National Analytical Management Program (NAMP)
U.S. Department of Energy Carlsbad Field Office

Radiochemistry Webinars

Actinide Chemistry Series

- *Environmental Chemistry of Uranium and Plutonium*

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Meet the Presenter…

Brian Powell

Dr. Brian Powell has extensive expertise with the mobility of radionuclides in soil and groundwater systems through his research in the Department of Environmental Engineering and Earth Sciences at Clemson University, as well as previous work at the Lawrence Livermore National Laboratory and the Lawrence Berkeley National Laboratory. He has a B.S. in Chemistry from the University of Montevallo, and a M.S. and Ph.D. in Environmental Engineering and Science from Clemson University. He holds memberships in the Association of Environmental Engineering and Science Professors, the American Geophysical Union, Sigma Xi, and the American Chemical Society.
At Clemson University, Dr. Powell teaches courses in Actinide Environmental Chemistry, Environmental Radiation Protection (Lecture and Laboratory courses), Introductory Health Physics, Geochemistry, and Geochemical Reaction Modeling. Dr. Powell's major research interest is to understand interrelated chemical, biological, and physical processes that control the fate and transport of radionuclides and trace metals in the environment. These processes include sorption by minerals, interactions with nano-colloids, complexation by organic ligands, and interactions with microorganisms. He has published over 20 refereed journal publications, 16 research reports, and made nearly 50 technical presentations on these topical areas. He has conducted sponsored research dealing with topics such as nuclear forensics, evaluation of nanoparticle behavior, sorption and environmental transport of plutonium, development of radiation detection and radiation laboratory courses, evaluation of radionuclide geochemistry in wetland and subsurface sediments, solid waste performance assessments at the Savannah River Site, measurement of thermodynamic parameters supporting advanced nuclear fuel cycle chemistry, and related topics. These projects have garnered over $5M in research awards. The knowledge gained from this work can be used to evaluate risk posed by subsurface contamination, to design remediation strategies for contaminated sites, and to facilitate the use of safe disposal practices.

CLEMSON UNIVERSITY

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Part 1: Plutonium Environmental Behavior

Dr. Brian A. Powell
Environmental Engineering and Earth Sciences
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National Analytical Management Program (NAMP)
U.S. Department of Energy Carlsbad Field Office

TRAINING AND EDUCATION SUBCOMMITTEE

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Outline

- Introduction: Brief overview of some sites
- Aqueous speciation in natural waters
  - Complexation with inorganic and organic ligands
  - Redox reactions
- Sorption to minerals and sediments
- Precipitation/Formation of nanoparticulates
- Colloid facilitated transport

Introduction – Pu-contaminated Sites

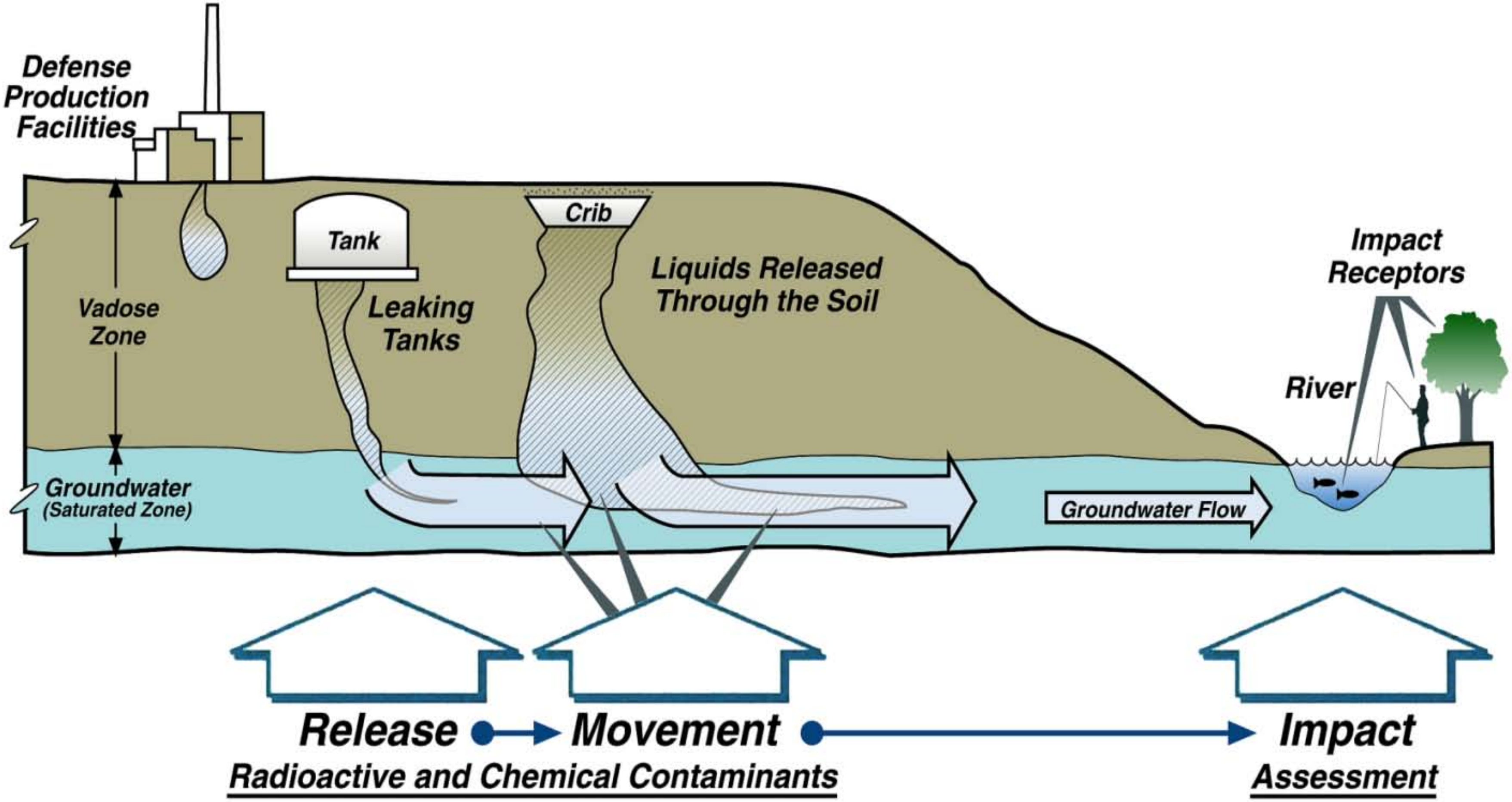
- DOE facilities have significant Pu deposits as a result of weapons production
- Hanford – 11.5 million m^3 of soil with Pu-laden waste
- Savannah River Site - 60 kg (1028 Ci) of ^{238}Pu is buried as low-level waste in shallow vadose zone disposal
- Nevada Test Site - approximately 2775 kg (8.3x10^5 Ci) of Pu (mostly ^{239}Pu by mass) remains in the subsurface as a byproduct of underground nuclear testing

