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Plutonium Speciation and Its Effects on Environmental Migration

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EXAFS Studies Performed in Collaboration with
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Actinide Environmental and Coordination Chemistry,
Chemistry and Environmental Divisions
Los Alamos National Laboratory

Plutonium Speciation and Its Effect on Environmental Migration

Overall Goal: Understand chemistry of Pu in environmental systems, to assist in remediation and risk assesment.

Detailed Research on Environmentally Important Plutonium Species
(Oxides, Hydroxides, Carbonates, ...)
Formation, Stability, Structure, Chemistry
Provides: Basis of Understanding
Thermodynamic Data for Modeling
Spectroscopic Signatures
Structural Details

Geochemical Modeling
Known Thermodynamic Data and Site Composition
Provides: Basis of Understanding, 'Snapshot'
Target Species for Research
Prediction of Solubility and Mobility

Characterization of Samples from a Contaminated Site
(Rocky Flats Environmental Test Site)
Provides: Reality!
Assistance in Evaluating Risks and Remediation

Mass Spectroscopy
Concentration
Isotopic Composition
Origin: Fallout vs. Site
Elemental

Separations and Counting
Concentration
Localization/Correlations
Macroscopic Environment

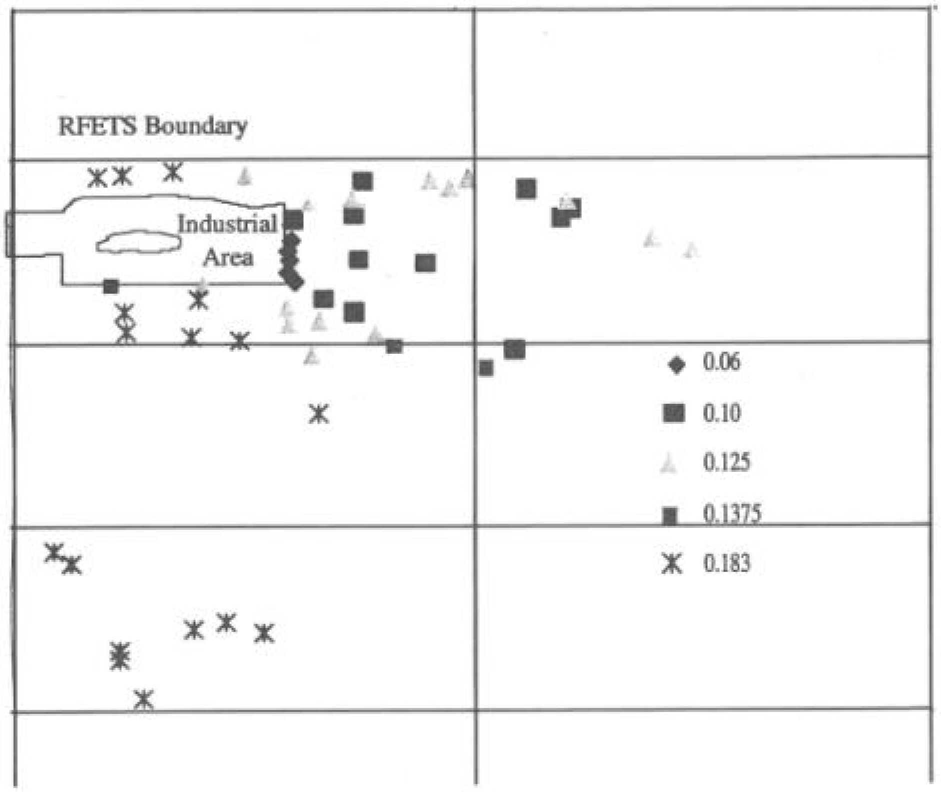
Electron Microscopy
Qualitative Concentration
Localization/Correlations
Morphology
Microscopic Environment

X-ray Absorbance Spectroscopy
Element
Oxidation State
Coordination Environment
Molecular Speciation

