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Surface complexation reactions in sandy porous media: Effects of incomplete mixing and mass-transfer limitations in flow-through systems

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Abstract:

Although mixing and surface complexation reactions are key processes for solute transport in porous media, their coupling has not been extensively investigated. In this work, we study the impact of mass-transfer limitations on heterogeneous reactions taking place at the solid-solution interface of a natural sandy porous medium under advection-dominated flow-through conditions. A comprehensive set of 36 column experiments with different grain sizes (0.64, 1.3 and 2.3 mm), seepage velocities (1, 30 and 90 m/day), and hydrochemical conditions were performed. The injection of NaBr solutions of different concentrations (1–100 mM) led to the release of protons via deprotonation reactions of the quartz surface. pH and solute concentration breakthrough curves were measured at the outlet of the columns and the propagation of pH fronts in the column setups was tracked inside the porous medium with non-invasive optode sensors. The experimental results show that the deprotonation of the reactive surfaces, resulting from their interactions with the injected ionic species, strongly depends on the hydrodynamic conditions and differs among the tested porous media despite their apparent similar surface properties. Reactive transport modeling was used to quantitatively interpret the experimental results and to analyze the effects of mass-transfer limited physical processes on surface complexation reactions, propagation of pH fronts, transport of major ions and spatio-temporal evolution of surface composition. A dual domain mass transfer formulation (DDMT) combined with a surface complexation model (SCM) allowed capturing the effects of incomplete mixing on the surface reactions and to reproduce the experimental observations collected in the experiments with high flow velocities. The SCM was parameterized with a single set of surface complexation parameters, accounting for the similar surface properties of the porous media, and was capable of describing the surface complexation mechanisms and their impact on the hydrochemistry over the large range of tested ionic strengths.

Keywords: column experiments, surface complexation, sandy porous media, incomplete mixing, dual-domain reactive transport modeling