Low-level Pu Burial Ground, SRNL

Yucca Flats, Nevada Test Site

Images: http://www.nv.doe.gov/nts/ and Powell et al., 2003

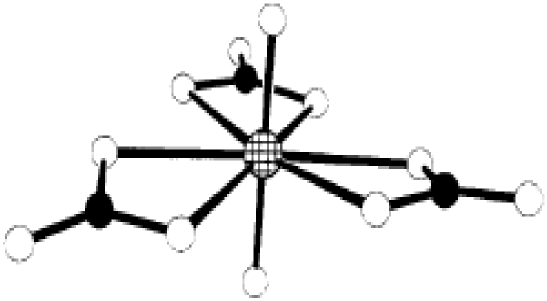
Need for Understanding U and Pu Geochemistry – Risk Evaluation



http://picturethis.pnl.gov

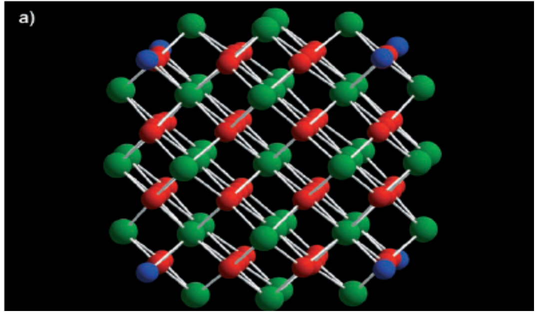
Major Reactions Influencing Pu and U Environmental Behavior

- Aqueous Complexation



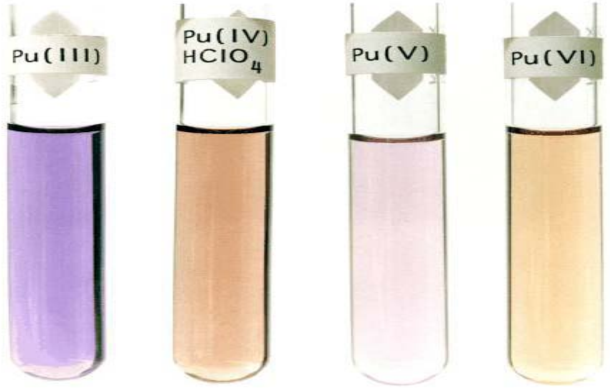
Soluble $UO_2(CO_3)_3^{4-}$ complex. Clark et al., *Chem. Rev.*, 1995, 95 (1), 25-48