$^{240}Pu/^{239}Pu$ *Ratios Determined Using TIMS*

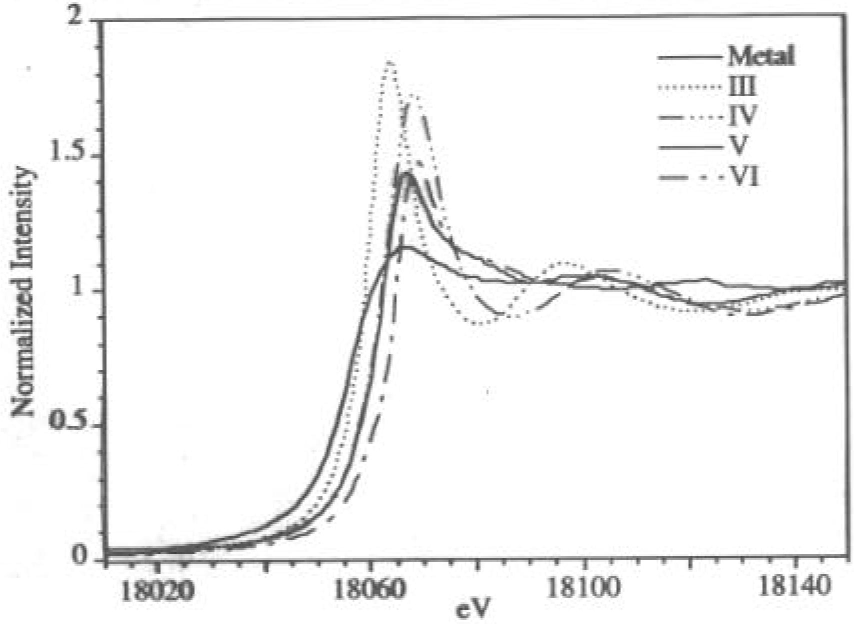
10 km grid

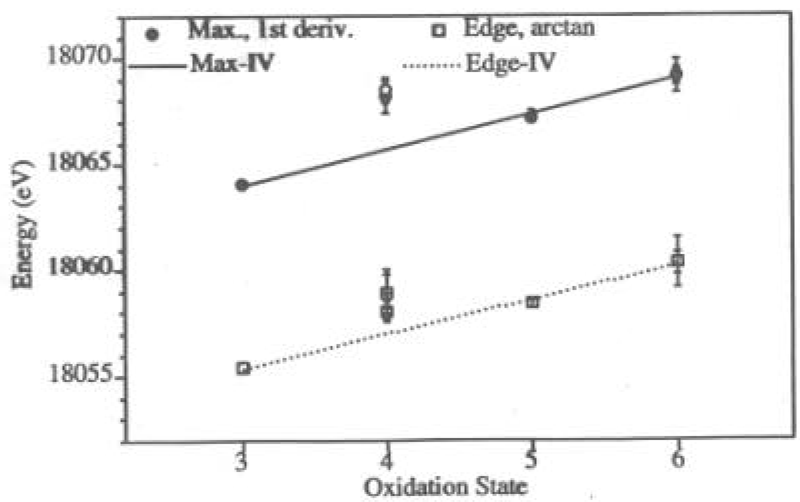
RFETS area is approximately 30 km^2



Plutonium migration from the site
does not appear to be rapid or significant

X-ray Absorption Spectra of Plutonium Metal and Aquo Ions





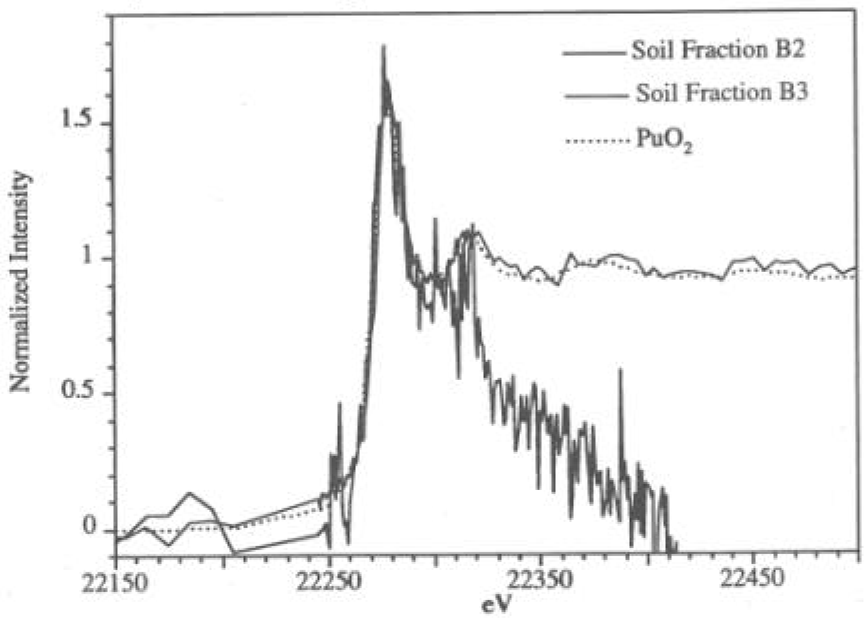
S. D. Conradson , I. A. Mahamid, D. L. Clark, N. J. Hess, E. A. Hudson,
M. P. Neu, P. D. Palmer, W. H. Runde, C. D. Tait*Polyhedron*, **1998**, *17(4)*, 599.

Size Fractionation, Radioactivity, and XAS Spectra of Soil Samples from 903 Pad Area, Collected 3/24/98

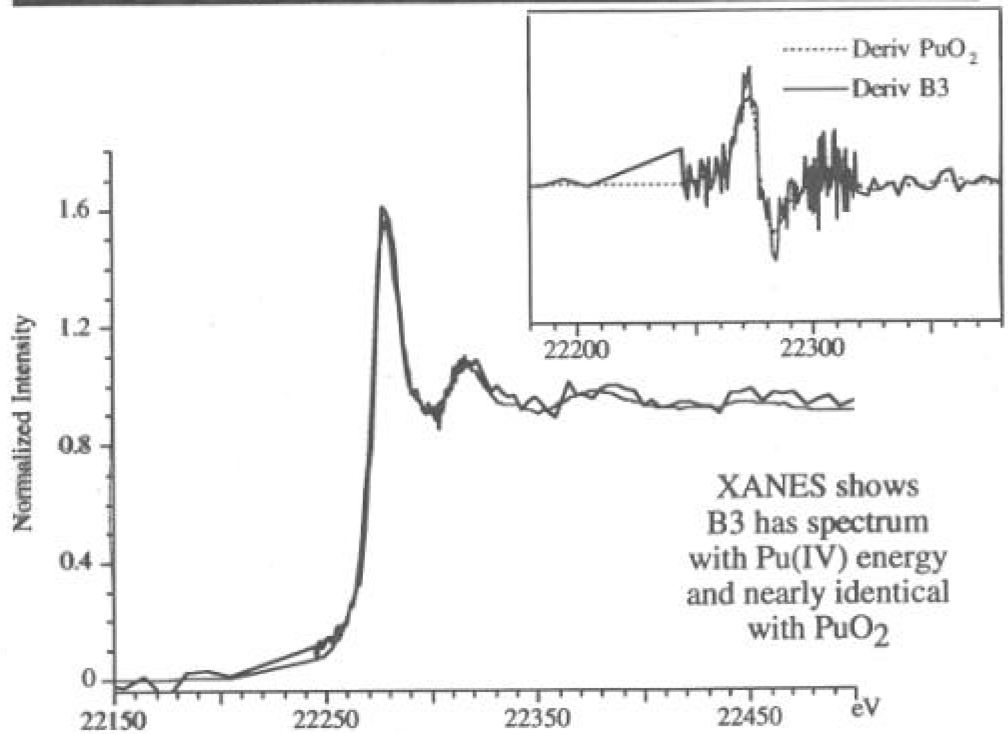
Fractionations of Soils and Gamma Counting Results

Fraction	Size	Net CPS/g (gross gamma, ^{241}Am)
0.0-0.5 ft.		
A1	> .0234 inch	------
A2	0.0234-0.0164 inch	9.00
A3	0.0116-0.0164 inch	22.97
A4	>0.0116 inch	8.83
0.8-1.5 ft.		
B1	> .0234 inch (>600μm)	------
B2	0.0234-0.0164 inch (415-600μm)	30.20
B3	0.0116-0.0164 inch (415-600μm)	41.71
B4	>0.0116 inch (300μm)	78.19

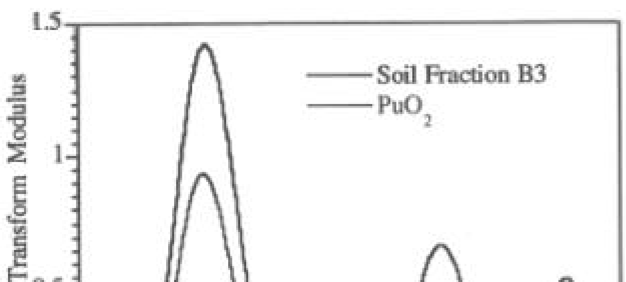
X-Ray Absorbance Spectra of Fractions Which Showed Pu Edge



X-Ray Absorbance of Soil Fraction B3



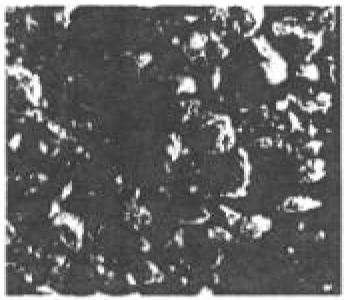
XANES shows B3 has spectrum with Pu(IV) energy and nearly identical with PuO_2



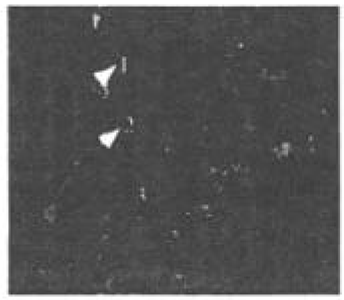
EXAFS shows Pu(IV) in B3 has ~8 oxygen 'neighbors' at 2.33Å

SEM Images and Element Mapping for Fraction B3

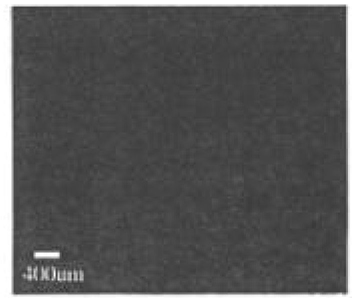
Normal SEM image



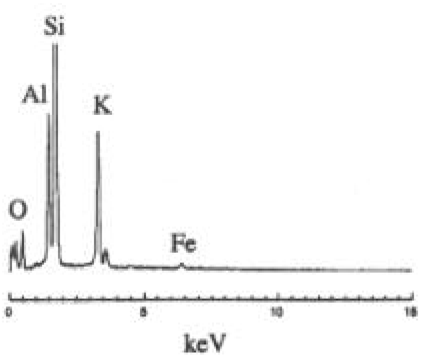
Pu-M element map



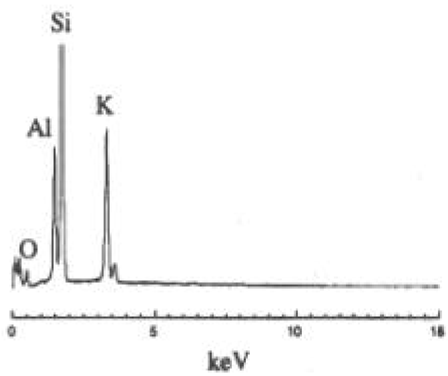
Pu-L element map



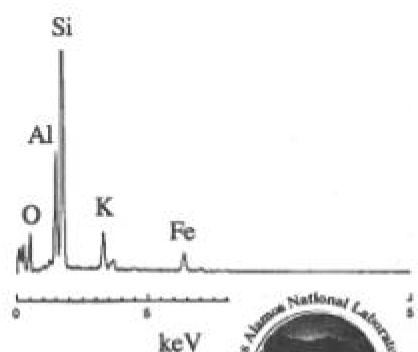
EDS pattern from spot # 1 in Pu-M element map



