Interrelation between diffusion and sorption in the transport of cations through highly compacted montmorillonite.

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Bentonites are planned to be used as the backfill material to embed canisters filled with high-level, long-lived intermediate-level radioactive wastes and spent fuel in the tunnels of a deep geological repository for radioactive waste. Besides various mechanical functions, the role of the bentonite buffer is to retard on a long-term the possible release of radionuclides into the far-field of the repository after canister failure. The clay fraction of bentonites is composed essentially of montmorillonite, a smectite-type clay mineral, which is composed of layers of octahedrally coordinated aluminium sandwiched by two layers of tetrahedrally coordinated silicium atoms in a 2:1 arrangement (often referred to as TOT sheets). An intrinsic property of these clays is their ability to swell in the presence of water, which leads to compacted bentonites having extremely low hydraulic conductivities. Consequently diffusion is assumed to be the dominant migration process of radionuclides across compacted bentonites. Despite the fact that diffusion data for many radionuclides are available in the literature, knowledge of the diffusion process of charged species through compacted clays is still rather poor on the basis of process understanding.

The diffusion of charged species in compacted bentonites compared to diffusion in free water is influenced by geometrical factors caused by the complex microstructure of these clays, which is characterised by a dense house-of-cards arrangement of clay platelets. These platelets are composed of stacks of TOT sheets. Owing to isomorphic substitution of aluminium and silicium atoms by cations with lower charges, these minerals contain a substantial excess of fixed negative charges at the surface which is compensated by aqueous counter cations. Different physico-chemical states of water can be distinguished in compacted smectitic clays. Water may be present as "free water" in the pore space between the clay platelets and is assumed to have similar properties to bulk water. In contrast, water present between the TOT sheets, the so-called interlayer water, is influenced by the large amount of charge compensating cations. For this reason, and because of the small pore size of the interlayer pores, the physico-chemical properties of interlayer water may differ distinctly from bulk water.

The overall aim of the work presented here is to understand the driving forces behind the diffusion of cations in compacted montmorillonite. For this purpose the diffusion of ^{22}Na and ^{85}Sr was measured in highly compacted montmorillonite by the classical through-diffusion technique combined with tracer profile analysis. The effect of clay thickness and external salt concentrations was investigated. High degrees of compaction were chosen so as to increase the ratio between interlayer water and free pore water in montmorillonite. As a main result of these investigations, conditional diffusion coefficients (^{c}D) calculated on the basis of the tracer concentration gradient in the aqueous phase in contact with the clay, and the sorption distribution ratios in these experiments, were found to decrease with increasing external salt concentration. In a logarithmic representation of these data, a

slope of -1 was obtained for the monovalent [22]Na, whereas the slope was -2 for the divalent [85]Sr (see Fig. 1).

Such an observation is somewhat unexpected. Diffusive transport is described by the mass flux of the substance under consideration, i.e. the amount of substance transported per unit of time and cross-sectional area. For the diffusion of sorbing species in porous media two parameters are commonly used to model the mass flux, an effective diffusion coefficient and the sorption distribution ratio (R_d). According to Fick's first and second laws the maximum possible mass flux is a function of the effective diffusion coefficient and the concentration gradient in the aqueous phase of the species under consideration. The sorption distribution ratio only determines the time needed to reach the maximum possible flux. On such a basis it is not possible to understand why the mass flux at steady state should be a function of the external salt concentration.

In the present contribution a possible explanation for these observations is proposed. It is postulated that the diffusion of the tracer cation through the interlayer is the dominant pathway in compacted swelling clays under the experimental conditions used. Further, the tracer concentration gradient in the interlayer water of the clay is the driving force determining the mass flux. Effective diffusion coefficients, based on such an interlayer tracer concentration gradient were found to be independent of the composition of the external aqueous phase. The latter gradient is assumed to be a function of the external salt concentration, according to the calculated distribution of the tracer cation between free pore water and the interlayer water via cation exchange. As a consequence of the proposed model, the retention of cationic radionuclides by cation-exchange does not only impact on the retention time in diffusion, but also the maximum possible mass flux. Future experiments aim at determining the range of applicability (e.g. range of degree of compaction, type of cations) of such an interlayer-diffusion model.
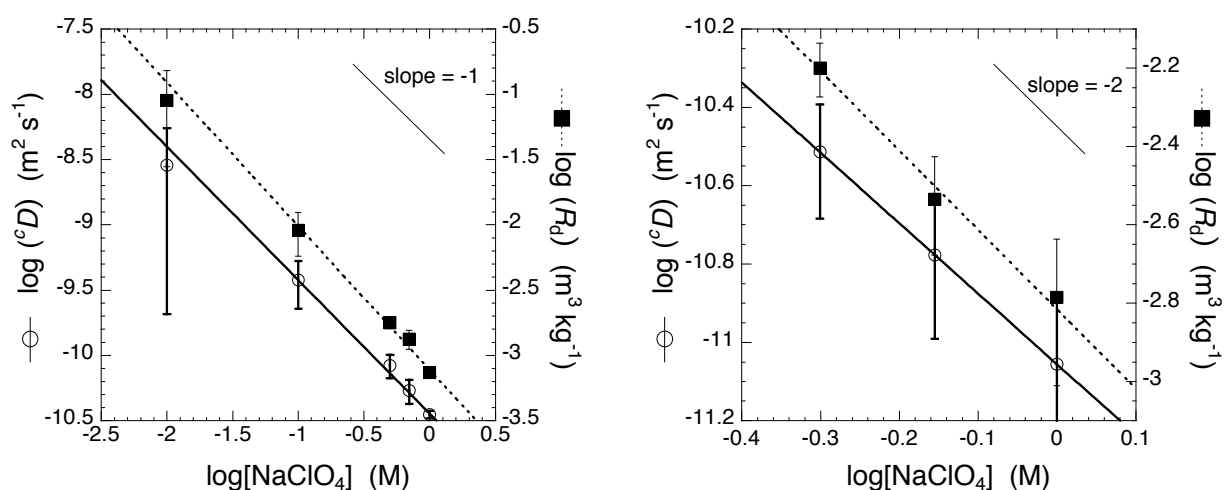

Figure 1. Logarithmic representation of the dependence of ^cD and R_d for [22]Na (left) and [85]Sr (right) in highly-compacted montmorillonite on the salt concentration in the water phase being in contact with the clay.