

The effect of surfaces and ligands on the reduction and reoxidation reactions of U studied in mixed-batch reactors and flow-through columns

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M. Boyanov (mboyanov@ice.bas.bg),^{1,2} D. Latta,^{1,3} M. Scherer,³ Y.Liu,⁴ C. Liu,⁴ B. Mishra,^{1,5} E. O'Loughlin,¹ K. Kemner¹

1. Biosciences Division, Argonne National Laboratory; 2. Institute of Chemical Engineering, Bulgarian Academy of Sciences; 3. Department of Civil and Environmental Engineering, The University of Iowa; 4. Pacific Northwest National Laboratory; 5. Department of Physics, Illinois Institute of Technology.

The speciation of uranium (U) is an important control on its mobility in natural systems. Factors such as the valence state and the molecular-scale environment of U influence its solubility and its susceptibility to leaching by groundwater. Subsurface systems contain a host of minerals, bacteria, and dissolved ligands; the interaction between them and U needs to be understood so appropriate reactions can be included in the Reactive Transport Models (RTMs) used to predict contaminant migration and to inform policy decisions.

The Argonne Subsurface SFA is continuing to provide the molecular-level understanding of the processes needed for the development of RTMs. Here, we study the transformations of U caused by changes in redox conditions that may result from a seasonal influx of organic matter or oxidized groundwater. We have shown previously that the precipitation of mononuclear U^{IV} in biostimulated systems is caused by the presence of phosphate in the medium. The reoxidation behavior of such U^{IV}-phosphate species is relatively unknown compared to uraninite. Using synchrotron x-ray spectroscopy we find that U^{IV}-phosphate oxidizes to U^{VI} at similar rates as uraninite. However, when ubiquitous ions such as calcium and phosphate are present in the groundwater the transformation pathways and rates change. In particular, uraninite and U^{IV}-phosphate oxidize slower because of the formation of a surface layer which inhibits further oxidation. Phosphate also changes the product of uraninite oxidation, which affects the subsequent stability of U^{VI}.

Our recent work also established that U^{IV} is stabilized as mononuclear species by the surfaces of metal oxides. While this finding may explain the observed predominance of mononuclear U^{IV} in field sediments, the contribution of the clay mineral fraction to this effect is unknown. Here, we investigate whether montmorillonite surfaces have a role in the stabilization of mononuclear U^{IV}. An Fe-free clay (SYn-1, 2-100 g/L loading) was reacted with U^{VI} and reducing conditions were established by addition of AH₂DS. Using synchrotron spectroscopy we find that U^{VI} is reduced to nano-particulate uraninite. The predominance of nano-uraninite even at high solids loading suggests that clays do not have as large a role as metal oxides in the stabilization of mononuclear U^{IV}.

An intermediate step in developing field-scale RTMs is testing their predictions in column experiments. The Argonne SFA is using x-ray accessible columns to compare the predicted and measured speciation under advective flow conditions. Results from a column consisting of ferrihydrite-coated packing material and a sulfide-containing influent will be presented.