EDS pattern from spot # 2 in Pu-M element map



EDS pattern from spot # 3 in Pu-M element map

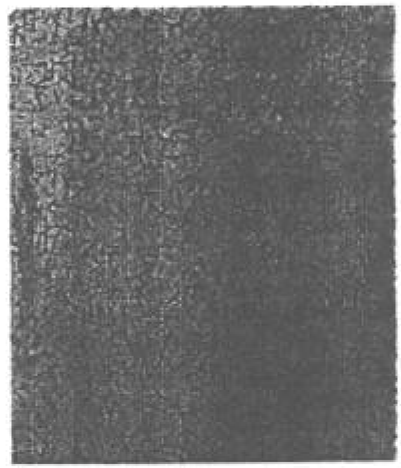


Actinide Environmental and Coordination Chemistry, Chemical Science & Technology Division.

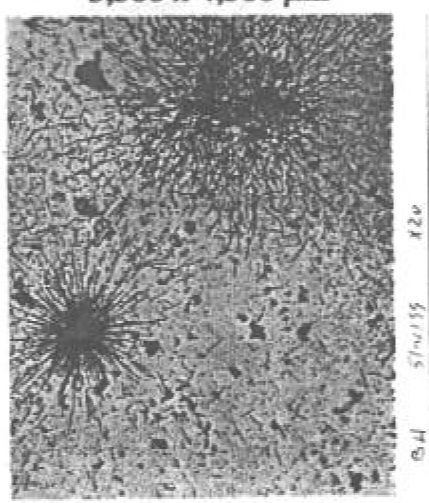
Radiographs of RFETS Soil Samples A3 and B4, 48 Hour Exposure Times

A3: Representative of soils
3,500 x 4,500 µm

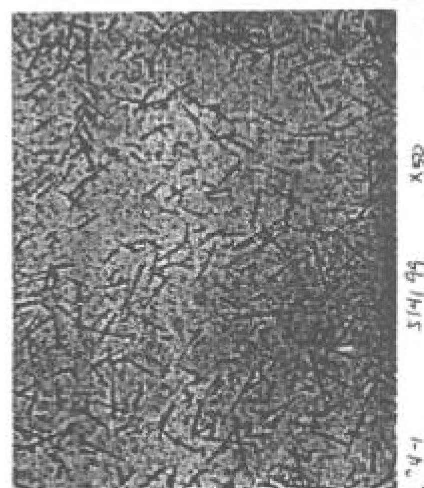
B4: 3,500 x 4,500 µm



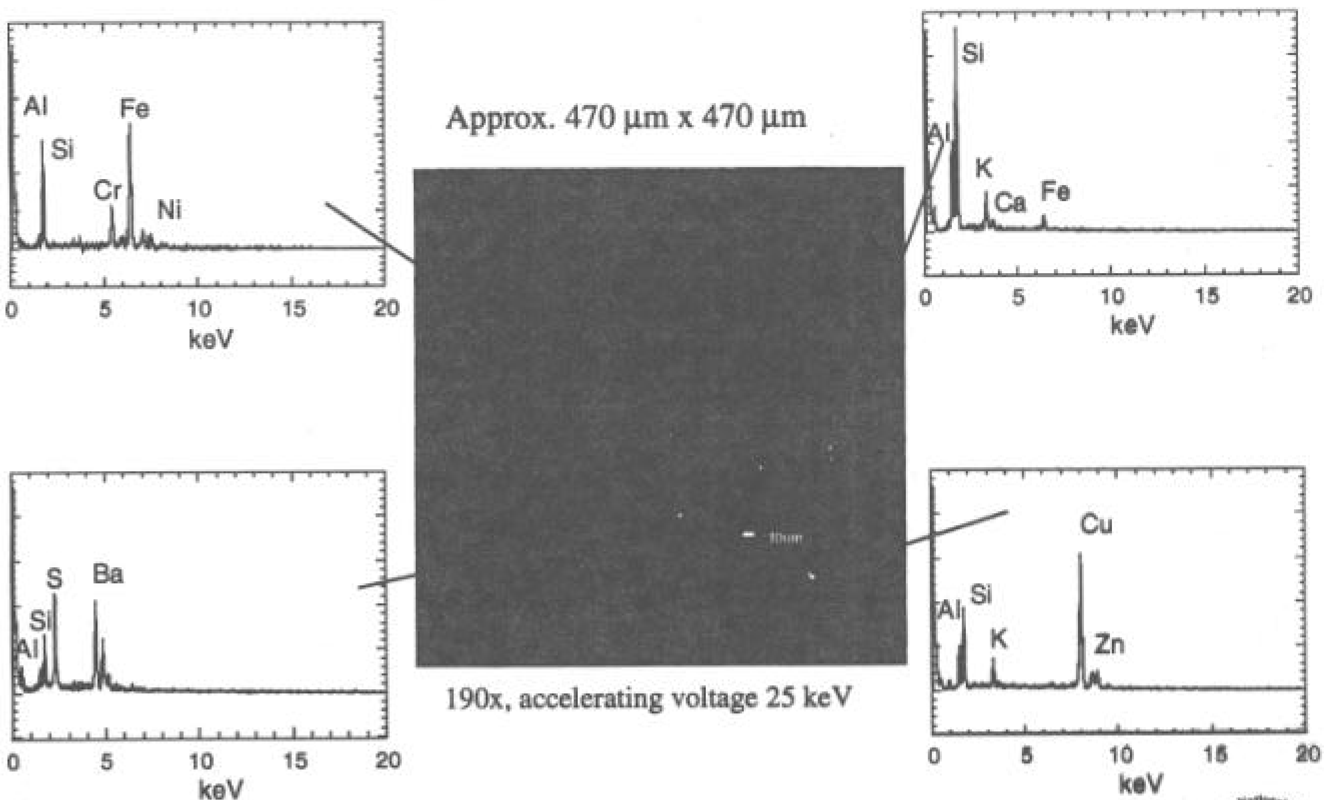
B4: Most localized and concentrated
3,500 x 4,500 µm



