Plutonium Speciation in Hanford Sediments and Redox Transformations Induced by Fe(II)

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Objective

This project focuses on the identification of the changes in the chemical form of Pu at different locations and with depth in the sediments at the Hanford site and how these chemical forms are altered in response to changes in redox conditions. The overall objective is to provide a baseline of knowledge on Pu contamination, reactivity, and the potential for future subsurface migration.

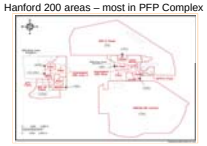
Approach

Review the available data on transuranic disposal at Hanford to gain a site wide perspective on important transuranic contamination issues. Where possible obtain and archive samples from field studies of transuranic contamination at Hanford. Conduct , in association with collaborators, detailed molecular level characterization studies of the chemical form of transuranics in the sediments. As part of the biogeochemical electron transfer science theme, conduct experimental laboratory studies on the transformations of the different chemical forms of Pu found in the sediments in response to changes in redox conditions that could occur at the site.

Review of Transuranic Contamination at Hanford

Hanford site – vast majority in 200 area
Pu-241 most important in term of activity

Hanford 200 areas – most in PFP Complex



PFP Complex Waste Sites – large quantities of both high salt and low salt waste disposed

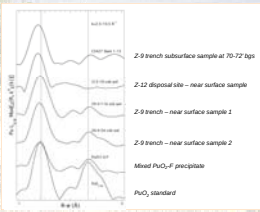
Obtaining subsurface materials

Obtained and inventoried samples from two different disposal locations (Z-9 and Z-12) and two sediment cores at the Z-9 site.

Speciation Studies: Chemical form of Pu changes with disposal location and depth in the subsurface.

X-Ray Absorption Spectroscopy

Chemical form changes with depth and disposal location



Fourier transform; c(R), modulus of k^3-weighted Pu L_3 EXAFS spectra using a sine window function.

Not Typical PuO_{2+x}

Pu-O distance significantly shorter for the Z-9 subsurface sample and for the sample at the Z-12 site. Only the near surface samples from the Z-9 site show the typical PuO_{2+x} distance. Inclusion of fluoride?

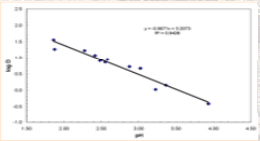
Subsurface sample shows non-typical very long range order.

Z-12 sample does not show any long range order (monomeric Pu?)

Potential Impact of Co-disposed organics (CCl_4)

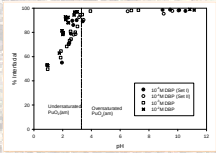
Pu partitions into the organic phase only at low pH. As pH increases the amount of Pu in the organic phase decreases. However, this loss of Pu from the organic phase is not found in the aqueous phase. Instead the Pu appears to accumulate at the organic/aqueous interface.

Distribution of Pu(IV) between organic and aqueous phases



Extraction of Pu(IV) by 0.001 M DBP in CCl_4 as a function of pH at I = 1.0 M of $NaNO_3$ and at room temperature. The distribution coefficient, D, equals the ratio of the concentration of Pu in the organic phase divided by the concentration in the aqueous phase.

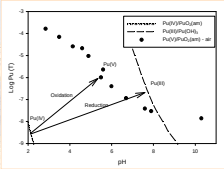
Accumulation of Pu at the organic/aqueous interface



Extraction studies of Pu(IV) in CCl_4 at different concentrations of DBP. Interfacial percentage is the difference between the total added and the amount recovered in the combined aqueous and organic phases.

Biogeochemical Electron Transfer Science Theme

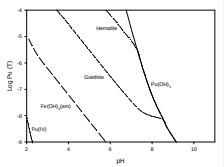
Pu in Hanford sediments has been found to exclusively occur in the solid phase. Hence one issue of primary concern is the potential for this solid phase Pu to be remobilized. **Oxidation/reduction reactions are the primary means for remobilization of Pu into the aqueous phase.**



Calculated PuO_2(am) solubilities with different Fe(II)products (Initial Fe(II)=0.001M)

Impact of oxidation and reduction reactions on the solubility of PuO_{2+x}(am) .