- Precipitation/Dissolution

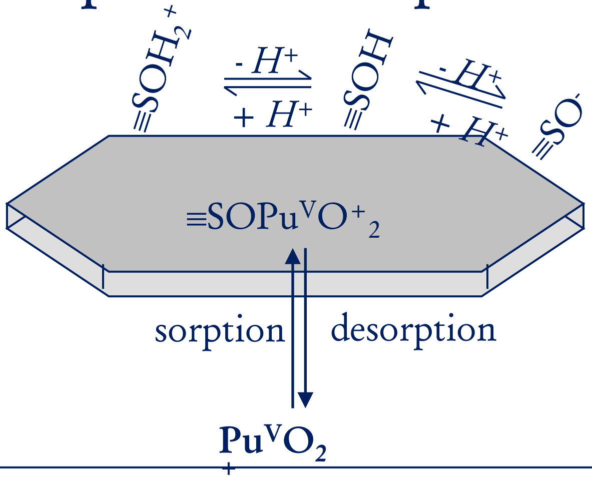


Pu(IV) “nanocluster“ Soderholm *et al.* 2008, Angew. Chem. Int. Ed., 47, 298 –302

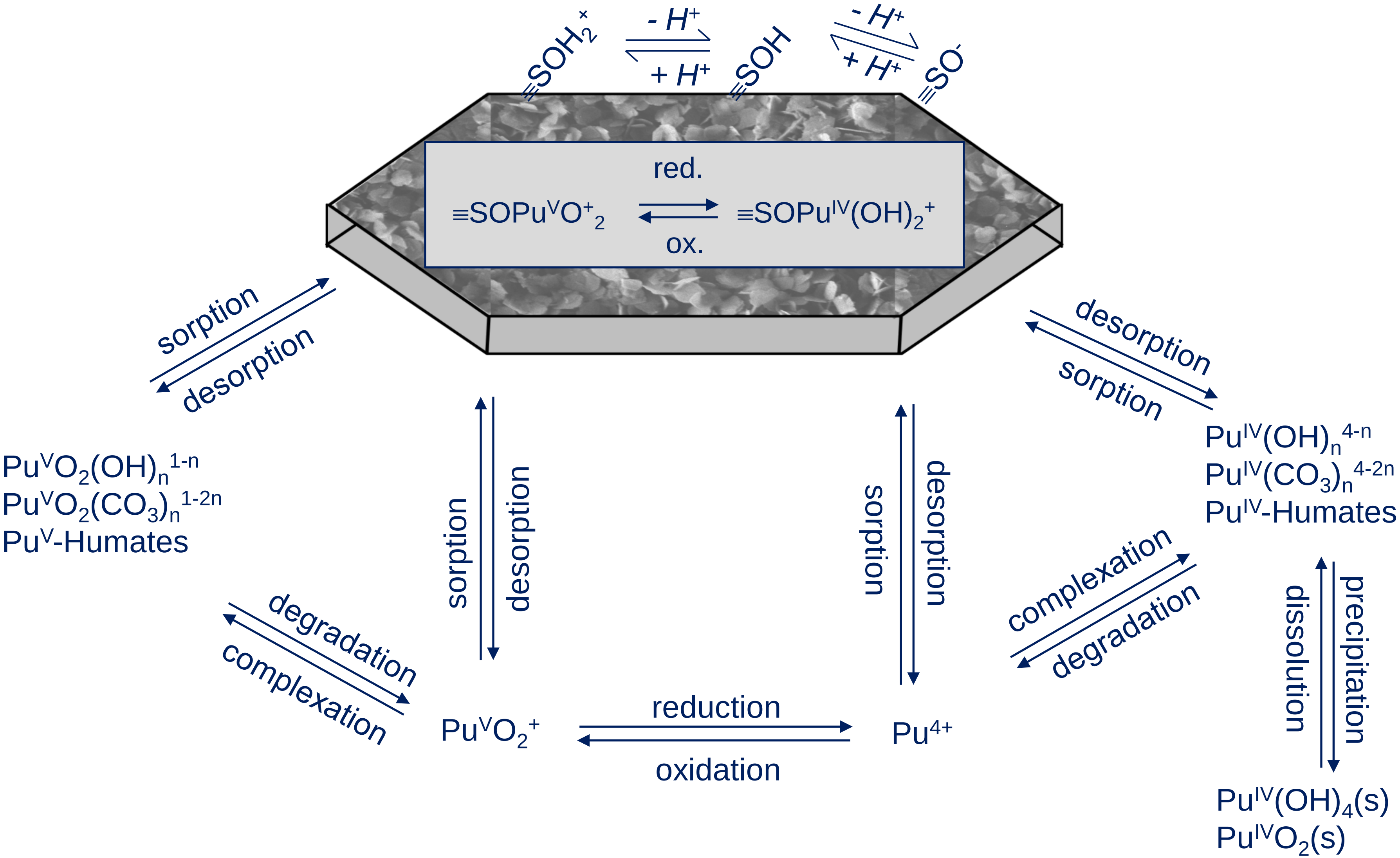
- Oxidation/Reduction



- Sorption/Desorption



Coupling of Geochemical Reactions



$\equiv SOH_2^+$ $\underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}$ $\equiv SOH$ $\underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}$ $\equiv SO^-$

