# Complex dynamics of water adsorbed on metal oxide surfaces

PETER T. CUMMINGS[1,2]*, LUKAS VLCEK[3],
EUGENE MAMONTOV[4] AND DAVID J. WESOLOWSKI[3]

[1]Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN, USA (*correspondence: peter.cummings@vanderbilt.edu)
[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA
[3]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA
[4]Neutron Scattering Science Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

Metal oxide-water interfaces are ubiquitous in geological formations, and the dynamics and structure at such interfaces are crucial to a wide range of chemical, geological, and biological processes. Despite the relative simplicity of the crystal surface structure, adsorbed water exhibits dynamics that are too complex for interpretation using traditional models of diffusion.

In the presentation, we will describe the use of molecular dynamics simulations to interpret findings of adsorption, quasi-elastic neutron scattering (QENS), and neutron spin echo (NSE) experiments [1-3]. The simulations investigate rutile ($\alpha$-$TiO_2$) and cassiterite ($\alpha$-$SnO_2$) surfaces with up to three layers of adsorbed water at temperatures between 200 K and 260 K. Atomic-level insight into the interfacial dynamics enables us to link structural features of the surface and adsorbed water, such as hydroxylation or layering, to dynamic processes observed in the neutron experiments. For instance, the simulation results explain a qualitative change in the overall dynamic behaviour caused by a change in the amount of adsorbed water. In addition to the motion of individual atoms and molecules we also investigate the collective dynamics of adsorbed hydrogen bonded groups of molecules and compare the results to recent NSE experiments.

[1] Mamontov, Vlcek, Wesolowski & Cummings *et al.* (2007) *J. Phys. Chem. C* **111**, 4328–4341. [2] Mamontov, Wesolowski & Vlcek *et al.* (2008) *J. Phys. Chem. C* **112**, 12334–12341. [3] Mamontov, Vlcek, Wesolowski & Cummings *et al.* (2009) *Phys. Rev. E.* **79**, Art. No 051504.

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# Multimodel simulations of the reactive transport of Uranium in small scale tracer tests

G.P. CURTIS[1]*, M. YE[2], M. KOHLER[3], P.M. FOX[1]
AND J.A. DAVIS[1]

[1]Water Resources Division, US Geological Survey, Menlo Park, CA 94025, USA (gpcurtis@usgs.gov, pfox@usgs.gov, jadavis@usgs.gov)
[2]Department of Scientific Computing, Florida State University, Tallahassee, FL 32306, USA (*correspondence: mye@fsu.edu)
[3]Department of Civil Engineering, University of Maine, Orono ME

The physical and geochemical heterogeneity of most aquifers causes reactive transport in aquifers to be complex and open to multiple interpretations. These complexities can be further complicated by spatial and temporal variations in groundwater chemistry. These factors were evaluated in two small-scale experiments that were conducted in an alluvial aquifer at a former uranium mill near Naturita, CO. The ambient groundwater chemistry at the tracer test site had a U (VI) concentration equal to 4 $\mu$M, an alkalinity equal to 8 meq/L and a pH of 7.1 and was close to equilibrium with calcite. The experiments were conducted by extracting contaminated groundwater from the aquifer and adjusting the alkalinity to either 25 meq/L or 2.5 meq/L and adding 6.2 mM KBr. U (VI) concentrations in the downgradient monitoring wells changed in proportion to the changes in alkalinity because of adsorption and desorption reactions.

Reactive transport simulations based on an equilibrium-controlled conceptual model that includes aqueous speciation reactions and a surface complexation model to describe U (VI) adsorption yield qualitatively good agreement with the observations. However, systematic differences between the simulations and observations are prevalent for all of the breakthrough curves and these deviations are consistent with kinetic or mass-transfer limitations. Several alternative conceptual models have been postulated and include (1) alternative representations of U (VI) adsorption reactions, (2) alternative approaches for simulating rate-limited adsorption and desorption and (3) alternative descriptions of the processes that affect the key major ions such as Ca and Mg including calcite dissolution kinetics and ion exchange. A multimodel analysis that includes alternative conceptualizations of these key geochemical processes is being evaluated to determine if model averaging reduces prediction uncertainty.