

Uranyl adsorption onto Montmorillonite: Complexity and ongoing challenges

JEFFREY G. CATALANO^{1*}
AND GORDON E. BROWN, JR.^{2,3}

¹Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130 USA
(*correspondence: catalano@wustl.edu)

²Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305 USA

³Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Lab, Menlo Park, CA 94025, USA

The fate and transport of uranium in contaminated soils and sediments may be affected by adsorption onto the surface of minerals such as montmorillonite. Montmorillonite adsorbs uranyl and other cations through two distinct mechanisms: cation exchange into the interlayer and specific adsorption onto edge surface functional groups. Binding of uranyl through cation exchange is dependent on ionic strength because of competition for sites with electrolyte cations and pH because of uranyl hydrolysis. Specific adsorption is less sensitive to ionic strength changes but highly pH-dependent. Complexation by carbonate is known to inhibit adsorption under alkaline conditions (pH >8). Thermodynamic models predict the distribution of uranyl between cation exchange and edge sites, but the models have not been spectroscopically verified and the effect of carbonate on surface speciation has not been investigated.

We have employed extended X-ray absorption fine structure spectroscopy to investigate the dependence of uranyl adsorption onto montmorillonite as a function of pH, ionic strength, and P_{CO_2} . These measurements demonstrate that under low ionic strength conditions cation exchange is a significant adsorption mechanism to higher pH values than past models predict. This may reflect the exchange of cationic uranyl hydrolysis products. These spectra also suggest that uranyl has a preference for [Fe(O, OH)₆] edge sites over [Al(O, OH)₆] sites. In addition, the data are consistent with the formation of uranyl carbonate ternary surface complexes. This work demonstrates that past thermodynamic models may underestimate the complexity of uranyl adsorption mechanisms on montmorillonite. Ongoing challenges include: assessing the additional exchangeable species beyond UO_2^{2+} as these are likely low charge and more sensitive to competing divalent electrolyte cations; determining the composition of edge sites as dissolution and neof ormation reactions may alter their composition relative to the bulk clay; and characterizing the extent of ternary surface complex formation induced by common ligands.

Fe(II)-induced structural transformations of hematite surfaces and their impact on contaminants

J.G. CATALANO^{1,2*}, P. FENTER², C. PARK³,
K.M. ROSSO⁴, A.J. FRIERDICH¹ AND B.T. OTEMUYIWA¹

¹Department of Earth & Planetary Sciences, Washington Univ., St. Louis, MO 63130 USA
(*correspondence: catalano@wustl.edu)

²Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439 USA

³Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439 USA

⁴Chemical & Materials Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352 USA

Reactions of Fe (II) at iron oxide-water interfaces affect contaminant fate, biogeochemical iron cycling, and iron isotope fractionation. Recent studies have demonstrated that these reactions involve electron transfer and atom exchange. Such processes must induce molecular-scale structural changes to iron oxides surfaces as they require the adsorption and oxidation of Fe (II). We have investigated the reaction of Fe (II) with specific surfaces of hematite under neutral (pH 7) and acidic (pH 3) conditions using X-ray reflectivity. Fe (II) induces structural changes that are independent of pH yet dependent on orientation, with (012) and (110) surfaces experiencing congruent layer-by-layer dissolution or growth and the (001) surface developing a <1 nm-thick discontinuous film formed that is structurally distinct from the hematite lattice. Resonant anomalous X-ray reflectivity measurements reveal that the concentration of adsorbed Fe (II) in this surface film at pH 7 was below the detection limit (i.e., <0.5–1 $\mu\text{mol}/\text{m}^2$). These observations suggest that Fe plays a catalytic role in a delocalized oxidative adsorption-desorption reaction, in which an electron from the adsorbing Fe (II) reduces and desorbs a lattice Fe (III) cation elsewhere.

We have further investigated the fate of sorbed As (V) and Ni (II) on hematite exposed to aqueous Fe (II). Fe (II) has no effect on As (V) speciation at the hematite surface, with bridging bidentate surface complexes present at both pH 4 and 7 independent of the presence of Fe (II). Similar systems containing goethite display identical behavior. In contrast, the speciation of Ni (II) changes from occurring as a surface complex in the absence of Fe (II) to being incorporated into the hematite structure in the presence of Fe (II). These contrasting effects of Fe (II) on contaminant speciation at iron oxide surfaces appear to reflect the compatibility of the contaminant species with the sorbent structure.