$\equiv SOPu^{V}O^{+}_{2}$ $\underset{ox.}{\overset{red.}{\rightleftharpoons}}$ $\equiv SOPu^{IV}(OH)_2^+$

sorption

desorption

$Pu^{V}O_2(OH)_n^{1-n}$
$Pu^{V}O_2(CO_3)_n^{1-2n}$
Pu^{V}-Humates

degradation

complexation

sorption

desorption

$Pu^{V}O_2^+$

reduction

oxidation

Pu^{4+}

sorption

desorption

desorption

sorption

$Pu^{IV}(OH)_n^{4-n}$
$Pu^{IV}(CO_3)_n^{4-2n}$
Pu^{IV}-Humates

complexation

degradation

dissolution

precipitation

$Pu^{IV}(OH)_4(s)$
$Pu^{IV}O_2(s)$

Aqueous Complexation - Outline

- Common oxidation states
- Common groundwater ions
- Hydration of the actinides
- Hydrolysis reactions
- Complexation with halides
- Complexation with oxyanions
- Complexation with natural organic matter

Equilibrium Constants

- Given reaction:

  aA + bB ⇔ cC + dD

- K^o is the equilibrium expression under standard conditions
- K^c is a concentration-based equilibrium constant
  based on the given solution conditions
- Stability constant notation (β^o and β^c) used for cumulative constants

$$K^o = \frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}$$

$$K^o = \frac{[C]^c\gamma_c^c[D]^d\gamma_d^d}{[A]^a\gamma_a^a[B]^b\gamma_b^b}$$

$$K^o = \frac{[C]^c[D]^d}{[A]^a[B]^b}\frac{\gamma_c^c\gamma_d^d}{\gamma_a^a\gamma_b^b}$$

$$K^o = K^c\frac{\gamma_c^c\gamma_d^d}{\gamma_a^a\gamma_b^b}$$

<u>Different names for the same thing (products over reactants)</u>

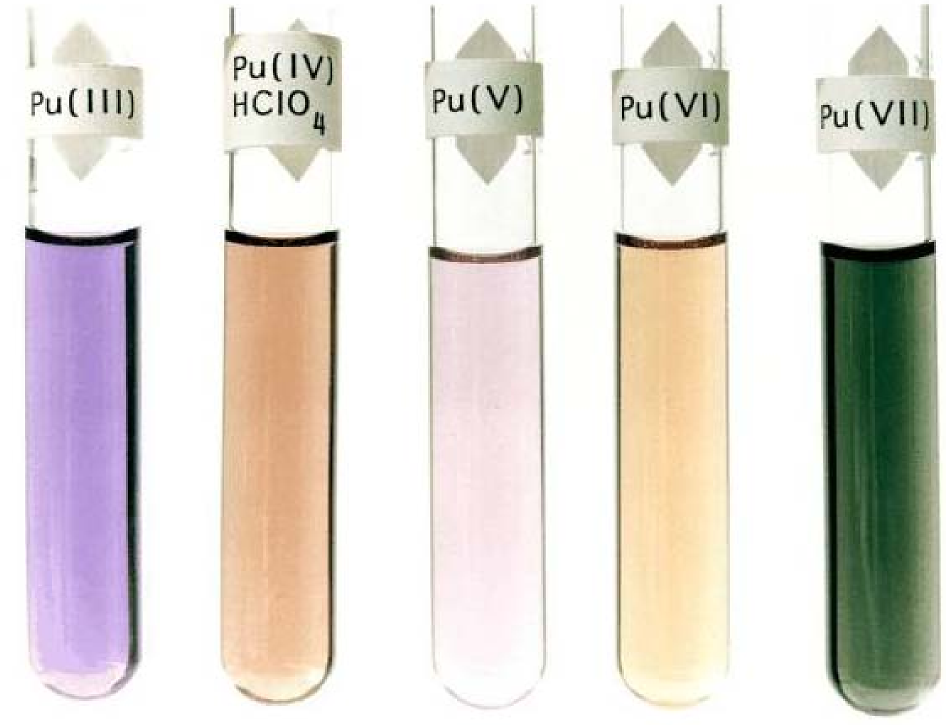
Stability constant = equilibrium constant = equilibrium for a metal-complex

Dissociation constant = acid/base dissociation (i.e., pK_a)

Hydrolysis constant = metal ion hydrolysis (i.e., reaction with water/OH^-)

