Reactivity of nano-biogenic uraninite in the subsurface: Dissolution rates and mechanisms

JOHN R BARGAR[1], KATE M. CAMPBELL[2],
HARISH VEERAMANI[3], JOANNE E STUBBS[1],
JUAN S LEZAMA-PACHECO[1], ELENA SUVOROVA[3],
KAI-UWE ULRICH[4], LISA Y. BLUE[4],
RIZLAN BERNIER-LATMANI[3] DANIEL E. GIAMMAR[4],
STEVEN B. YABUSAKI[5] AND PHILIP E. LONG[5]

[1]Stanford Synctrotron Radiation Lightsource, Menlo Park, CA, 94025 USA
(*correspondence: bargar@slac.stanford.edu)
[2]US Geological Survey, Boulder, CO 80303, USA
[3]Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland
[4]Washington University, St. Louis, MO 63130 USA
[5]Pacific Northwest National Laboratory, Richland, WA 99352 USA

Biogenic uraninite is of potentially great significance to naturally and artificially bioreduced sediments and uranium ore deposits. The stability of this phase is believed to be compromised by its nano size. Since other forms of U (IV) are thought to be *more* prone to oxidation than uraninite, the stability of this solid can be viewed as a limiting case, a first-order scientific question likely to impact the success of stimulated bioremediation approaches. Trace and major-ion solutes strongly moderate uraninite stability, and their spatial/temporal variability in groundwater is difficult to capture in laboratory analog studies. Evaluation of kinetic parameters for nano-biogenic-uraninite dissolution in the field and meaningful testing of hypotheses developed from previous laboratory work therefore requires stability studies under *bona fide* groundwater conditions. Consequently, biogenic uraninite corrosion by molecular oxygen was studied in groundwater at Rifle, Colorado. The Rifle IFRC site is ideal for such investigations because of the availability of wells with contrasting DO concentrations, extensive historical groundwater data, and good site infrastructure.

Nano-uraninite synthesized by U (IV) reduction by proteobacteria isolated from Rifle groundwater was deployed in wells and subsequently analyzed to assess dissolution rates and compositional/structural changes. Net U loss is remarkably slow, at least 100-fold slower than those obtained in laboratory experiments, and is impacted by associated organic matter. Fundamental controls over this behavior will be discussed. This study indicates that nano-biogenic uraninite is relatively stable in groundwater, even under oxic conditions.

Influence of organic acids on U(VI) adsorption onto kaolinite

M. BARGER* AND C.M. KORETSKY

Department of Geosciences, Western Michigan University, Kalamazoo, MI 49008, USA
(*correspondence: michelle.l.barger@wmich.edu)

Use of uranium as a nuclear fuel may result in release of the toxic radionuclide to the environment. Adsorption of aqueous UO_2^{2+} on sediment solids may significantly influence the mobility of U in the subsurface. Such reactions may in turn be effected by the formation of strong organic complexes, either via competition with aqueous U (VI) complexes or by enchancement due to formation of ternary complexes on solid surfaces. In this study, U (VI) adsorption on kaolinite is investigated as a function of pH and ionic strength in the presence and absence of organic ligands.

All experiments were conducted under open atmosphere at room temperature and pressure using ~500 mL batch reactors. 10^{-5} M U (VI), background electrolyte (0.001 to 0.1 $NaNO_3$) and organic acid (initially 0, 10 or 20 mg/L fulvic acid) were combined and a control aliquot (~10 mL) withdrawn. Next, 2 g/l kaolinite (KGa-1b) was added to the reactor, the pH was adjusted to 3 with HNO_3 and the slurry was equilibrated under constant stirring for 30 min. The slurry pH was then titrated upwards, at ~0.3 pH intervals, using small additions of 0.1 M NaOH. At each interval, a 10 mL aliquot of the well mixed slurry was pipetted into a 15 mL centrifuge tube, and equilibrated for a further 24 hrs on a rotator, after which the pH was remeasured. Each tube was then centrifuged and the superntant syringe-filtered (0.45 μm nylon) and prepared with nitric acid and an internal standard (3 ppm In). Supernatant U was measured by ICP-OES using matrix matched standards.

U (VI) adsorbs strongly on the kaolinite, from no detectable uptake at pH ~3 to nearly 100% adsorption at pH between 5.5 and 7.8, with subsequent desorption occurring at higher pH. Adsorption increased with decreasing ionic strength. Particularly in 0.1 M $NaNO_3$ experiments, U (VI) adsorption was slightly decreased in the presence of fulvic acid at alkaline pH, perhaps due to competition with aqueous U (VI)-fulvic acid complexes. In contrast, adsorption was enhanced at lower pH in the presence of fulvic acid, suggesting that ternary complexes may form on the kaolinite surface. Future experiments will be completed with other organic acids (e.g. NTA, citric acid, EDTA and oxalic acid).