Reduction of U(VI) by Fe(II): Influence of Fe- and Al-(oxyhydr)oxides on redox catalysis

S. D. TAYLOR*[1], M. C. MARCANO[1], K. M. ROSSO[2] AND U. BECKER[1]

[1]Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109, USA
[2]Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352, USA
(*correspondence: sdtaylor2015@outlook.com)

One approach to limit the transport of uranium is to reduce $U(VI)_{aq}$ to $U(IV)O_{2(s)}$ with the common natural reductant Fe(II). The abiotic reduction of U(VI) by Fe(II) (in an anoxic, neutral pH environment) has been shown to be kinetically inhibited in the absence of a solid substrate. Mineral surfaces, such as those of schoepite [1] and iron oxides, catalyze U(VI) reduction by Fe(II) [2]. However these surface-mediated redox processes are not well understood.

The reduction of U(VI) by Fe(II) in suspensions with isostructural semiconducting Fe- and insulating Al-(oxyhydr)oxides was specifically investigated to understand the effect of the electronic properties of the minerals on their catalytic efficiency. A combination of experiments with quantum-mechanical atomistic modeling including kinetic Marcus theory was applied to characterize the structure, thermodynamics, and reaction mechanisms between actinide/metal complexes and mineral surfaces. Experimental results continue to show that U(VI) reduction to U(IV)/U(V) by Fe(II) is catalyzed in the presence solids. The catalytic abilities of the isostructural Fe- and Al-(oxyhydr)oxide substrates differ; U(VI) reduction by Fe(II) is more than ten times faster in the presence of semiconducting Fe (hydr)oxides than in the presence of insulating Al (hydr)oxides. *Ab initio* calculations on periodic surfaces show the semiconducting Fe oxide surface offers charge-transfer pathways, where the mineral acts as a medium through which electrons can be moved through, that can significantly contribute to the Fe oxides' enhanced catalytic abilities.

Previously, there have been little to no quantitative data on the thermodynamics and kinetics of redox reactions in the presence of insulating and semiconducting surfaces. To describe the kinetics of mineral-catalyzed redox reactions *ab initio* electron transfer calculations are being applied for the first time to these ternary, coadsorbed systems. This alternative method provides significant insight into the kinetics and thermodynamics for charge-transfer pathways on mineral surfaces influencing the migration of radionuclides/metals.

[1] Taylor et al. (2015) *GCA* **156**, 154-172. [2] Liger et al. (1999) *GCA* **63**, 2939-2955.