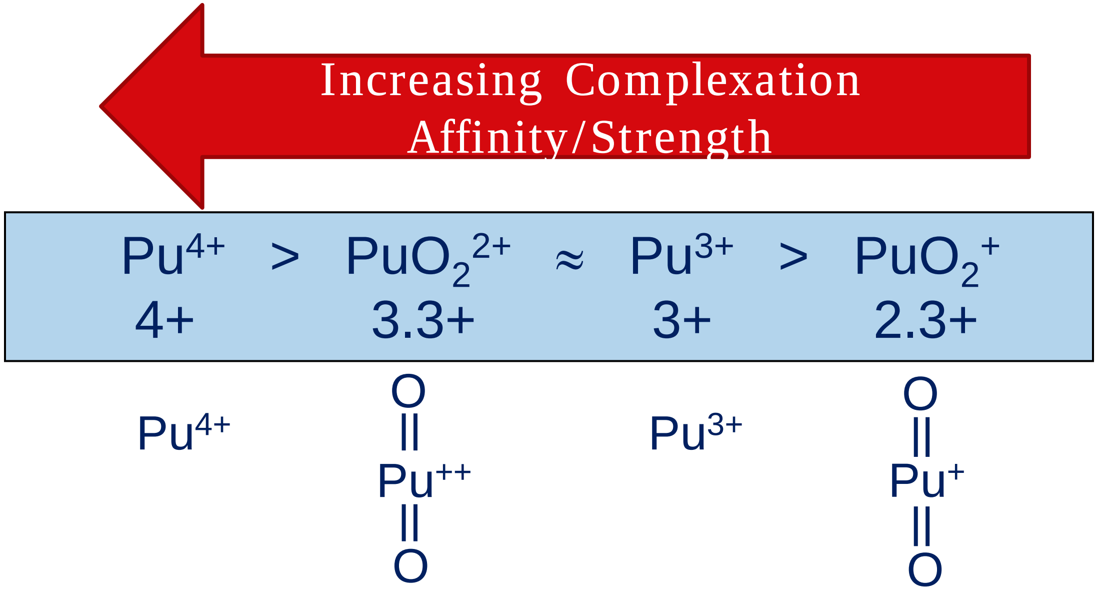
Pu Oxidation States

- Under environmental conditions, Pu(III), Pu(IV), Pu(V), and Pu(VI) are expected to be stable
- Pu(IV) and Pu(V) appear to be the dominant oxidation states
- These two oxidation states represent the extremes of mobility of Pu in the environment as Pu(IV) is insoluble and relatively immobile, while Pu(V) is generally soluble and mobile



Influence of Effective Charge

- Most processes concerned with plutonium in oxidation states III-VI
  - Pu(III) and Pu(IV) present as free ions
  - Pu(V) and Pu(VI) present as actinyl ions PuO_2^{+} and PuO_2^{2+}
- Overall effective charge of the ions does not follow formal charge (Rao and Choppin, 1984)



Increasing Complexation Affinity/Strength

$Pu^{4+} > PuO_2^{2+} \approx Pu^{3+} > PuO_2^{+}$

4+ 3.3+ 3+ 2.3+

Pu^{4+}

$O=Pu^{++}=O$

Pu^{3+}

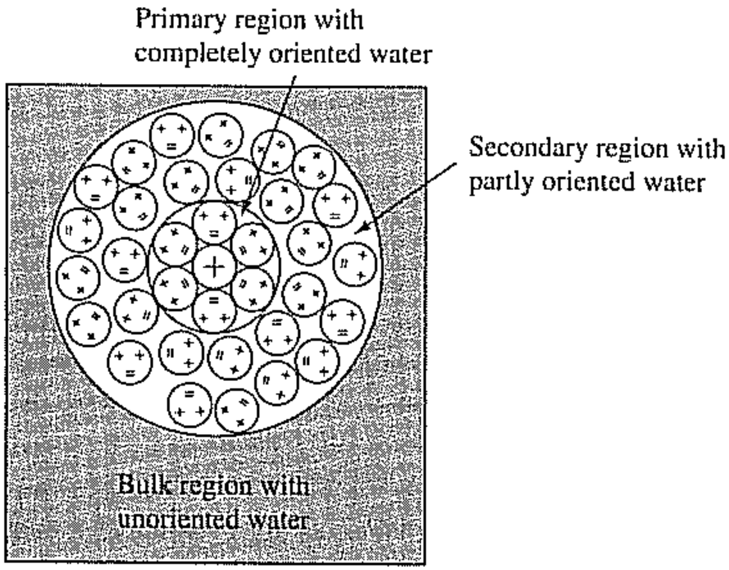
$O=Pu^{+}=O$

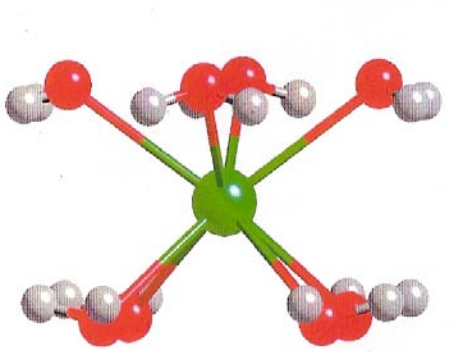
General Solution Chemistry Trends

- In neutral pH (5-9) natural waters, actinide ions hydrolysis readily. Therefore, solubility is generally limited to $<10^{-6}$ M, with the notable exception of pentavalent actinides
- Hydrolysis leads to $An(OH)_4(s)$ and $AnO_2(s)$, which may have a colloidal character
- Other dissolved heavy elements are present at solubility concentrations of the actinides. Therefore, significant competition for chemical reactions exists (i.e. competition between Fe(III) and Pu(IV))
- Complexing ions such as carbonate, phosphate, humic substances, etc., may stabilize actinides as monomeric ions
- All the above reactions are highly dependent on the oxidation state of the actinide
- Stability of oxidation states varies for each actinide and the components within natural waters. Redox chemistry between actinides is not necessarily comparable. However…
- Chemical behavior between oxidation states is generally similar

