

## Surface speciation of sulfate at a water-ferrihydrite interface

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Surface speciation is important for understanding the adsorption mechanisms and the long-term behavior of dissolved toxic species as well as the bioavailability of nutrients. In addition, the speciation influences the physicochemical property of the minerals, such as solubility of nano particles [1] and dissolution rate of mineral [2]. Ferrihydrite is low crystalline ferric hydroxide widely distributed in soils and rivers. It is also thought to be an effective anion adsorbent because of its high-specific surface area and positively-charged surface in natural water. Sulfate ( $\text{SO}_4^{2-}$ ) is common anion in soils and rivers. It is reported that sulfate competes with phosphate, carbonate, trace metal and organic acid adsorption [3,4]. The present study aims to reveal the surface speciation of sulfate at the electrolyte solution-ferrihydrite interface under various pH and ionic strength conditions by means of *in situ* IR spectroscopic analysis (ATR-FTIR) and surface complexation modeling (Extended Triple Layer Model: ETLM [3, 5]).

IR spectra of sulfate adsorbed on ferrihydrite were fitted by Gaussian functions based on the assignments by Peak *et al.* [4]. The number and position of the peaks from IR spectra showed there are inner-sphere and outer-sphere sulfate complexes. Outer-sphere complex is dominant under the examined pH (4 to 9) and ionic strength ( $I = 0.01$  to  $0.1$ ) conditions, although the contribution decreases with increase of ionic strength and decrease of pH. The coordination environment was estimated by ETLM analyses of independent surface charge data of ferrihydrite in  $\text{Na}_2\text{SO}_4$  solutions as function of pH and ionic strength. The coordination environment of outer-sphere species was determined to be  $(>\text{FeOH}_2^+)_2\text{SO}_4^{2-}$  (bidentate deprotonated outer-sphere species) while that of inner-sphere species was  $>\text{FeOSO}_3^-$  (monodentate deprotonated inner-sphere species). ETLM prediction using these two sulfate surface species and these reaction equations quantitatively reproduced the surface speciation as function of pH and ionic strength obtained by the ATR-IR analyses.

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## Modeling cesium diffusion in a claystone formation

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Diffusion experiments performed at different scales with reactive tracers provide a good opportunity to test and verify reactive transport models. Recently, considerable progress has been made to describe the diffusion of cations and anions in clay media [1] by accounting for the different porosities and diffusivities 'seen' by the different ionic and uncharged species. Thus, simultaneous diffusion of tritium, iodide and sodium from an *in situ* experiment in Opalinus Clay was successfully modeled using the PHREEQC code with the newly developed multicomponent diffusion option [1].

Cesium, a safety-relevant radionuclide is known to sorb rather strongly to claystone, but on the other hand displays a high effective diffusivity. Two *in situ* diffusion experiments (DI-A1 and DI-A2), in which a number of tracers including also  $\text{Cs}^+$  were carried out in the Mont Terri URL. The results of these were modelled with simple diffusion models and empirical expressions for sorption (e.g. [2]). Here we report the refined modelling of the  $\text{Cs}^+$  diffusion data from the two *in situ* experiments using the multicomponent diffusion model of [1] and accounting for recent laboratory  $\text{Cs}^+$  diffusion data on small-scale samples [3].

A dual porosity model, which is consistent with structural data of the clay, is shown to be necessary to describe the *in situ* data. Moreover, the results show the importance of including the specific hydraulic properties of the borehole filter and the annular space between filter and rock in the modeling description. When these effects are accounted for, then a remarkable consistency in diffusion and sorption parameters between the different *in situ* tests and the small-scale lab tests is obtained. Also, the results are consistent with batch sorption data performed at low solid/liquid ratio, thus indicating the same cesium sorption capacity at high S/L ratios at different spatial scales.

[1] Appelo & Wersin (2007) *EST* **41**, 5002-5007. [2] Wersin *et al.* (2008) *Appl. Geoch.* **23**, 678-691. [3] Appelo *et al.* (in prep.).