

Relevance of diffuse layer, Stern-layer and interlayer transport in diffusion experiments with various clays and ions

PHILIPP KREJCI¹, THOMAS GIMMI^{1,2}, LUC VAN LOON¹
AND MARTIN A GLAUS¹

¹Paul Scherrer Institut

²University of Bern

Presenting Author: thomas.gimmi@geo.unibe.ch

Clays and clay rocks are important parts in the multi-barrier system of repositories for radioactive waste. Understanding the transport behaviour of ions through clays is crucial to assess the long-term safety of clay barrier systems. Many experimental studies revealed that diffusion of cations and anions in clays cannot be explained by pore diffusion alone, as diffusion coefficients derived from experiments were higher for cations and lower for anions than expected for pure pore diffusion. This can be attributed to the interactions of cations and anions with the negatively charged clay surfaces.

Several transport codes were further developed to include transport in the diffuse layer near charged surfaces in addition to pore diffusion in 'free' porewater. This allowed for a better description of many experimental data. However, cations with the same charge (e.g., Na⁺ and Cs⁺) should show the same enrichment in the diffuse layer and thus similar diffusion coefficients according to such models, whereas experimental data show partly large differences. It is thus likely that the overall diffusion of cations is not only affected by transport in the diffuse layer, but also – to various degrees – by transport of cations sorbed on other sites (e.g., Stern layer, interlayers).

Here we explore the capabilities of a transport model that can include diffusion in 'free' porewater, diffuse layer, Stern layer and interlayers. The code Flotran was extended to account for these processes by considering modified diffusion coefficients for each ion and coupling through Nernst-Planck. The extended model was applied to diffusion of Cs⁺ in Opalinus Clay at various Cs background concentrations, and of HTO, Cl⁻, Na⁺, Sr²⁺, and Cs⁺ in bentonite at three different bulk densities and in Opalinus Clay with different ionic strengths of the pore solution.

Based on pore structure models and parameters taken from the literature where available, the experimental data could generally be well predicted. Moreover, the contributions of different pore compartments to the overall diffusive transport could be quantified. Significant differences in the contributions of diffuse layer, Stern layer, interlayer and 'free' porewater to diffusion were evidenced for the different clay materials and the different ions.