Modelling diffusion of sorbing cations in Opalinus Clay

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Significance

Natural and engineered clay barriers play an important role in retardation of radionuclides or other contaminants. Transport of sorbing cations (e.g., Na and Sr) through these clay barriers cannot be described consistently with classical Fickian diffusion theory as implemented in most available transport codes.

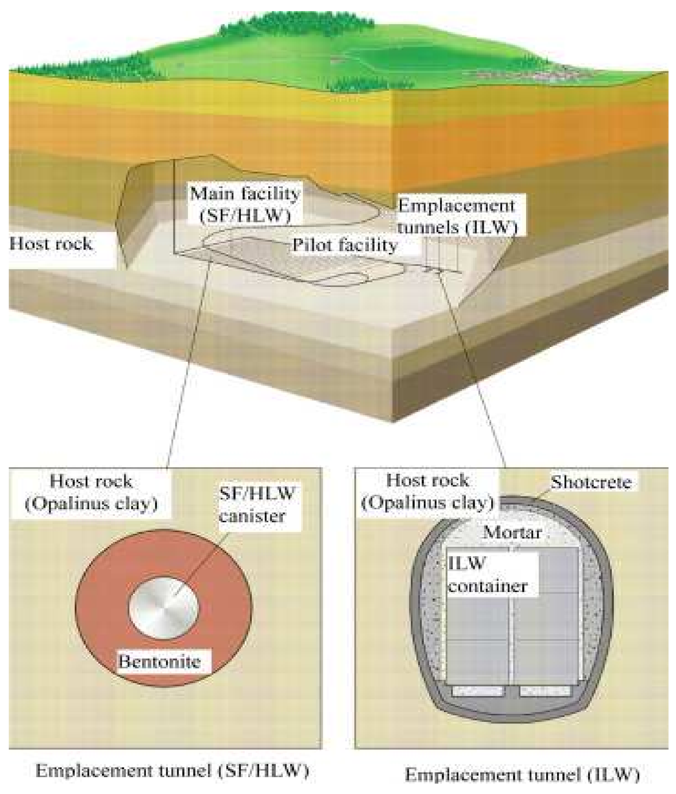

Figure 1: Swiss radioactive waste repository concept (from Delage, et al., 2010)

Sorption sites and transport mechanisms

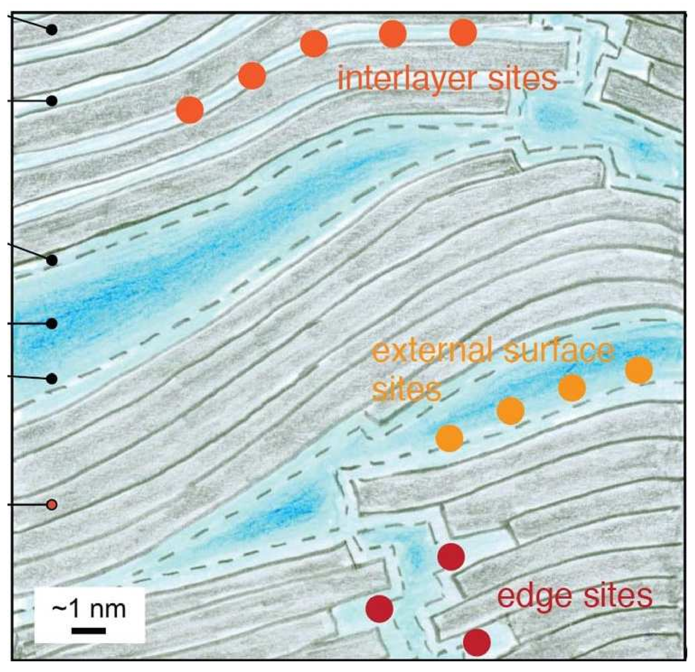

Figure 2: Illustration of different pore environments and sorption sites (edge, external and internal planar) in clay