B4: 1,400 x 1,800 µm

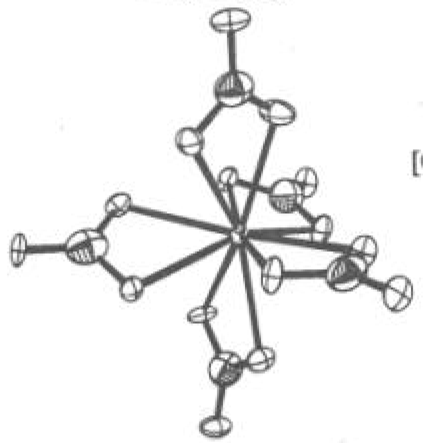


SEM Backscattered Electron Image and EDS of Soil Particle in Fraction B4



Single Crystal XRD Structures of An(IV) Pentacarbonate Complexes

$Pu(CO_3)_5^{6-}$

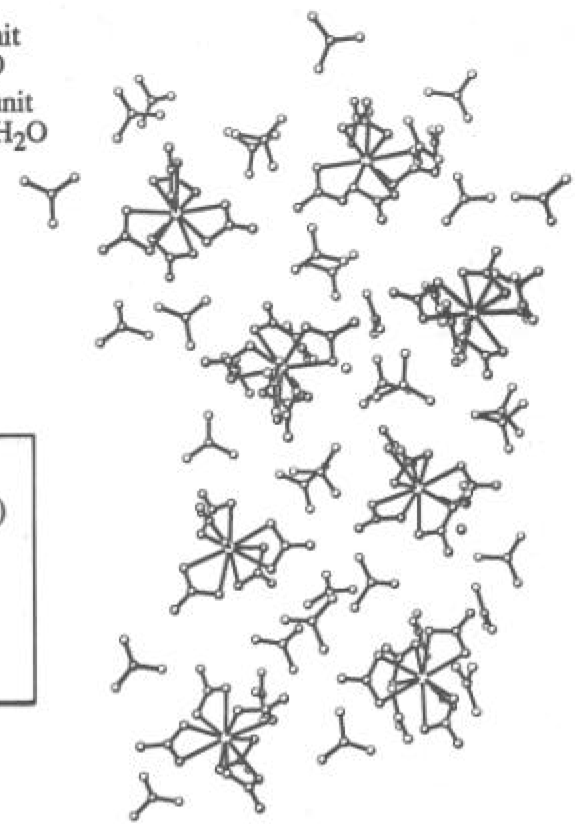


Triclinic, P_1
Pu: Z=2, 1 Pu/assy. unit
$Na_6Pu(CO_3)_5 \cdot 12H_2O$
Np: Z=16, 8 Np/assy. unit
$[C(NH_2)_3]_6Np(CO_3)_5 \cdot xH_2O$

Distance (Å)	Th	Np	Pu
Pentacarbonato	2.493(11)	2.431(9)	2.415(7)
Hexanitrato	2.57	2.51	2.49
Atomic R	0.94	0.87	0.86

Th to Np dec. less than atomic R (0.06 vs 0.07)
Np to Pu dec. more than atomic R (0.02 vs 0.01)

$[C(NH_2)_3]_6Np(CO_3)_5$



References

Voliotis, P. S.; Rimsky, A Acta Cryst. **1975**, B31, 2615.
Voliotis, P. S.; Rimsky, A Acta Cryst. **1975**, B31, 2612.
Clark, D. L.; et al. Inorg. Chem. **1998**, **37**, 2893-2899.
Allen, P. G.; et al. Inorg. Chem. **1996**, **35**, 2841-2845.

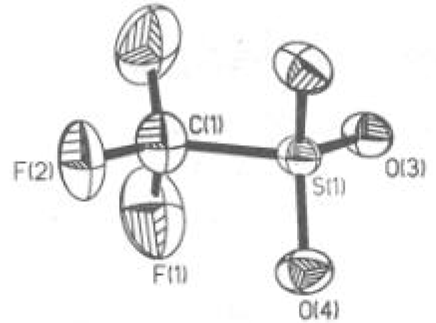
Single Crystal X-ray Structure of Aquo Pu(III)

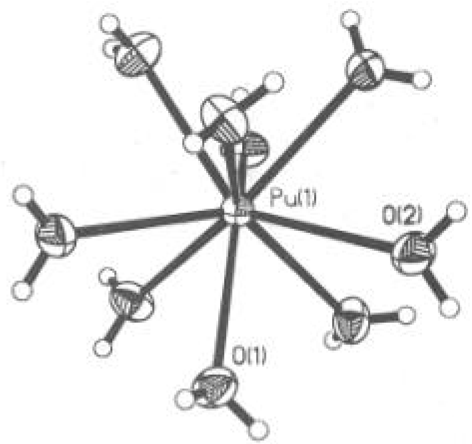
$Pu(H_2O)_3][CF_3SO_3]_3$

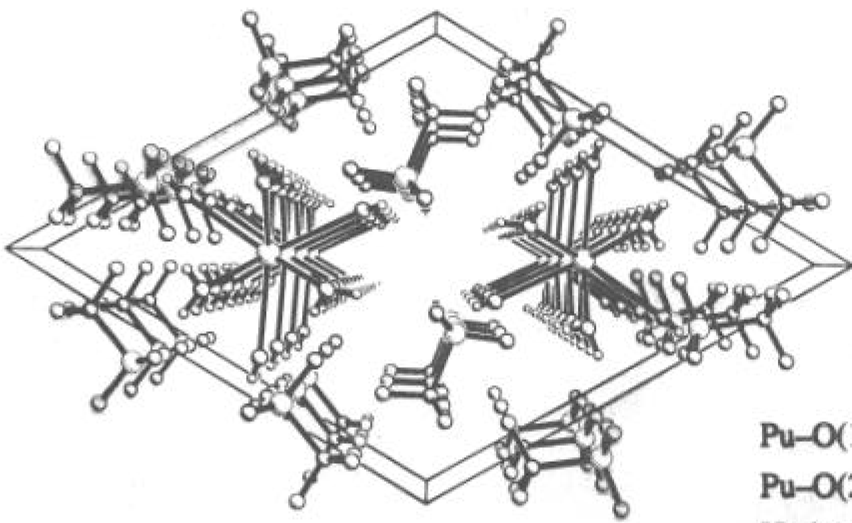
Hexagonal, P6(3)/m, Z = 2

a = 13.9283(6), b = 7.3816(4)

R_1 = 0.0243, wR_2 = 0.0452







Pu–O(1)	2.476(2)Å
Pu–O(2)	2.574(3)Å
Hydrogen Bonds	1.997-2.125Å

Characterization of Colloidal Pu(IV) Hydroxide

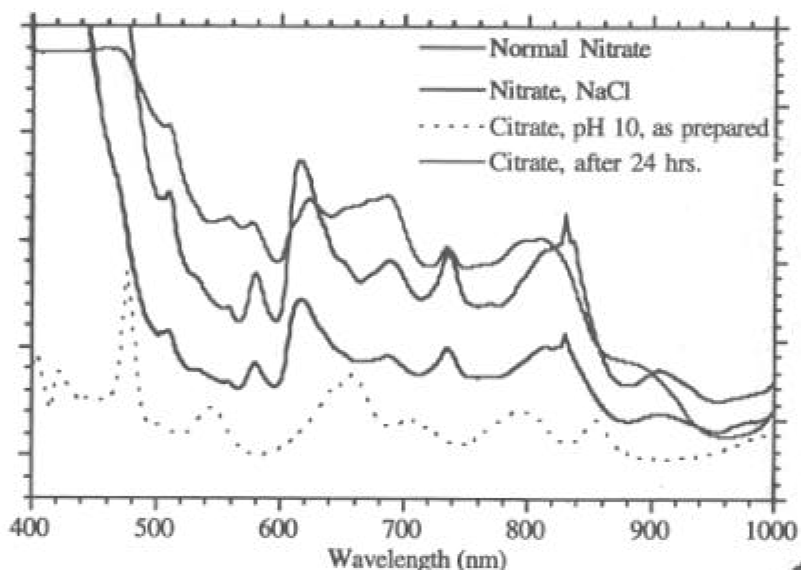
Synthesis:

