The ionic strength – EDL effect on diffusion in clay. Modeling an in situ experiment at Mont Terri.

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In the DR-A experiment (Mont Terri, CH), synthetic porewater (NaCl-dominated, I=0.36) was circulated through a borehole for 189 days, leading to the out-diffusion of several tracers into the Opalinus Clay. The solution was then replaced with a higher-salinity solution (0.50 M NaCl + 0.56 M KCl) and circulated for another 540 days, leading to the diffusion of Cs^+, Ca^{2+}, Mg^{2+} and Sr^{2+} back into the borehole and to an increase in the out-diffusion of I^-, Br^- and ^3H (HTO). These results were interpreted using the CrunchClay code, which includes a mean electrostatic potential model for the Electric Double Layer. Species-specific diffusion (Nernst-Planck) occurs through both bulk and EDL porosities. A 1D radial model considered a single pore diffusion coefficient ($D_p=10^{-9}$ m^2/s) for cations and HTO in the bulk porosity, and a smaller D_p (3×10^{-10} m^2/s) for anions. D_p values in the EDL were smaller (10^{-11} m^2/s), except for K^+ and Cs^+ (2×10^{-10} and 5×10^{-10} m^2/s). Well-established multisite cation exchange was used to calculate sorption of cations on the clay.

The model reproduced the experimental results well. The increase in ionic strength caused a decrease in the EDL porosity and a consequent increase in the out-diffusion of I^-, Br^- and HTO. High K^+ caused the displacement of Cs^+, Ca^{2+}, Mg^{2+} and Sr^{2+} from the exchange complex. The calculated tracer distribution profiles in the rock were consistent with measurements. Differences in D_p between bulk and EDL porosities may be caused by the different geometries of the diffusion pathways near the clay surfaces (EDL) and those in the centers of the pores (bulk). Pore throats where EDLs from opposite walls overlap may be the reason for the smaller D_p values for anions in the bulk porosity.

The model has shown the capability to consider changes in conditions affecting important radionuclide contaminants (e.g. $^{137}Cs^+$, $^{90}Sr^{2+}$, $^{129}I^-$). Coupled multicomponent diffusion together with the electrostatic properties of the charged surfaces are essential in the development of predictive models for ion transport in clays.