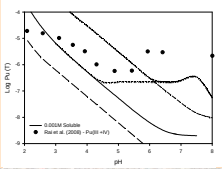
Oxidation produces Pu(V) aqueous species and reduction Pu(III) species.



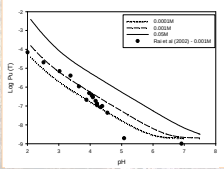
Reduction of PuO_{2+x} to Pu(III) by Fe(II) depends dramatically upon the nature of the Fe(III) reaction product formed.

Identification of the Fe(III) reaction product key to determining the remobilization of subsurface Pu.

Thermodynamically possible changes in PuO_2(am) solubilities with addition of solids (Initial Fe(II) 0.001M)



PuO_2(am) solubilities with different initial soluble Fe(II) concentrations



Potential impact of formation of different Fe(III) reaction products and comparison with existing experimental data

Summary and Conclusions

Transuranic contamination at Hanford occurs primarily in the 200 area in the central plateau. The highest levels of contamination are located near the Z-plant complex where in some cases the transuranics (Pu and Am) have migrated deep into the subsurface. We have found the Pu in the sediments to occur exclusively as Pu(IV) but not exclusively as the expected Insoluble PuO_{2+x}. The exact chemical form varies with disposal location and with depth in the sediment. The mechanism of subsurface migration remains unknown. Our recent results indicate that transport in the organic phase, or at least the organic/aqueous interface is a potential, but previously unrecognized, transport vector. Since Pu is found almost exclusively in the solid phase, remobilization into the aqueous phase is a primary concern. The most likely mechanism of remobilization is via redox reactions involving the Pu(IV) compounds. Our initial work in this area, as part of the biogeochemical electron transfer science theme, focuses on redox reactions between Pu(IV) compounds and Fe(II). The extent of this potential remobilization mechanism is critically dependent on the nature of the Fe(III) reaction product as well as the initial chemical form of Pu(IV).

Future Research

Our current research direction is focused both on defining the chemical form of Pu in the sediments and evaluating potential remobilization mechanisms. Our studies with the contaminated materials utilize XAS measurements of Pu speciation, NMR measurements of P speciation, and analysis of individual particles by our collaborators at LLNL using NanoSIMS. Our studies as part of the biogeochemical electron transfer science theme focus on redox reactions between Pu(IV) compounds and Fe(II). Specifically, reduction reactions of PuO_{2+x} by Fe(II) yielding different Fe(III) reaction products including ferrihydrite, goethite, magnetite, and titanomagnetites.

Key Contributions

- **Summary report on transuranic contamination at Hanford -** *K.J. Cantrell (2009) Transuranic Contamination in Sediment and Groundwater at the U.S. DOE Hanford Site. PNNL-18640.*
- ***Note to the DOE site contractor*** *summarizing potential transuranic sites at Hanford where future sample collection would present scientific opportunities.*
- ***Obtaining subsurface samples*** *with high Pu concentrations from two disposal sites and with depth in two cores. Samples available to collaborators.*
- ***Pu contamination and characterization activities***
  - *A.R. Felmy , K.J. Cantrell and S.D. Conradson. Plutonium Contamination Issues in Hanford Soils and Sediments; Discharges from the Z-Plant (PFP) Complex. Chemistry and Physics of the Earth (in press).*
- ***Pu speciation research*** *- Rai D., D.A. Moore, A.R. Felmy, K.M. Rosso, and H. Bolton Jr. $PuPO_4$(cr,hyd.) Solubility product and Pu^{3+} Complexes with Phosphate and Ethylenediaminetetraacetic Acid. Journal of Solution Chemistry (in press).*
- ***Integration of Pu research*** *into the Biogeochemical electron transfer science theme in the PNNL SFA.*

External Collaborations

- **LLNL (M. Zavarin and A. Kersting)**
- **UNLV (K. Czerwinski**
- **WSU/Moscow State University (S. Kalmykov and S.B. Clark)**
- **LANL (D. Clark)**

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