$0.10\ M\ ^{239}Pu$ in $4\ M\ HNO_3$, hydrolyze, precipitate '$Pu(OH)_4$', wash repeatedly, peptize using dilute nitric acid, heat (80°C). Final solutions ~0.03 M Pu, $0.02\ M\ HNO_3$, pH 1.74. Solution conditions included saturated NaCl, $4\ M\ NaNO_3$ and 0.1 M Na citrate, $4\ M\ NaNO_3$

Multi-method characterization:

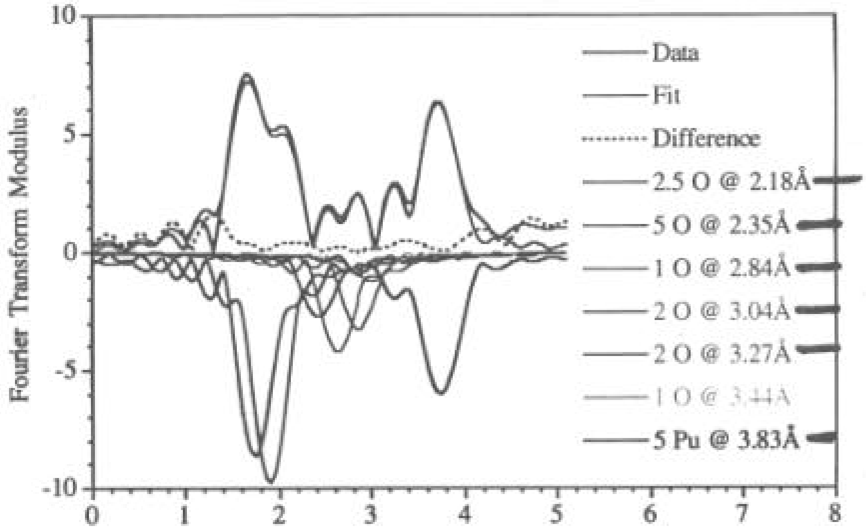
Optical Absorption Spectroscopy, Field Flow Fractionation, Dynamic Light Scattering, Extended X-ray Absorption Fine Structure, and Scanning Electron Microscopy.

Optical Absorbance Spectra

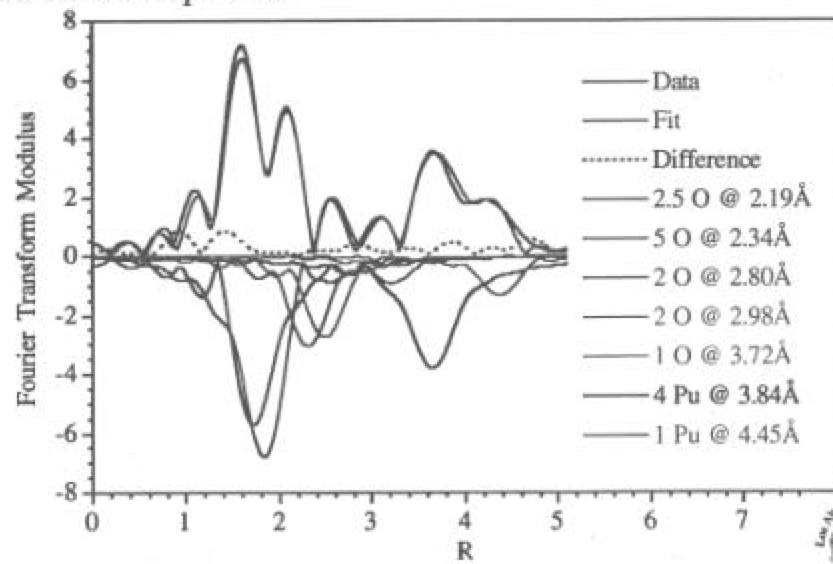


EXAFS of Pu(IV) Colloids

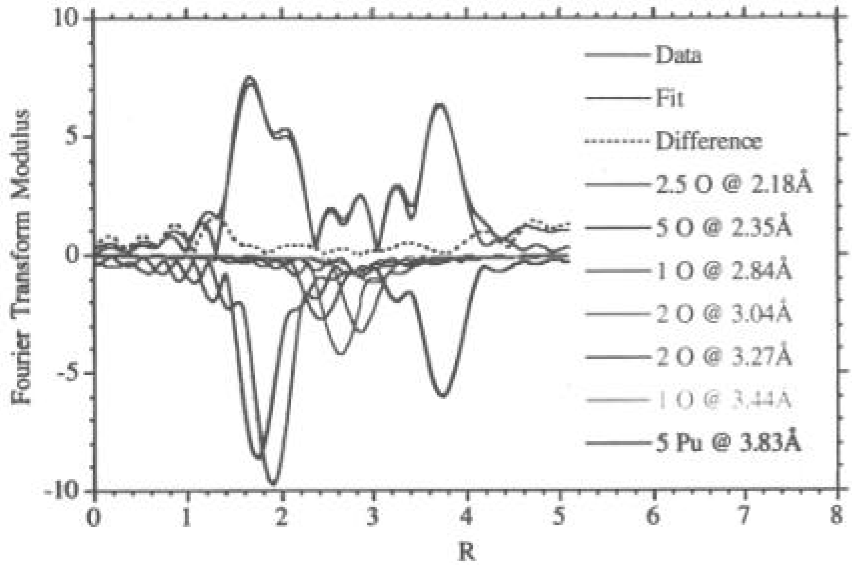
Nitrate Preparation

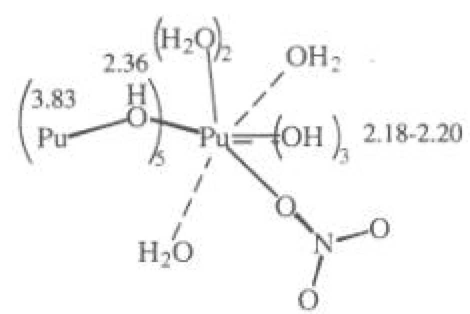


Nitrate/Citrate Preparation



EXAFS of Colloidal Pu(IV) Hydroxide





R, Å	n	type
2.18-2.20	2.5	OH^-, terminal
2.36	4.6	O^{2-}, OH^-, bridge
2.83	1.3	NO_3^-, monodentate
3.04	2.3	H_2O, terminal
3.26	2.1	H_2O, terminal
3.43	2.0	H_2O, outer sphere
		NO_3^-, N.
3.83	5.1	Pu

