

Surface complexation of U(VI) by Fe and Mn (hydr)oxides

David M. Sherman, Chris G. Hubbard and Caroline L. Peacock

Department of Earth Science, University of Bristol, Bristol BS8 1RJ UK.

Abstract. Sorption of U(VI) to iron and manganese (hydr)oxides is a fundamental control on the mobility of uranium in oxic soil and groundwater. Surface complexation models for these sorption reactions are needed to enable reactive transport simulations of U in the environment. We have been investigating the sorption of U(VI) to iron and manganese (hydr)oxide minerals using classical batch sorption experiments, EXAFS spectroscopy and first-principles (quantum mechanical) calculations of the structures and energetics of U surface complexes. EXAFS spectra of U surface complexes are complicated by multiple scattering and the poor resolution of U-carbonate complexes. We argue that previous models for surface complexation need to be reassessed. Instead, we show that on goethite (α -FeOOH) and ferrihydrite ($\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$), we can model both our EXAFS and our sorption experiments using three surface complexes, $(>\text{FeOH})_2\text{UO}_2(\text{H}_2\text{O})_3$, $>\text{FeOCO}_2\text{UO}_2$, and $(>\text{FeOH})_2\text{UO}_2\text{CO}_3$. Using these complexes, we fit our batch sorption experiments to a surface complexation models for U on goethite and ferrihydrite with a 1pK model for surface protonation, an extended Stern model for surface electrostatics and inclusion of all known $\text{UO}_2\text{-OH-CO}_3$ aqueous complexes in the current thermodynamic database. The models give an excellent fit to our sorption experiments done in both ambient and reduced CO_2 environments at surface loadings of 0.02-2.0 wt. % U. We find that we can model the EXAFS and batch sorption experiments of U(VI) on birnessite as an inner-sphere $(>\text{Mn}_2\text{O})_3\text{UO}_2^{++}$ and $(>\text{Mn}_2\text{O})_3\text{UO}_2\text{CO}_3$ complexes over vacancy sites. In the

environment, U(VI) and its carbonate complexes will be preferentially sorbed by iron(III) (hydr)oxides over manganese(IV) oxides.