**Introduction**

- The molecular-scale speciation and reactivity of U(IV) products of microbial U(VI) reduction is crucial to the stability and fate of U in naturally reduced sediments and to the success of in-situ bioremediation strategies.
- Uraninite (UO₂) and U(IV) bound to biomass (i.e., monomeric U(IV)) are products of microbial U(VI) reduction in the field.
- Biogeochemical processes, molecular structure and composition, and diffusive transport processes can profoundly affect the stability of U(IV) species in subsurface environments.
- This portion of the SLAC SFA project has integrated laboratory and field scale experiments to assess the reactivity of U(IV) species.

**Objectives**

1. Measure the mobilization of U from U(IV) species under different chemical conditions.
2. Evaluate the effect of groundwater cations on the rates and mechanisms of UO₂ dissolution under environmentally relevant conditions.
3. Identify the impact of diffusive limitations on the oxidative dissolution of UO₂ at experimental conditions relevant to uranium-contaminated aquifers.
4. Quantify UO₂ dissolution rates in situ in the subsurface.

**Hypotheses**

- Different U(IV) species respond to chemical extractants in unique ways that can serve as a foundation toward understanding their reactivity in bio-reduced sediments.
- Groundwater cations can interact with UO₂ in subsurface environments to increase its stability.
- The rate of U release resulting from oxidative UO₂ dissolution limitations will control diffusive transport limitations.
- Dissolution of UO₂ in subsurface aquifers rich in carbonate proceeds via oxidation and loss of surface U atoms and U(IV) does not accumulate in corrosion products.

**Mobilization of U from Different U(IV) Species**

- Synthesis of U(VI) and molecular U(OH)₄ has similar low degrees of mobilization in water soluble, ion exchangeable, and ligand extractable experiments. These behaviors of biogenic U(IV) were similar to those observed in U(VI) and monomeric U(IV).
- Monomeric U(IV) was more susceptible than biogenic UO₂ to oxidative mobilization.

**Effect of Groundwater Cations on UO₂ Dissolution**

- UO₂ dissolved from a suspension in water 100 mM NaCl, pH 8.3, in the absence of NaCl, 45% monomeric U(IV) and 55% unreacted UO₂.
- EDDS, and chemical extractions.
- Efflux from field experiments performed at the Old Rifle, Colorado site.
- Zn: supersaturation with respect to ZnCO₃.
- Two types of biogenic UO₂ obtained from SSF and Shewanella oneidensis.
- UO₂ dispersed from synthetic UO₂ in the subsurface and strongly inhibit its oxidative dissolution.

**Effect of Diffusive Limitations on UO₂ Dissolution**

- Continuous stirred reactor was used at 0.01 M MOPS buffer at pH 7.8, residence time = 24 hours.
- UO₂ placed in dialysis-covered membrane tubes as suspensions or embedded in polyacrylamide gels (gel pucks) for mass balance measurements.
- Two types of biogenic UO₂ obtained from Shewanella oneidensis strain MR-1.
- UO₂ deployed for 270 and 630 months in wells B-02 (oxic well) and P-103 (naturally reducing).

**Materials**

- Synthetic U(VI)
- Biogenic UO₂ (consisted of 55% biogenic UO₂ and 45% monomeric U(IV))
- These materials were first acid digested to determine total U content.

**Chemical Extractions**

- Water soluble: Deionized water (0.01 M MOPS buffer at pH 7.8, residence time = 24 hours)
- Ion exchangeable: Ammonium-nitrate: 0.01 M NH₄NO₃ + 0.01 M MOPS buffer at pH 7.8, residence time = 24 hours
- Ligand extractable: Sodium Fluoride (0.1 M NaF + 0.01 M MOPS buffer at pH 7.8, residence time = 24 hours)

**Conclusions**

- Water soluble UO₂ dissolved in water 100 mM NaCl, pH 8.3, in the absence of NaCl, 45% monomeric U(IV) and 55% unreacted UO₂.
- EDDS, and chemical extractions.
- Efflux from field experiments performed at the Old Rifle, Colorado site.
- Zn: supersaturation with respect to ZnCO₃.
- Two types of biogenic UO₂ obtained from SSF and Shewanella oneidensis strain MR-1.
- UO₂ deployed for 270 and 630 months in wells B-02 (oxic well) and P-103 (naturally reducing).

**Objectives**

1. To study the rates and processes controlling oxidative dissolution of UO₂ in aquifers with diffusive limitations to mass transfer.
2. To develop a decay model for biogenic UO₂ dissolution over long-time-scales (e.g., 5 years for complete dissolution).

**Hypotheses**

- Different U(IV) species respond to chemical extractants in unique ways that can serve as a foundation toward understanding their reactivity in bio-reduced sediments.
- Groundwater cations can interact with UO₂ in subsurface environments to increase its stability.
- The rate of U release resulting from oxidative UO₂ dissolution limitations will control diffusive transport limitations.
- Dissolution of UO₂ in subsurface aquifers rich in carbonate proceeds via oxidation and loss of surface U atoms and U(IV) does not accumulate in corrosion products.

**Impact**

- Interactions with divalent groundwater cations can affect the longevity of UO₂ and the mobilization of U(IV) in remediated subsurface environments.
- Diffusive limitations to transport can substantially prolong the lifespan of UO₂ at oxidic conditions. Laboratory-measured rates can be useful for predicting U mobility in diffusion-limited field settings once limitations are taken into account.
- Monomeric U(IV) and biogenic UO₂ respond similarly to complexing and ion exchanging extractants, but monomeric U(IV) is more labile at oxidizing conditions.

**Ongoing Work**

- Aqueous chemistry experiments to investigate the mobilization of U in biogenic UO₂ with and without biogenic humic material.
- XAS characterization of synthetic UO₂, biogenic UO₂, and monomeric U(IV) before and after chemical extractions.
- Chemical extractions of sediments and biogenic UO₂ materials obtained from field experiments performed at the Old Rifle, Colorado site.

**Products/Papers**

- Seven presentations at national and international conferences.

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