

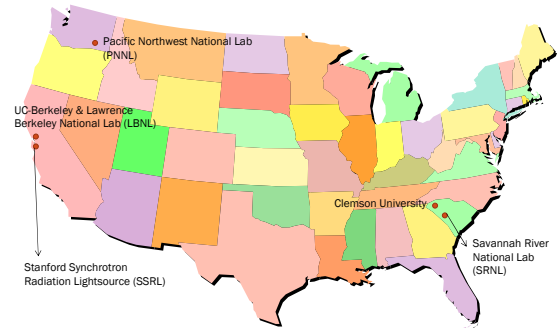
Influence of Iron Redox Transformations on Plutonium Sorption to Sediments

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Collaborator Map



Objective

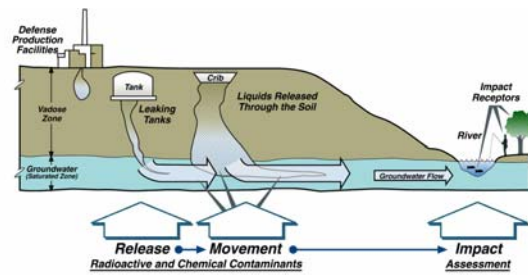
to impose changes on Fe mineralogy within a sediment and relate them to changes in Pu(V) surface-mediated reduction to Pu(IV)

Hypothesis

with increasing vigor of treatments (temp and time), the amount of iron in the soil decreases, resulting in a mineral phase that is less reactive

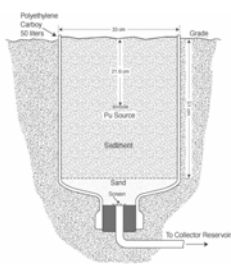
this will correspond to decrease in the rate and extent of Pu(V) surface-mediated reduction to Pu(IV)

Vadose Zone



<http://picturethis.pnl.gov>

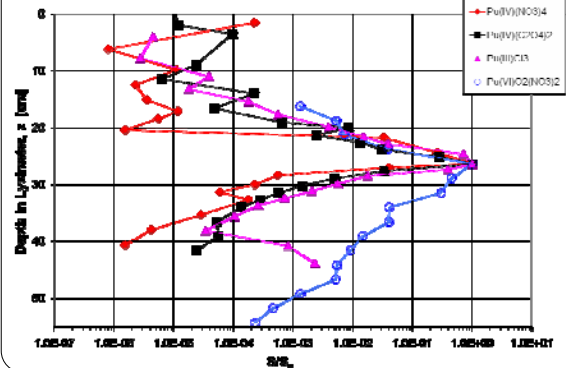
Pu Lysimeters at SRNL



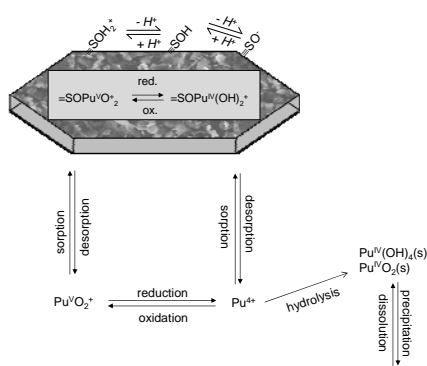
| Pu Source | Years in Ground |
|--|-----------------|
| $\text{Pu}^{\text{III}}\text{Cl}_3$ | 11 |
| $\text{Pu}^{\text{IV}}(\text{C}_2\text{O}_4)_2$ | 11 |
| $\text{Pu}^{\text{IV}}(\text{NO}_3)_4$ | 11 |
| $\text{Pu}^{\text{IV}}\text{O}_2(\text{NO}_3)_2$ | 2 |



