A Donnan diffusion model for the description of Sr adsorption kinetics to hydrous ferric oxide

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Sorption of ions by hydrous ferric oxide (HFO) often shows a fast initial sorption reaction followed by a much slower sorption process. The second step is diffusion controlled with a rate that may be explained by electrostatic interactions in the material's pores. HFO is made of small crystallites that are aggregated, generating pores in the nanometer range. The pores may be large enough to contain unbound water but small enough to be electrically charged due to the overlapping of the electric diffuse layers inside the pores. The Donnan diffusion model describes this case. It uses a Donnan electrostatic model to calculate the pore solution chemistry, which is influenced by pH and sorption dependent surface charge. Ion diffusion in the pore water is calculated from the gradients in Donnan concentrations and Donnan potentials. Surface chemical equilibria were described with a 1-pK basic Stern surface complexation model based on the CD-MUSIC model [1]. The model was implemented with ORCHESTRA [2]. To test the Donnan diffusion model, dense aggregates of HFO [3] were packed in a chromatographic column and equilibrated with an electrolyte solution of 10^{-2} M $NaNO_3$ to a given pH (pH 4 and 7). Then an identical solution, containing additionally 10^{-4} M Sr was injected. To interpret the sorption behavior, Sr breakthrough curves were recorded and compared with the predictions of the Donnan-diffusion model. The initial part of sorption was fast, which may be explained by diffusion in large pores. An unexpected result was that the fraction of pores with fast diffusion depended on pH, so that this fraction had to be determined specifically for every experiment. For the diffusion limited part of sorption, good correspondence between model and experiment indicated that electrostatically constrained diffusion did influence sorption kinetics significantly and that the model was applicable.

References

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Mixing solutions, precipitation and changing permeability in porous media

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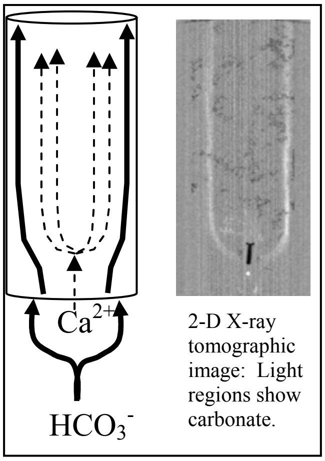
Modifying subsurface permeability and altering flow paths is important for many environmental applications. Experiments have been conducted to evaluate different approaches for generating *in situ* supersaturation states for calcite and controlling the spatial distribution of calcite precipitation within porous media. One such approach is diffusive mixing along parallel flowstreams of reactants as shown in the figure. A solution of calcium chloride was injected through a porous diffuser into the interior of a 5cm diameter sand column with a background flow of sodium bicarbonate. Mixing occurred along the interface between the two solutions. X-ray tomography was used to image the three dimensional distribution of calcium carbonate solids in the column. Calcium carbonate propagated along the interface between the solutions as mobile colloids or was deposited in the pores, thereby separating the two solutions. Complex resistivity is also being used to detect the formation of calcite. A similar experiment in two dimensions allowed direct observation of the mixing zone using colored dyes and spectral analysis.



2-D X-ray tomographic image: Light regions show carbonate.

An additional approach under investigation has been to generate at least one of the reactants *in situ*. For example, we have been testing the use of immobilized urease enzyme to generate carbonate ions from urea hydrolysis as an abiotic analog to a remediation approach for immobilization of strontrium-90 based on co-precipitation in calcite (Smith, R.W. et al. EMSP project). The long-term goals of these experiments are to understand flow-precipitation coupling and how the impact on system permeability can be controlled, at scales from the pore level to the field.