Reactive transport modelling of a long-term core infiltration experiment with claystone

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Argillacious rocks have low hydraulic conductivities (10^{-14}-10^{-13} m/s), large sorption and ion exchange capacities, are homogeneous, and are thus consdiered as host rocks for deep storage of radioactive waste in several countries. Constraining multicomponent transport parameters for dissolved species are of importance in this context.

A three-year advective-diffusive experiment under a hydrostatic confining pressure with a preserved drill core from Opalinus Clay (mid Jurassic, Switzerland) was used to (1) displace the *in situ* pore water with an artificail pore water [1], and (2) to monitor the breakthrough of tracres (^{2}H, ^{18}O, ^{36}Cl, Br) and major chemical components (this study). A multi-component reactive transport model (PHREEQC) was used considering explecitly free porewater and pore water affected by clay-bound diffuse double layers [2], species-specific diffusion coefficients, ion-exchange, and slected carbonate / silicate equilibria.

A much faster break-through is observed for Br^- (an Cl^-) compared to ^{2}H due to anion-exclusion effects and the advective flow regime. While the break-through of individual tracres can be modelled with a classical 1D advection/diffusion approach constraining accessible porosities and effective diffusion coefficients, an adequate multi-component reactive transport model does require the consideration of different types of accessible porosities, e.g. including a diffuse-double layer model [2]. The elution behaviour of cations is constrained by multi-component ion exchange and ionic-strength effects that can drive some of the eluted cation concentrations distinctly above those of the infiltrating solution.

[1] Mäder *et al.* (2004) *Proceedings of the 11th International Symposium on Water-Rock Interaction*, 445-449, Balkema. [2] Appelo and Wersin (2007). [2] Appelo and Wersin (2007) *Env. Sci. Tech.*, **41**, 5002-5007.

Adsorption of transgenic Cry1Ab protein to the silica-water interface

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Bt crops are genetically modified to produce insecticidal Cry proteins against pests. Bt crops release Cry to soils. Little is known about adsorption of Cry to soil particles, albeit this process governs Cry fate and bioactivity in soils. The aim of this work was to systematically investigate and model the adsorption of model protein Cry1Ab to silica (SiO_2) as a function of solution chemistry. To this end, we combined solution-depletion experiments coupled to immunological protein detection with *in situ* real time adsorption measurements using quartz crystal microbalance (QCM-D).

Electrostatics governed the adsorption of Cry1Ab (isoelectric point (IEP) = 6.4) to SiO_2 (point of zero charge = 2-3) at I = 50 mM (NaCl). Favorable electrostatics at pH 5 and 6 resulted in fast and pronounced adsorption. At pH 5 and c(Cry1Ab) = 10 μg mL^{-1}, a protein monolayer formed on the SiO_2 surface. Conversely, at pH 7 and 8, no adsorption was detected, due to electrostatic repulsion. At I = 10 mM, electrostatics still governed Cry1Ab adsorption. Yet, protein-protein interactions and/or entropic effects facilitated adsorption resulting in a protein bi-layer and a monolayer on SiO_2 at pH 6 and 7, respectively. Also, at pH 8, detectable amounts of Cry adsorbed despite unfavorable electrostatics. Adsorption at both I= 10 mM and 50 mM was highly concentration dependent and reversible. Desorption rates increased with increasing pH of the rinsing buffer. Control experiments involving two additional proteins (bovine serum albumin (IEP 4.6) and hen egg white lysozyme IEP = 10.5)) and positively and negatively charged polymers as adsorbents confirmed the dominant role of electrostatics in Cry1Ab-SiO_2 interactions.

Irreversible sorption of BSA to SiO_2 pointed to structural unfolding of BSA on the surface, resulting in a larger contact area and hence an increase in the activation energy of desorption. Conversely, reversible sorption of Cry1Ab suggested that this protein remained in near native conformation and that an adsorption-desorption cycle of did not result in irreversible structural changes in Cry1Ab and hence loss of its bioactivity. This was confirmed in diet incorporation bioassays using the susceptible pest organism *Ostrinia nubilalis*, where effect concentrations for 50% growth inhibition of the test organisms were only slightly higher for SiO_2-adsorbed than freely dissolved Cry1Ab.