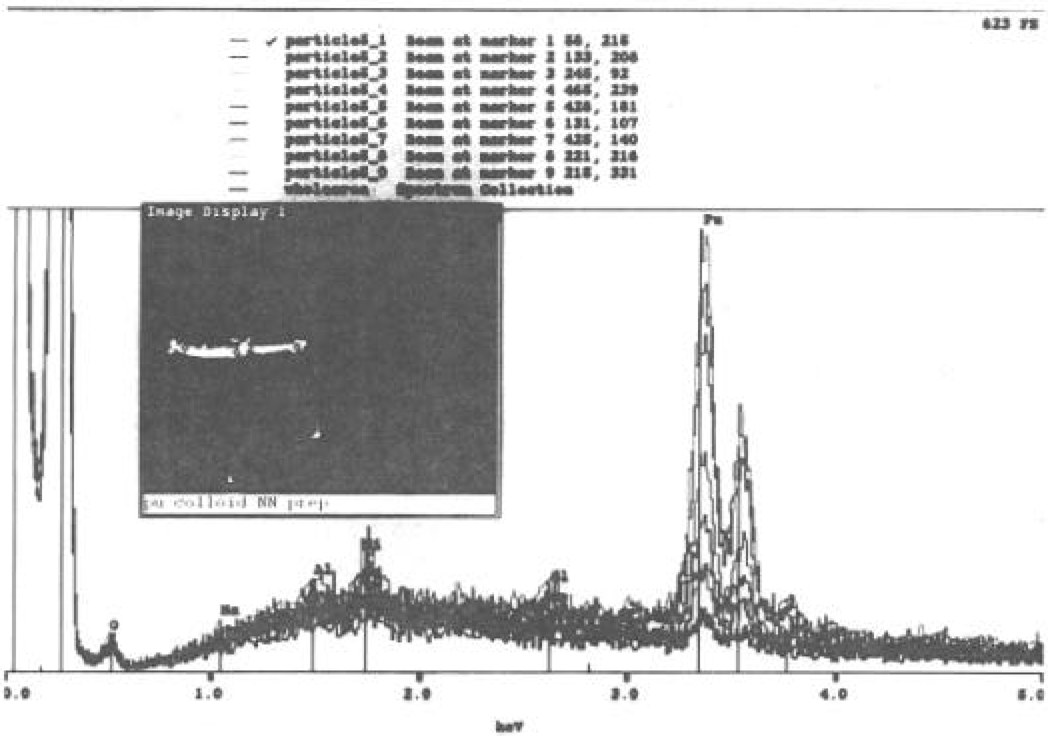


Image Display 1
pu colloid NN prep
Pu
0.0
1.0
2.0
3.0
4.0
5.0
keV

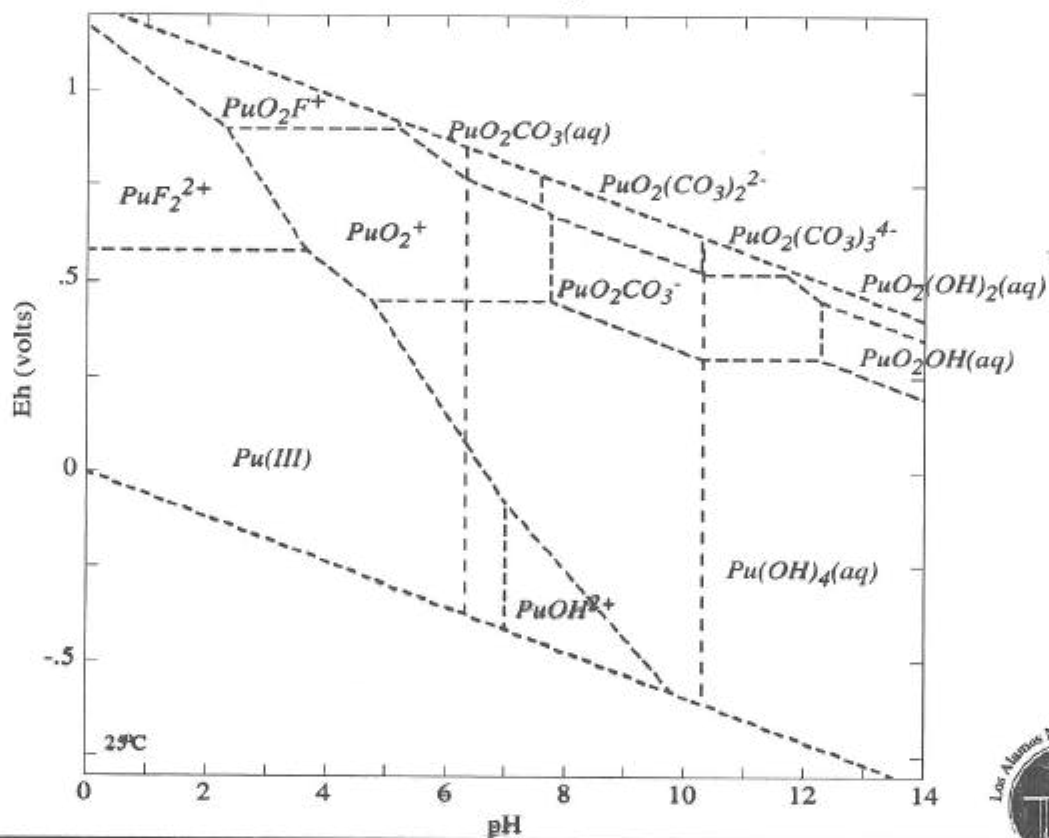
Size Determination Results

Colloidal Product	Size (LS), Å	Size (FFF), Å	Diff. Coeff., cm^2/s
Normal, Nitrate Media	150	20	1.9×10^{-6}
Saturated Sodium Chloride, 4 M Nitrate	150	25	
0.1 M Sodium Citrate, 4 M Nitrate	50	45	9.7×10^{-7}

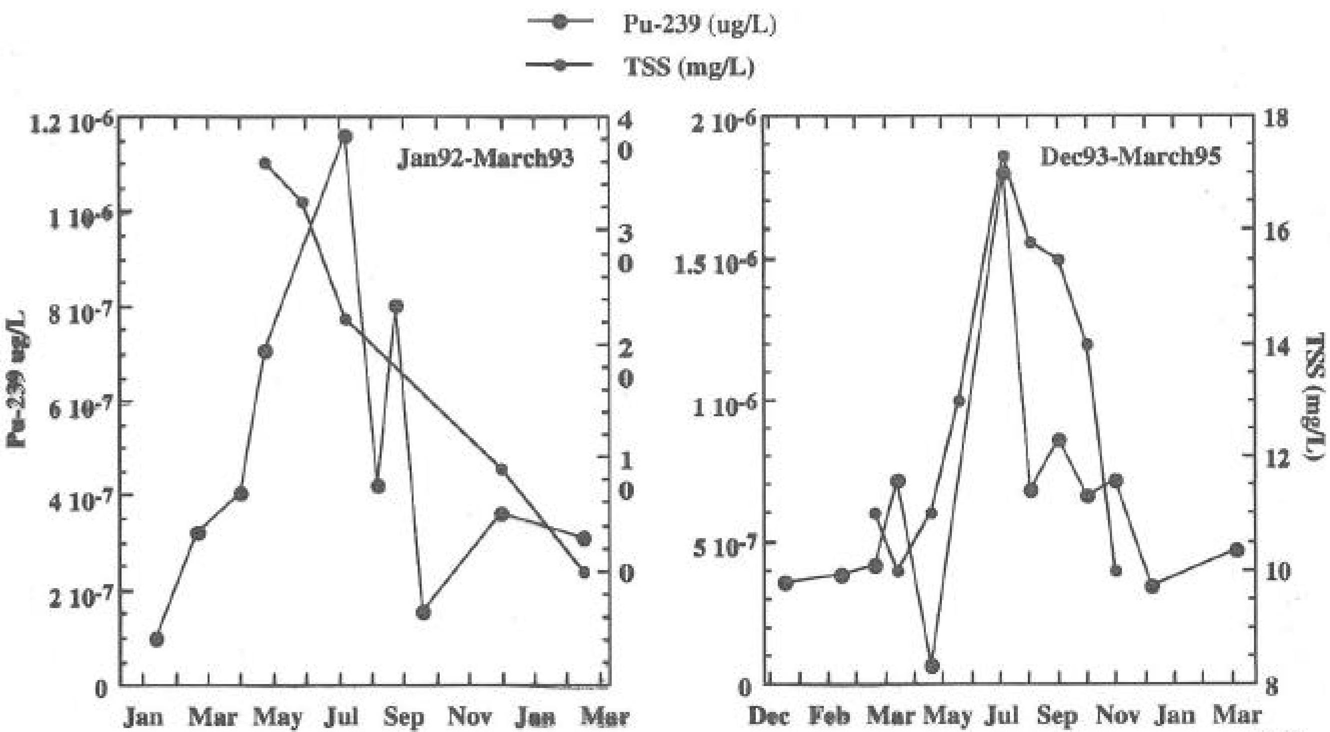
- Measurements from FFF can be considered the smallest unit size.
- Measurements from dynamic light scattering (DLS) are more representative of intrinsic particle size with no shear stresses.
- Unit sizes from the nitrate and citrate/nitrate preparations are 20 and 45Å. The 'nitrate' colloids easily aggregate to form particles of 150Å size.
- Upon evaporation of the solution to one fifth the initial volume, 'nitrate' colloids easily aggregate to ~200Å size particles and 'citrate' colloids aggregate to ~350Å size with a bimodal distribution.