Distribution of Pu in Lysimeters



Plutonium Sorption/Desorption



Approach

- Chemically treat vadose zone sediment with various complexants and reductants to selectively leach and/or reduce iron oxide and phyllosilicate phases
- Characterize iron mineralogy by Mössbauer spectroscopy
- Characterize Pu oxidation state speciation by X-ray Absorption Near Edge Structure (XANES), solvent extraction, and lanthanum fluoride coprecipitation
- Relate changes in Pu(V) sorption and reduction kinetics to changes in solid phase Fe mineralogy and Fe oxidation state

Sediment Characteristics

| Sediment ID | Description of Chemical Treatment | Treatment Objective | Surface Area (m ² g ⁻¹) |
|-------------|--|--|--|
| WS | untreated <53-µm sediment | control | 32.7 |
| HH | hydroxylamine-hydrochloride-25°C-0.5 hours, <53-µm sediment | soluble manganese oxides & amorphous Fe(III) oxides | 33 |
| AAO | Acid ammonium oxalate in the dark, <53-µm sediment | soluble poorly-crystalline iron oxides | 30.4 |
| DCB1h-25°C | dithionite-citrate-bicarbonate-25°C-1 hour, <53-µm sediment | Amorphous and crystalline iron oxides + phyllosilicate Fe(III) | 31.2 |
| DCB4h-25°C | dithionite-citrate-bicarbonate-25°C-4 hours, <53-µm sediment | Same as above | 36.5 |
| DCB4h-70°C | dithionite-citrate-bicarbonate-70°C-4 hours, <53-µm sediment | Same as above | Not measured |

