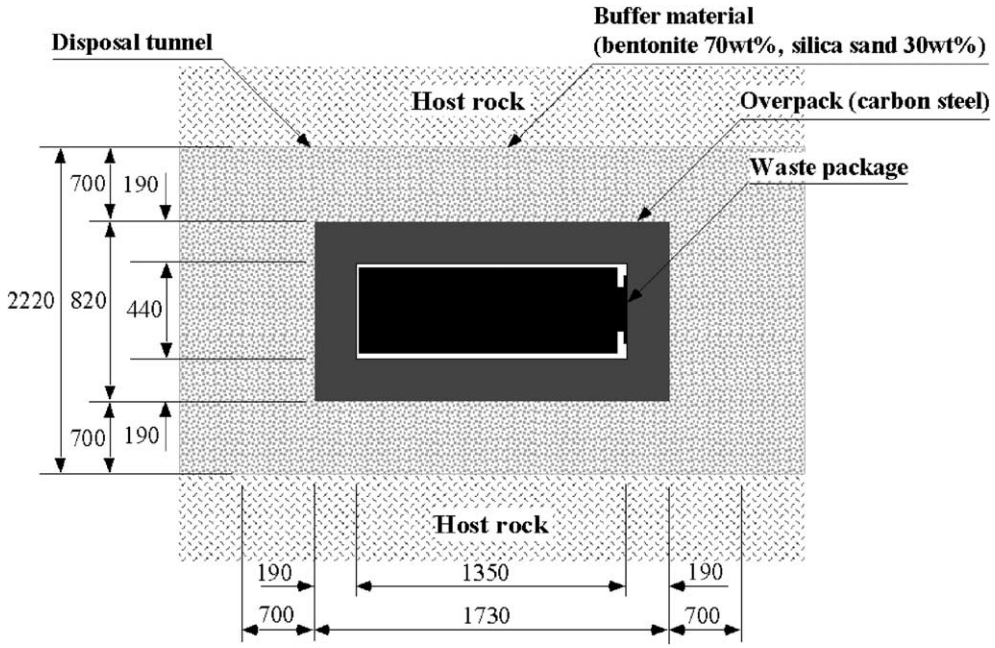

Fig. 1. Design example of multi-barrier system for HLW geological disposal (e.g., JNC, 2000a).