Multi-scale modelling of ions and water diffusion in clays

S.V. CHURAKOV

Paul, Scherrer Institute, Villigen-PSI, CH-5232, Switzerland (sergey.churakov@psi.ch)

Materials with low hydraulic permeability such as clays are major components in engineered and natural barriers for waste disposal sites. Migration of ions and water through such barrier systems over safety relevant times are predicted solving diffusion equation on continuum scale. Natural clay, however are highly heterogeneous in terms of porosity and mineralogical composition. These heterogeneities are manifested at different scales and consequently have strong influence on diffusion of solutes. To fully understand the mechanism of ion transport in clays the solute migration has to be addressed using complementary simulations and measurements capable of resolving the transport and chemical phenomena on different scales.

In clays, up to 50-70% of fluid accessible pore space is attributed to the interlayer and the diffuse double-layer porosity where solution properties, namely the mobility of ions and water, are strongly influenced by mineral surfaces. The transport through such nanopores is readily addressed by molecular simulations. At the sub-micrometer scale the individual interlayers are interconnected thought the macrospores. Molecular simulations with explicit solvent approach are not feasible at this scale anymore. Instead pore scale stochastic approaches are used to assess the influence of pore geometry and topology on the effective diffusion coefficient of the sample. Finally, state-of-the-art X-ray tomography measurements can provide 3D mineral distribution in a sample non-destructively at a resolution down to few micrometers. These data are directly used in transport simulations to reveal the consequences of mineralogical and textural heterogeneities in clays and their influence on the effective transport parameters of clay samples. Such a multi-scale treatment of transport phenomena using complementary modelling and measurement techniques is a necessary condition for accurate and reliable prediction of radionuclides migration over geological space and time domains.

Two step up-scaling of molecular diffusion coefficients in clays

S.V. CHURAKOV[1]*, TH. GIMMI[1,2] AND M TYAGI[1]

[1]Paul, Scherrer Institute, CH-5232 Villigen-PSI, Switzerland (*correspondence: sergey.churakov@psi.ch)
[2]University of Bern, CH-3012 Bern, Switzerland

Mass transport in rocks with low hydraulic conductivity such as clays originates from Brownian motion of molecules and ions in the solution and their interaction with the surface of the minerals. Up-scaling these molecular phenomena to the continuum scale, which is required for large-scale and long-time predictions, is particularly challenging because the considered scales differ by orders of magnitude. To address the up-scaling problem we developed a two-step simulation approach which enables us to derive macroscopic diffusion coefficients of water and ions for continuum equations from pore scale molecular diffusion coefficients [1]. Our starting point for the up-scaling procedure is local pore diffusion coefficients derived from molecular dynamics simulations for specific local environments, such as the interlayer or edge regions of clay particles. We then assign these local diffusion coefficients to different types of porosity of a model clay structure and obtain the structure-averaged effective diffusion coefficient of the sample by random walk simulations. Our model clay rock is composed of compacted grains of clay minerals. The space between the grain boundaries forms micro-pores. To generate such structures, a kinetic Monte Carlo method is employed on a grid to obtain closely packed grains of desired shapes, sizes and orientations. By varying the composition and geometrical properties of the clay model we have investigated the effects of mineralogical heterogeneities and of anion exclusion on the diffusion coefficients measured in laboratory experiments. Our up-scaling concept is general and can be used for up-scaling molecular diffusion coefficients for porous materials with almost arbitrarily complex structures.

[1] Churakov & Gimmi, (2011) *J. Phys. Chem. C* **115**, 6703-6714.