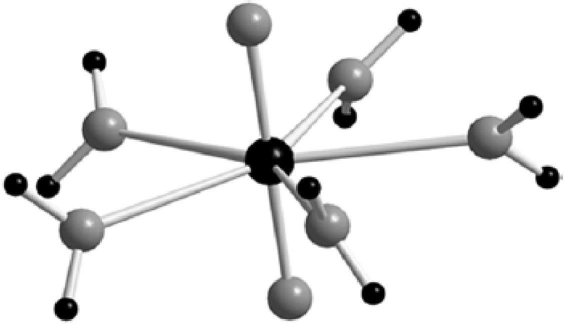
Actinide Hydration – An(H_2O)$_x$

- Complexation reactions with water
- f-element salts are fairly soluble in water
- Strong ion-dipole interactions create a primary hydration sphere
- Additional hydration layers created from additional dipole-dipole interactions
- Hydration state and number is influenced by effective charge (see next slide)





An(IV), $N_{H2O} = 8$



An(VI), $N_{H2O} = 5$

Vallet et al., 2001

Influence of Effective Charge on Hydration

Choppin and Wong, Aqu. Geochem., 4, 77-101, 1998

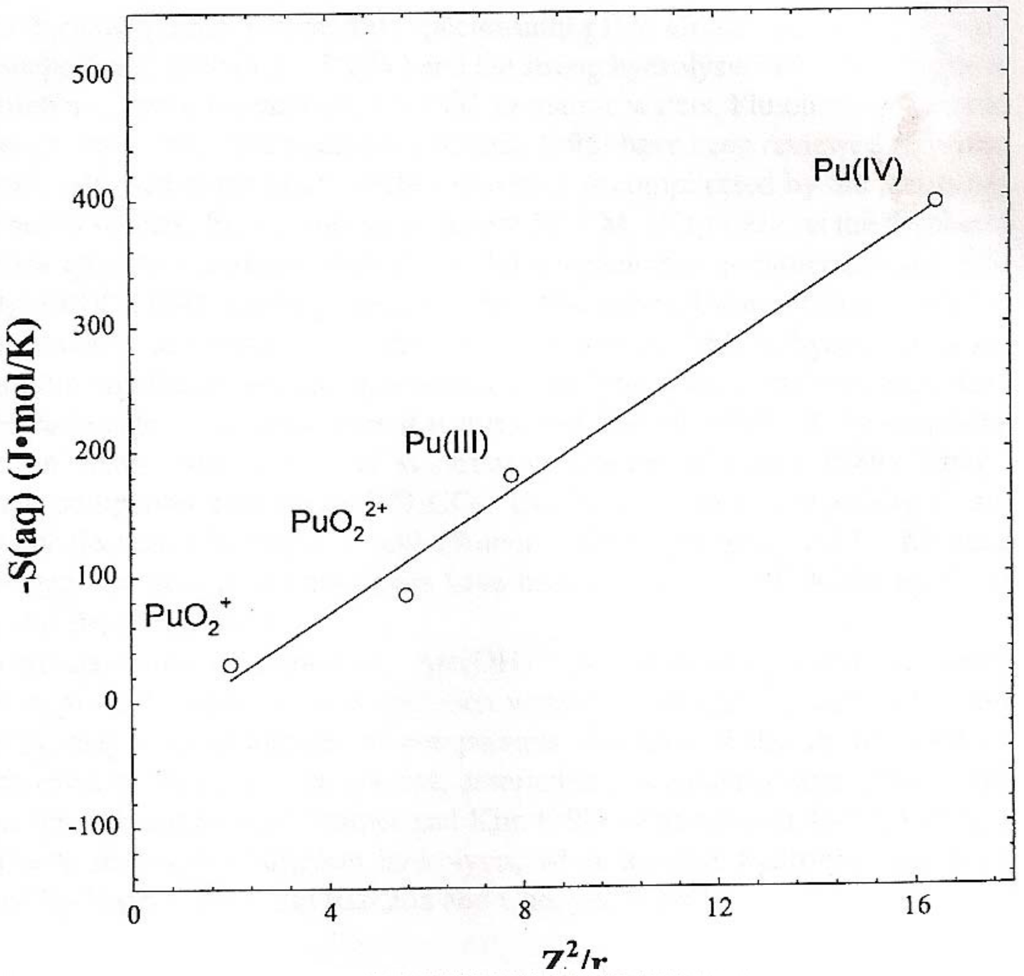
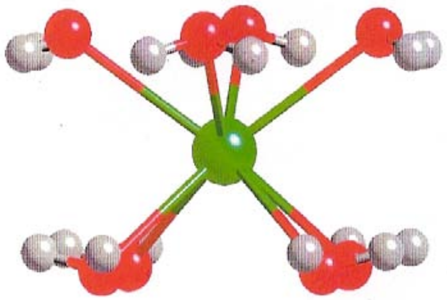


Figure 2. Correlation between $-S^\circ_{(aq)}$ and where radius r is based on coordination numbers (CN): $CN_{Pu(V)} = 4$; $CN_{Na(I),Ca(II)} = 6$; $CN_{Pu(IV)} = 8$; $CN_{Pu(III)} = 9$. Adapted from Morse (1991).