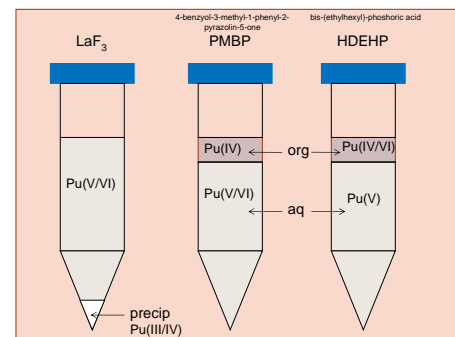
Treated Sediments

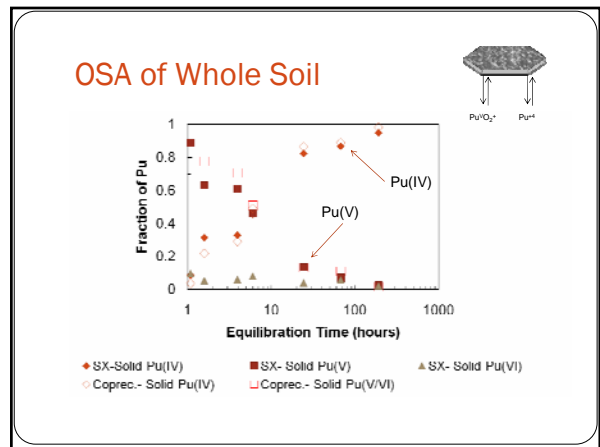
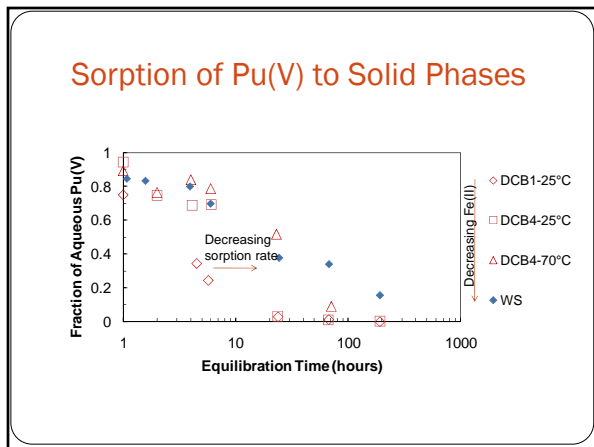
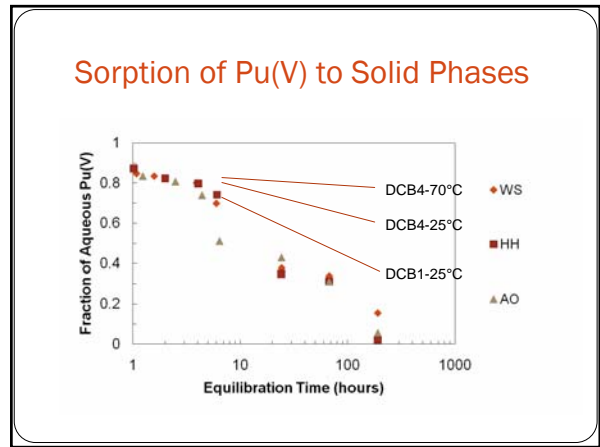
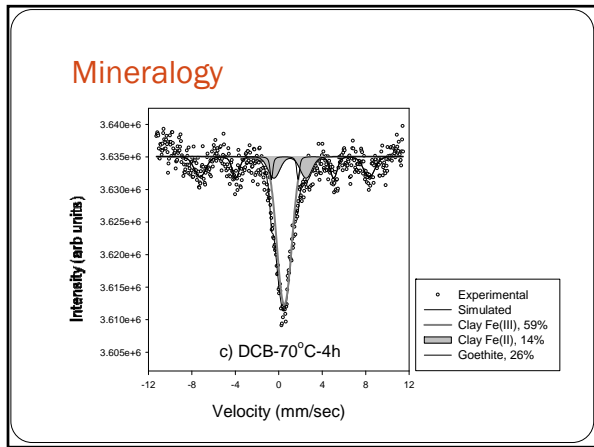
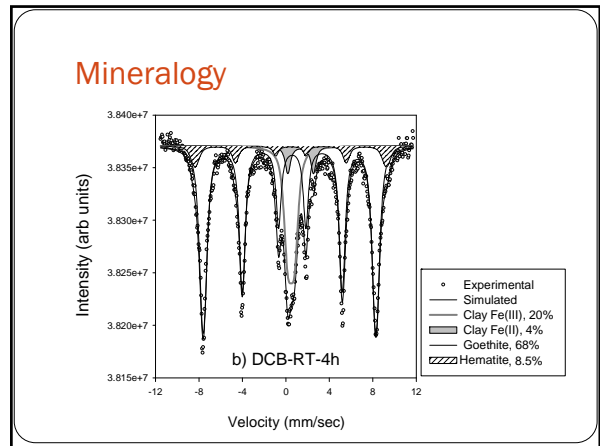
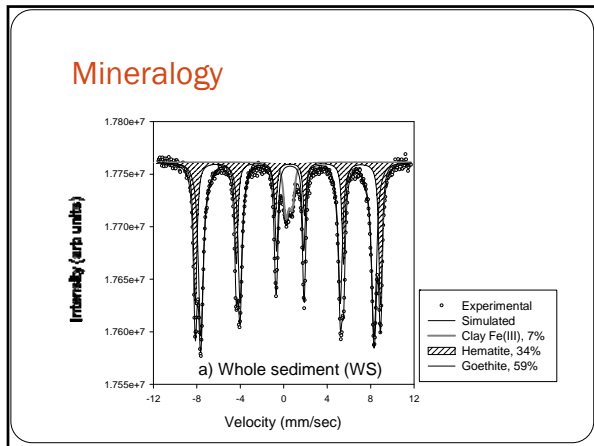