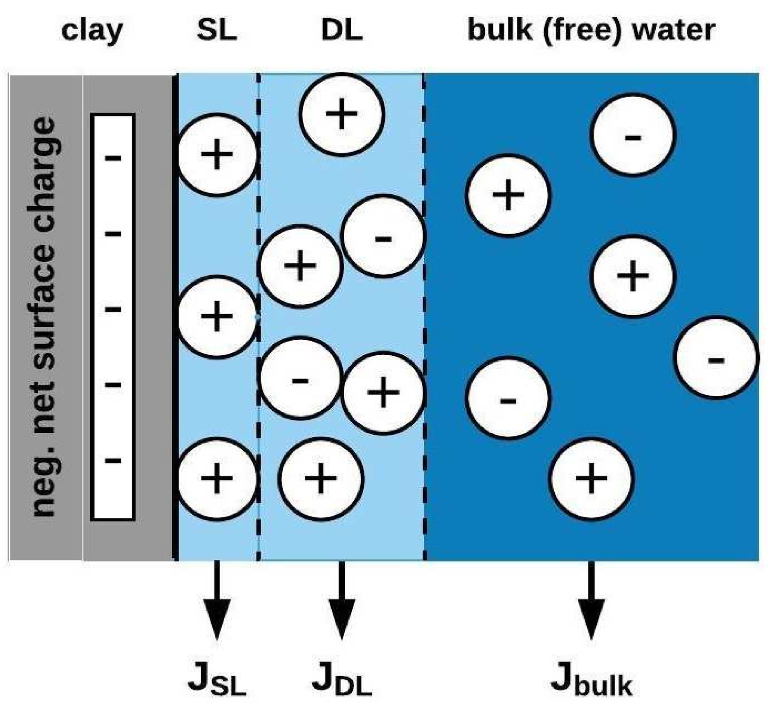

Figure 3: Schematic representation of the concept of a triple-layer model; Stern (SL) and diffuse (DL) layer cations can contribute to the overall mass flux

Multi-site surface diffusion model

The process of surface diffusion (SD) was newly implemented in the transport code FLOTRAN (Lichtner, 2007). SD accounts for a (partial) mobility of sorbed cations on site *i*. Pore and surface diffusion can be combined in a single effective diffusion coefficient (Gimmi & Kosakowski, 2011):

$$D_{e,c} = \frac{\varepsilon D_0}{\tau_p} + \sum_i \rho_{bd} \frac{\partial S_i}{\partial C} \frac{\mu_{s,i} D_0}{\tau_s}$$

(with porosity ε, tortuosity τ for each pathway and $\tau_p = \tau_s$, mineral density ρ_{bd}, diffusion coefficient D_0 in water, derivative of the sorption isotherm $\partial S / \partial C$).

The relative surface mobility $\boldsymbol{\mu_s}$ has to be derived from experiments.

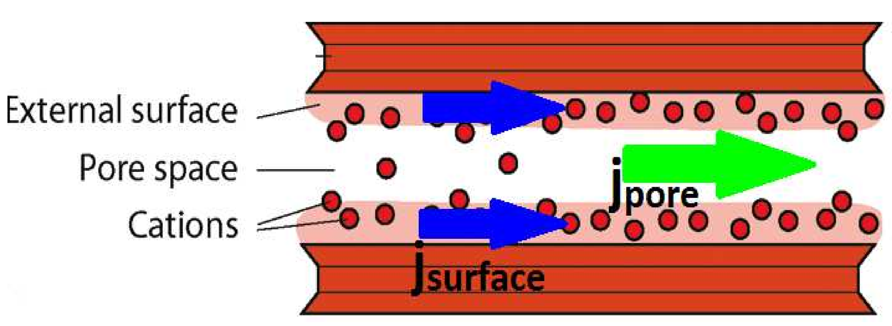

Figure 4: Schematic representation of pore and surface diffusion in a clay pore

Diffusion experiment

Diffusion of Na and Sr was experimentally determined parallel to the bedding of an Opalinus Clay sample (for experimental set-up see Van Loon, et al., 2004).

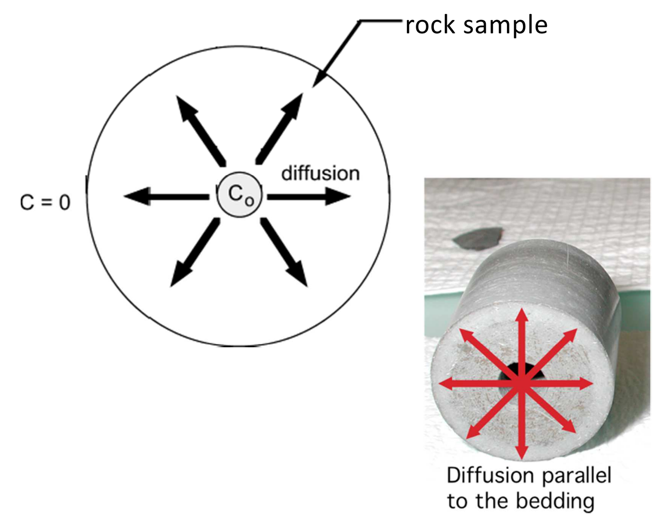

Figure 5: Experimental set-up for radial diffusion (top view)

Modelling results

The surface mobility μ_s on planar sorption sites was estimated to 0.4 for Na and to 0.05 for Sr. The SD model with the μ_s matches the experimental fluxes.