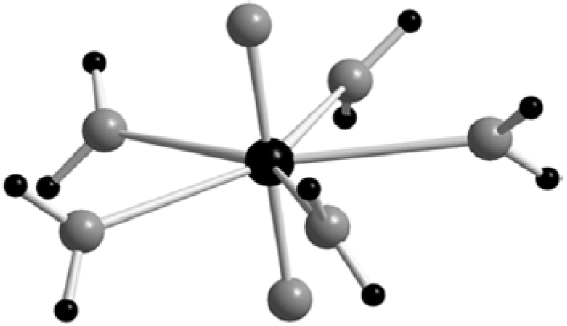
- Energy of hydration increases with decreasing ionic radius for a fixed charge
- More negative entropy for Pu(IV) versus Pu(VI) and Pu(V) indicates increased hydration

Actinide Hydration

- Pu(III) - data indicate 9-10 hydrating waters with a Pu-O coordination number of 9 or 10
- Pu(IV) – 8 hydrating waters with an Pu-O coordination number of 8
- Pu(V) – 5 coordinating waters with an overall Pu-O coordination number of 7 (5 waters and 2 axial oxygen atoms)
- Pu(VI) – 5 or 6 coordinating waters with an overall coordination number of 7 or 8 (5 or 6 waters with 2 axial oxygen atoms)



An(IV), $N_{H2O} = 8$



An(VI), $N_{H2O} = 5$
Vallet et al., 2001

Ref: Table 28.3 The Chemistry of the Actinide and Transactinide Elements, 2006

Actinide Hydrolysis

- General reaction

$$xAn^{z+} + yH_2O \Leftrightarrow An_x(OH)_y^{xz-y} + yH^+$$

$$\beta^o = \frac{\{An_x(OH)_y^{xz-y}\}\{H^+\}^y}{\{An^{z+}\}^x\{H_2O\}^y}$$

- Occurs for all actinide ions
  - An(IV) – begins in acidic (~pH 1) solutions
  - An(III), An(VI) – begins in weakly acidic to neutral solutions
  - An(V) – begins above pH 8

- Note: reaction can be written as

$$xAn^{z+} + yOH^- \Leftrightarrow An_x(OH)_y^{xz-y}$$

$$\beta^{o*} = \frac{\{An_x(OH)_y^{xz-y}\}}{\{An^{z+}\}^x\{OH^-\}^y}$$

- β^o and β^{o*} are related through the water dissociation constant

- Strength of hydrolysis will follow the same trend with regard to effective charge:
  - An(IV) > An(VI) > An(III) > An(V)