Eh-pH Diagram for Pu in Natural Water

[Pu] = 10 μM $[HCO_3^-] = 10^{-2.55}$

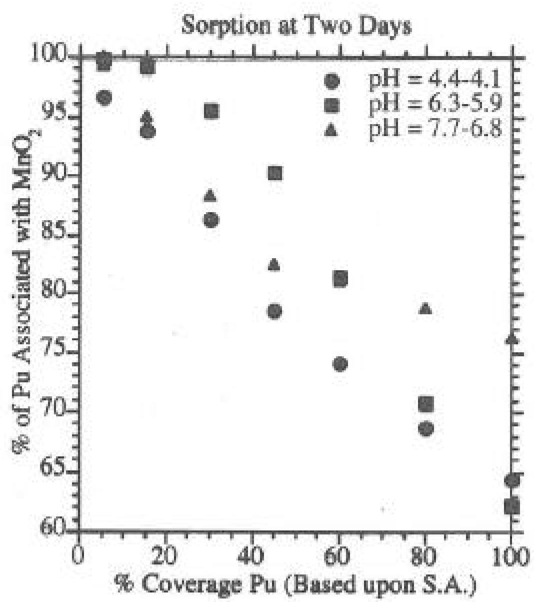


Seasonal Variation of ^{239}Pu and TSS in Surface Water of the C2-Pond at the Rocky Flats Environmental Test Site



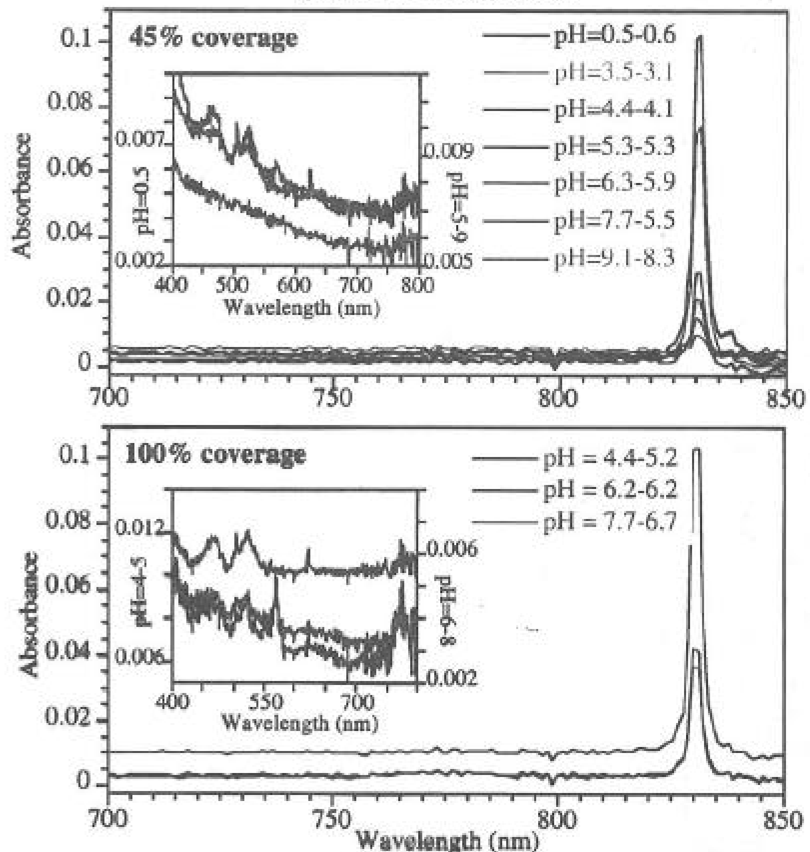
Pu(V) Combined with MnO_2 and Resultant Oxidation to Pu(VI)

% Pu(V) Sorbed as a Function of Amount Added

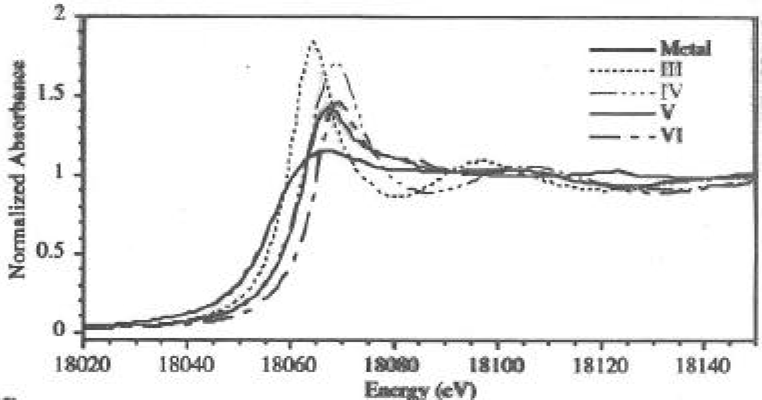


Optical Absorbance Spectra of Solution After Contacting Solid

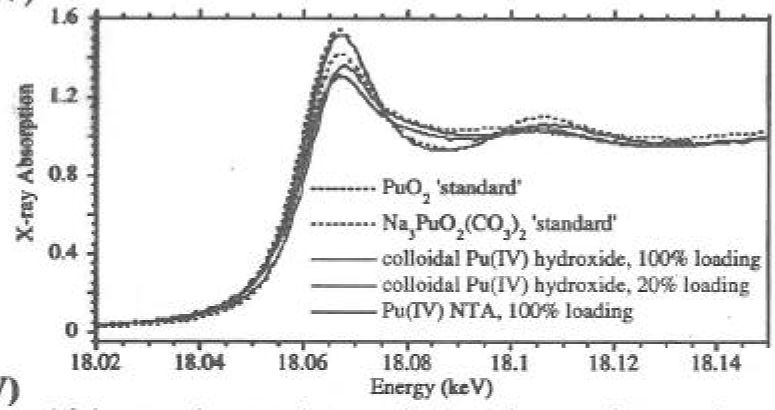
pH, initial and after 2 days



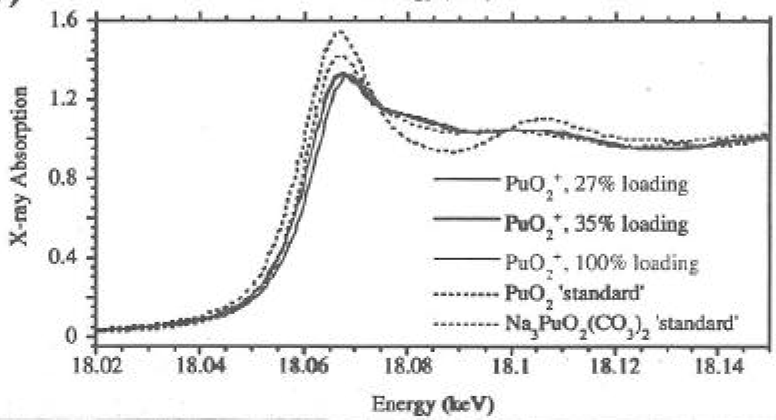
X-ray Absorbance of Pu Species Sorbed Onto MnO_2



