



## Impact of multicomponent ionic transport on pH fronts propagation in saturated porous media

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Multicomponent ionic interactions have been increasingly recognized as important factors for the displacement of charged species in porous media under both diffusion- [1,2] and advection-dominated flow regimes [3,4]. In this study we investigate the propagation of pH fronts during multicomponent ionic transport in saturated porous media under flow-through conditions. By performing laboratory bench-scale experiments combined with numerical modeling we show the important influence of Coulombic effects on proton transport in the presence of ionic admixtures. The experiments were performed in a quasi two-dimensional flow-through setup under steady-state flow and transport conditions. Dilute solutions of hydrochloric acid with  $MgCl_2$  (1:2 strong electrolyte) were used as tracer solutions to experimentally test the effect of electrochemical cross-coupling on the migration of diffusive/dispersible pH fronts. We focus on two experimental scenarios, with different composition of tracer solutions, causing remarkably different effects on the propagation of the acidic fronts with relative differences in the penetration depth of pH fronts of 36% between the two scenarios and of 25% and 15% for each scenario with respect to the transport of ions at liberated state (i.e. without considering the charge effects). Also significant differences in the dilution of the distinct ionic plumes, quantified using the flux-related dilution index at the laboratory bench scale [5], were measured at the outflow of the flow-through system. The dilution of the pH plumes also changed considerably (26% relative difference) in the two flow-through experiments only due to the different composition of the pore water solution and to the electrostatic coupling of the ions in the flow-through setups. Numerical transport simulations were performed to interpret the laboratory experiments. The simulations were based on a multicomponent ionic formulation accurately capturing the Coulombic interactions between the transported ions in the flow-through system. The results of purely forward simulations show a very good agreement with the high-resolution measurements performed at the outlet of the flow-through setup and illustrate the importance of charge effects on pH fronts propagation in porous media.

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