Unsaturated Porous Media Experiments on Nanoconfinement Influences of Water Films and Capillarity on Diffusion and Flow

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Despite decades of research, the scale at which water film thicknesses and pore sizes in geologic media begin to impart significant deviations from bulk liquid water properties in diffusive transport and viscous flow remains unclear. Two experimental approaches are presented here, one examining diffusion in adsorbed water films, and the other examining capillary imbibition of water.

In diffusion through the aqueous phase in unsaturated porous media, lower limits of transport have been associated with either the thickness of adsorbed films becoming too restrictive, or with a low water saturation at which a percolation limit is encountered. In hydrophyllic materials, the former explanation is the physical basis for the latter. Previous, we measured ion (Rb^+) diffusion in quartz sands over a wide range of water saturations, with an emphasis on conditions associated with water film thicknesses ranging from 1 μm to 1 nm [1]. We found that diffusion path tortuosity accounted the mobility of this nonreactive cation. We have more recently been investigating ion diffusion in water films with sub-nm thickness, and find a very sharp decrease in effective diffusion coefficients relative to that associated with tortuosity, indicative of restricted ion mobility within films $\leq$ 3 water layers in thickness.

Measurements of water imbibition into unsaturated nanoporous media provides another means to test influences of confining interfaces. We compare experiments of water imbibition into shales with predictions based on a new scaling relation applicable over 10 orders of magnitude in permeability. Over this very wide range, a simple scaling relation provides satifactory predictions for water imbibition in hydrophilic media having characteristic hydraulic radii as fine as ~10 nm. These results collectively indicate that macroscopic scaling of diffusion and liquid phase flow is reliable in nonreactive nanoporous systems.

[1] Tokunaga *et al.* (2017) *Environ. Sci. Technol.* **51**, 4338-4346.