Characterization of Uranium Species in Sediments under Iron and Sulfate Reducing Conditions Using Synchrotron-Based Techniques

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OBJECTIVES:

- To determine the chemical structure of uranium (IV) complexes found in subsurface sediments at Old Rifle, Colorado, a former uranium mill.
- To understand the biochemical process of uranium reduction under ironic and sulfuric reduction conditions.

INTRODUCTION:

- Large uranium plumes still persist in groundwater at legacy Department of Energy (DOE) due to past uranium extraction and processing.
- At Old Rifle, >34 million gallons of groundwater is contaminated with uranium.
- Such contamination is particularly problematic because it occurs at depth, is present in large volumes, and cannot be easily accessed for clean-up.
- One method of remediation being investigated is the bioreduction of soluble U(VI) to insoluble U(IV) complexes or uraninite (UO$_2$) through the in-situ stimulation of metal-reducing bacteria.
- Uranium complexes produced by metal-reducing bacteria can be characterized using X-ray absorption spectroscopy (XAS) and X-ray microscopy (XRM).

METHODS AND RESULTS:

- Columns containing subsurface sediments from the Rifle test site were amended with acetate and uranium and flushed with groundwater for various duration.

<table>
<thead>
<tr>
<th>Conditions of Sediment Columns</th>
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<tbody>
<tr>
<td>Column ID</td>
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<tr>
<td>-----------</td>
</tr>
<tr>
<td>2B</td>
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<tr>
<td>4A</td>
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<td>4E</td>
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- During the initial days of amendment, iron reduction by metal-reducing bacteria is the dominant metabolic process.
- After ~30 days of amendment, shift to sulfate-reduction as the dominant terminal electron accepting process due to the growth of the sulfate-reducing bacteria population.

X-Ray Microscopy

- Uranium coat visible around Fe-S containing sediment in all three columns.

DISCUSSION:

- Uranium is shown to be highly associated with Fe-S coatings; uranium complexes bound to Fe-S structure
- Fe XANES of the sediment cross-section of column 2B and 4A show that the iron complexes contain Fe(II); XRM images show that the S is highly associated with Fe → possible iron complex is Fe(II)-S.
- As duration of sulfate reduction increases, sulfate concentration in sediment increases; however, uranium coating decreases → decrease in U(IV) production as sulfate-reducing bacteria dominate reducing process.

FURTHER STUDIES:

EXAFS on sediments need to be taken to distinguish the uranium complexes. Sediments will be amended at different time points during the transition between iron-reduction to sulfate-reduction phase.

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