Sorption of Pu(V) to Solid Phases

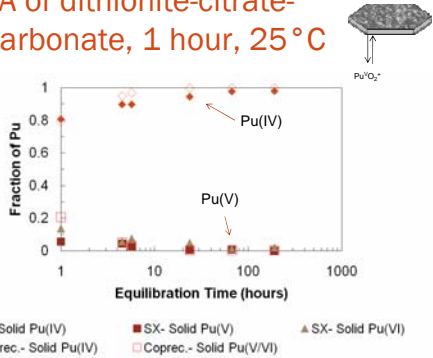
- 5 g/L sediment
- Ionic strength = 10mM NaCl
- pH = 5.3
- [Pu(V)] = 10⁻¹⁰ M
- After equilibration period:
 - Centrifuge to leave <100nm particles in supernatant
 - Aliquot of supernatant for LSC
 - Remaining supernatant passed through 3K MWCO centrifugal filter (1-5nm)
 - Oxidation state analysis (OSA) of filtrate
 - Wet sediments resuspended in 0.3M HCl for 15 min. to quantitatively leach Pu(V/VI)

Oxidation State analysis procedure

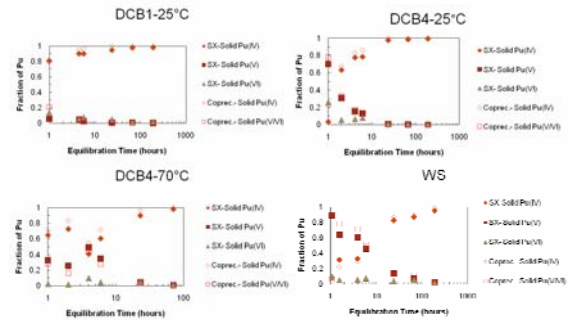




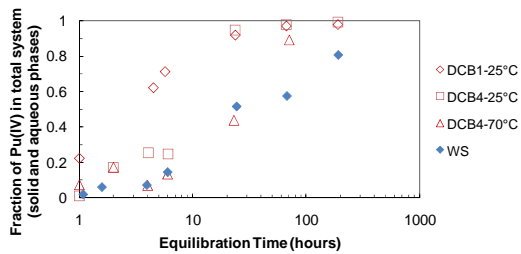
OSA of dithionite-citrate-bicarbonate, 1 hour, 25 °C



OSA Comparison



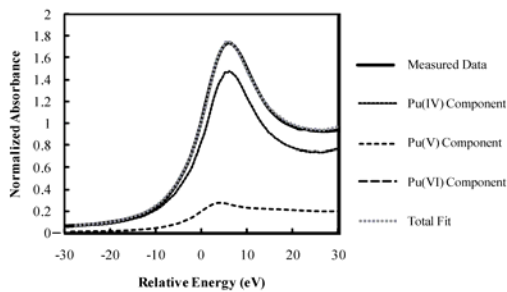
Sediment Reactivity



Trends

- Mössbauer results indicate that **increasing treatment temperature and reaction times decreased overall amount of iron in the system**:
 - WS > HH > AAO > DCB1-25°C > DCB4-25°C > DCB4-70°C
- Mössbauer results also indicate that the fraction of Fe(II) in the system followed:
 - DCB1-25°C > DCB4-25°C > DCB4-70°C
- Sorption data indicate that the amount of Fe(II) in the system **increased the rate of Pu(V) surface-mediated reduction to Pu(IV)**:
 - DCB1-25°C > DCB4-25°C > DCB1-70°C ≥ WS

XANES



Photoelectric Effect and X-ray Absorption Edge

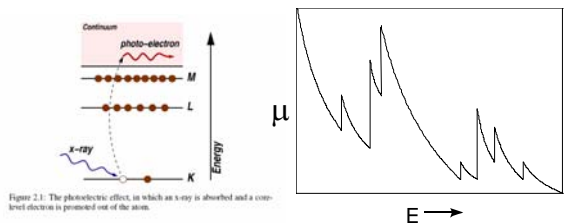
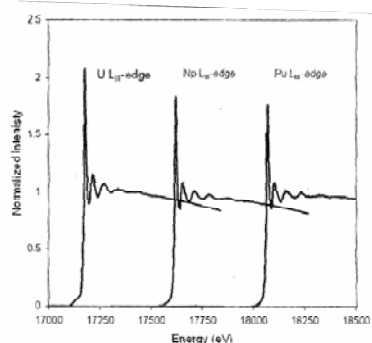


Figure 2.1: The photoelectric effect, in which an x-ray is absorbed and a core-level electron is promoted out of the atom.