Pu(IV)

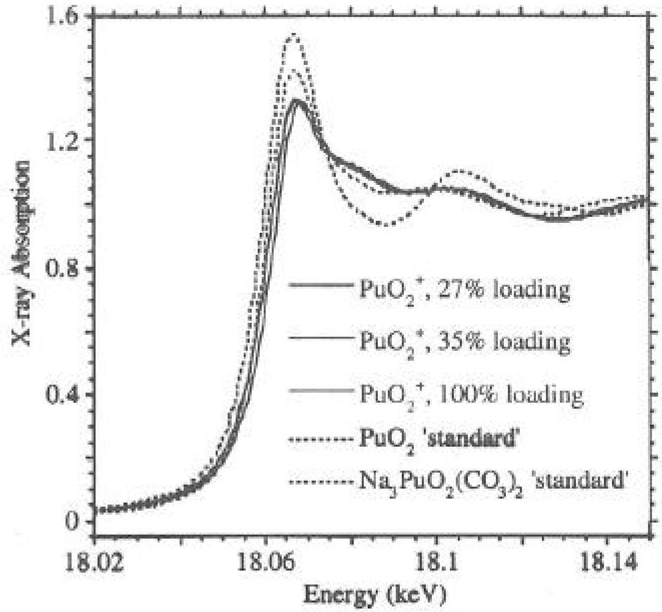


Pu(V)

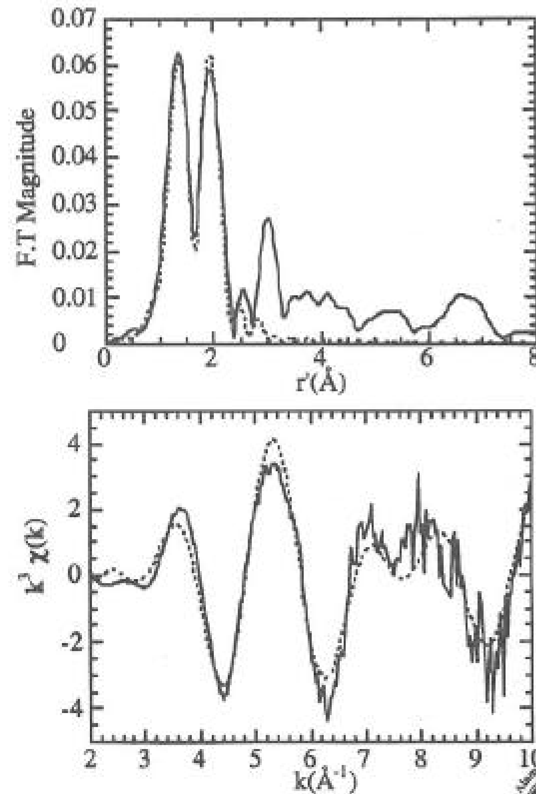


X-ray Absorption Spectra of Pu(V) Sorbed Onto MnO_2

XANES



EXAFS of 27% loading sample

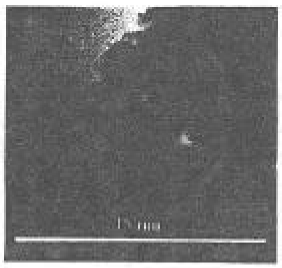


Two Shell Fit of 27% Loading Sample
Clearly Pu(VI) !

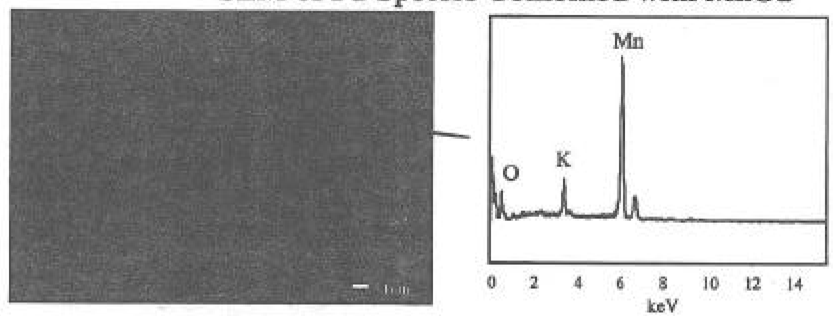
# of Oxygens	R (Å)	
1.92	1.75	Sigma = 0.0057
4.34	2.38	Eo = 11.999

Electron Microscopy of Pu Sorbed Onto MnO_2

TEM of MnO_2
100,000 x
Prior to Sorption



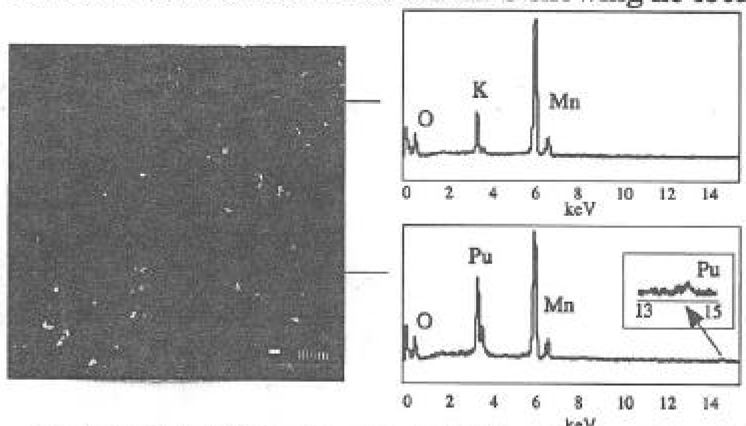
SEM of Pu Species Combined with MnO2



PuO_2^+, 100% loading sample, 2500x,
backscattered electron mode and EDS showing no localized Pu.

SEM of Sorption Samples

- PuO_2^+ sorption delocalized
- Colloidal Pu(IV) hydroxide sorption islocalized--aggregated or surface precipitation.



Colloidal Pu(IV) hydroxide, 20% loading sample, 200x,
backscattered electron mode and EDS showing localized Pu.

Detailed Research on Environmentally Important Plutonium Species

- Colloidal Pu(IV) Hydroxide
  - First study of structural details.
  - Colloids formed in the presence of strong chelating agents.
  - Colloids formed in high ionic strength.
  - Not all evidence suggests transformation to PuO_2 on the same time scale.
- Actinide Carbonates
  - Structural study of An(IV) carbonate species.
  - Extensive spectrophotometric (thermodynamic) data on An(VI).
- Pu(III) Aquo Structure
- Pu Sorption onto MnO_2
  - Pu(V) species appear to oxidize to Pu(VI)!
  - Pu(IV) hydroxide appears to oxidize to mixture of Pu(V/VI)!!
  - Pu(IV) sorbed as NTA complex--remains Pu(IV).

Characterization of Samples from RFETS Site

- TIMS isotopic data from site and CO samples proves site Pu is localized within and directly east of the site.
- XAS of soil samples most concentrated in Pu contain predominantly PuO_2.
- SEM and radiography show Pu is delocalized.
- Water samples from drainage ponds are too dilute for most analyses, consistent with PuO_2 dominating the geochemistry.
- Results communicated to RFETS and concerned citizens.

Geochemical Modeling

- Database critically evaluated.
- Speciation predicted for range of Eh and pH.

New Project

- Hanford and INEEL interactions.
- Continue research on important species.
- Use database and site data to predict speciation.

Acknowledgements

Brian Scott--*Single Crystal X-ray Diffraction*

J. Doug Farr & Roland Schulze--*Collaborators on Colloid Size Determinations*

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Actinide Environmental and Coordination Chemistry,
Chemical Science & Technology Division.
Los Alamos National Laboratory