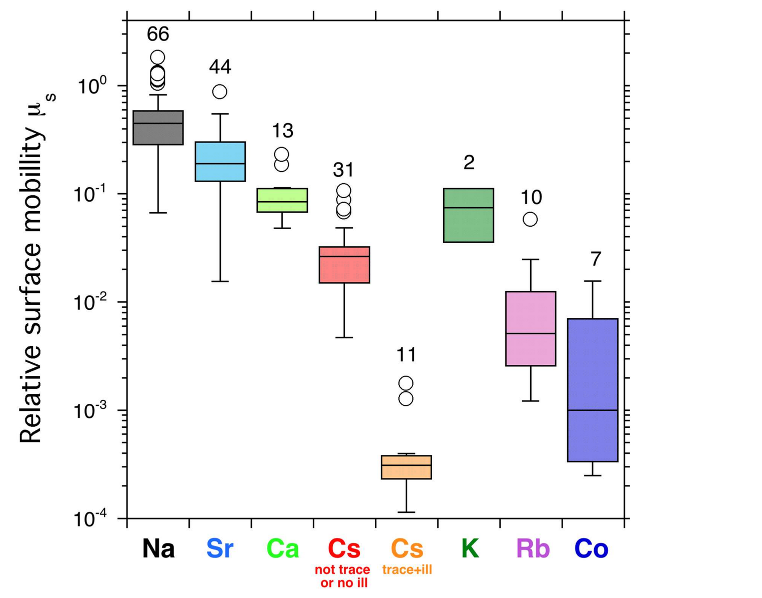

Figure 6: Literature values of surface mobilities μ_s for different cations (Gimmi and Kosakowski, 2011)

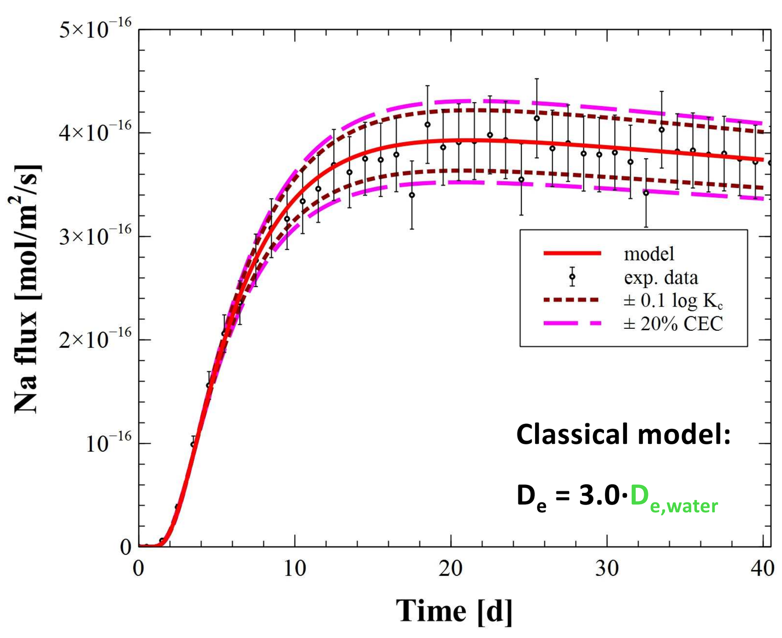

Figure 7: Na flux at the outer boundary of the OPA sample

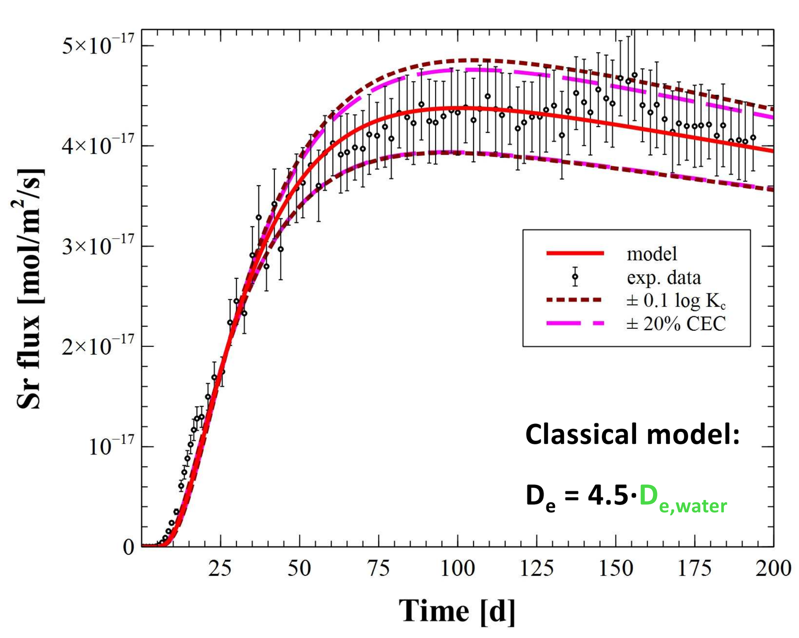

Figure 8: Sr flux at the outer boundary of the OPA sample

Conclusion

The surface diffusion model successfully describes the Na and Sr diffusion in Opalinus Clay. The estimated mobilties agree well with literature values.

Acknowledgement

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References

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