X-ray Absorption Spectroscopy (XAS)



XANES Spectra of Actinide Oxidation States

Chemistry of the Actinide and Transactinide Elements, 2006

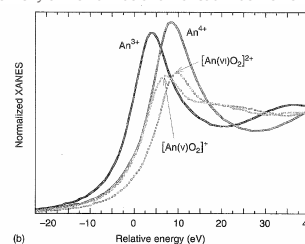
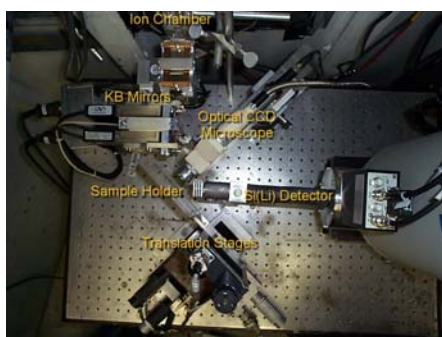


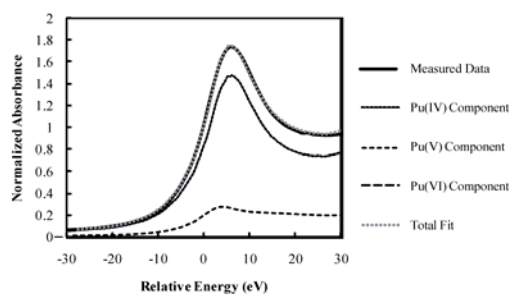
Fig. 28.2 (b) Representative XANES data as a function of oxidation state and coordination environment. The trivalent and tetravalent spectra show about a 4 eV difference in the edge energy, as do the pentavalent and hexavalent dioxo moieties. However, a comparison of tetravalent with pentavalent dioxo spectra show very small, sometimes negative shifts in the edge energies, as shown. In addition, the shapes of the spectra are different. The trivalent and tetravalent species tend to have a larger white-line feature whereas the dioxo coordination of the higher oxidation states produces multiple scattering that results in the shoulder at higher energy of the edge peak itself (Hudson et al., 1995a).

National Synchrotron Light Source Beamline X26A



XANES – Whole Soil

XANES ~ 87% Pu(IV)
SX ~ 85% Pu(IV)
LaF₃ ~ 86% Pu(IV)



Conclusions

- Sediments from the SRS facilitated surface-mediated reduction of Pu(V) to Pu(IV)
- In all of the treated sediment samples, the aqueous phase was dominated by Pu(V) while the solid phase was dominated by Pu(IV)
- The amount of Fe(II) in the sediments decreased with the vigor of DCB treatments
- Decrease in Fe(II) concentration correlated with a decrease in the rate of Pu(V) reduction to Pu(IV)
- Implications for DOE sites?

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- Portions of this research were performed under appointment of the OCRWM Graduate Fellowship Program.
- Mössbauer spectroscopy measurements were conducted at the Environmental Molecular Sciences Laboratory (EMSL).
- XANES spectroscopy was carried out at the Stanford Synchrotron Radiation Lightsource.
- L.K. Schwaiger for assisting in XANES data collection
- Tom Resch (PNNL) for help with particle size separations

Silica-²⁴²Pu and silica-²³⁸Pu comparison

- Expected similar results from binary systems
- Solutions contain same Pu activity, but different concentrations
 - ²⁴²Pu = 10⁻⁸ M ; 22000 cpm/L
 - ²³⁸Pu = 10⁻¹⁰ M ; 26000 cpm/L
- Calculating theoretical H₂O₂ concentration
 - ²⁴²Pu alpha energy (MeV)= 4.90
 - ²³⁸Pu alpha energy (MeV)= 5.50
 - A 4 MeV alpha particle produces 1.64 H₂O₂ per 100 eV energy loss