Comparison of Pu Hydrolysis vs Oxidation State

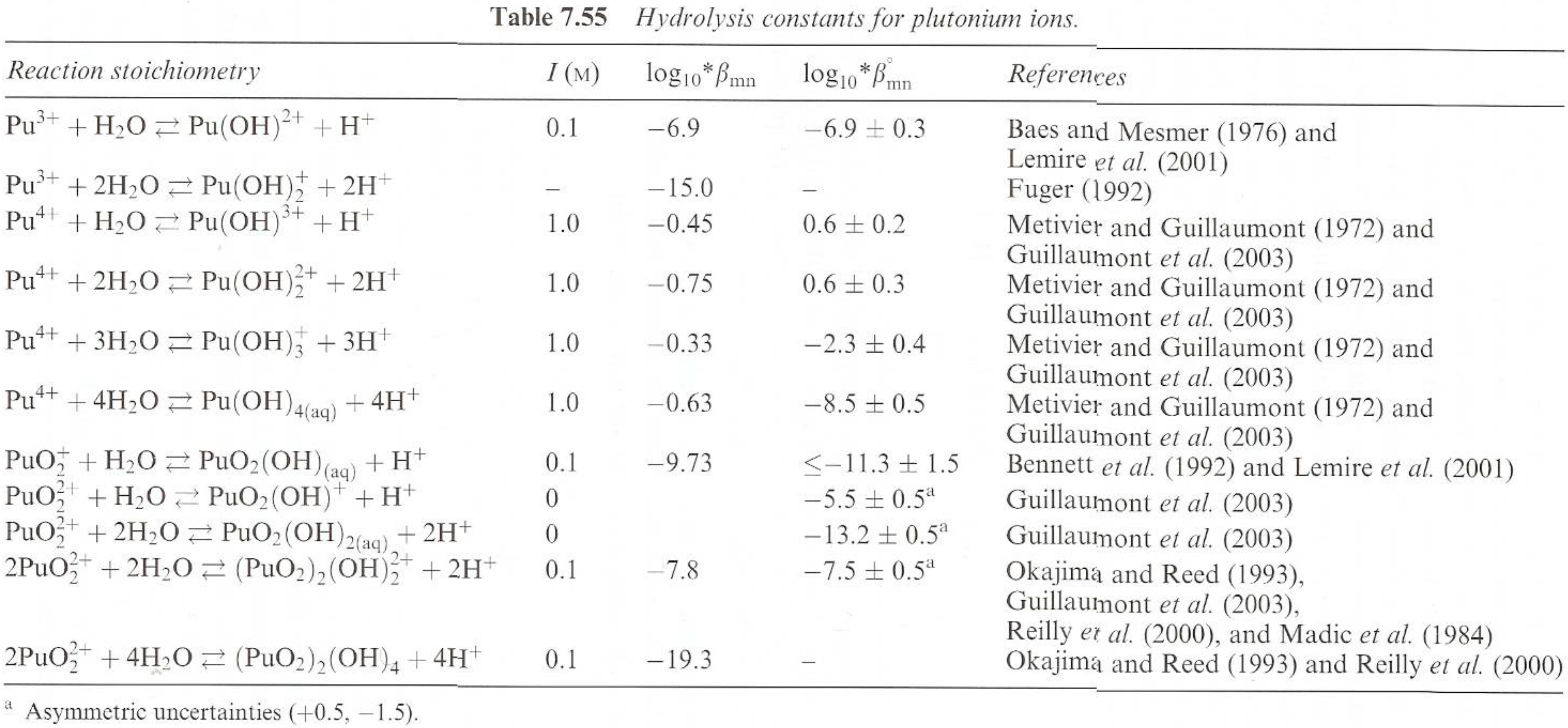


Table 7.55 *Hydrolysis constants for plutonium ions.*

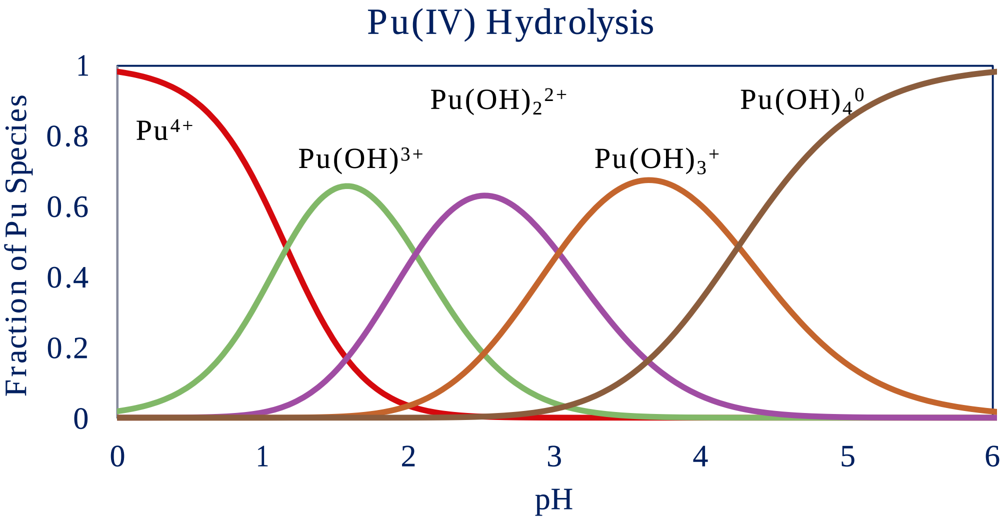
Reaction stoichiometry	I (M)	$\log_{10}{}^*\beta_{mn}$	$\log_{10}{}^*\beta^\circ_{mn}$	*References*
$Pu^{3+} + H_2O \rightleftarrows Pu(OH)^{2+} + H^+$	0.1	−6.9	−6.9 ± 0.3	Baes and Mesmer (1976) and Lemire *et al.* (2001)
$Pu^{3+} + 2H_2O \rightleftarrows Pu(OH)_2^+ + 2H^+$	–	−15.0	–	Fuger (1992)
$Pu^{4+} + H_2O \rightleftarrows Pu(OH)^{3+} + H^+$	1.0	−0.45	0.6 ± 0.2	Metivier and Guillaumont (1972) and Guillaumont *et al.* (2003)
$Pu^{4+} + 2H_2O \rightleftarrows Pu(OH)_2^{2+} + 2H^+$	1.0	−0.75	0.6 ± 0.3	Metivier and Guillaumont (1972) and Guillaumont *et al.* (2003)
$Pu^{4+} + 3H_2O \rightleftarrows Pu(OH)_3^+ + 3H^+$	1.0	−0.33	−2.3 ± 0.4	Metivier and Guillaumont (1972) and Guillaumont *et al.* (2003)
$Pu^{4+} + 4H_2O \rightleftarrows Pu(OH)_{4(aq)} + 4H^+$	1.0	−0.63	−8.5 ± 0.5	Metivier and Guillaumont (1972) and Guillaumont *et al.* (2003)
$PuO_2^+ + H_2O \rightleftarrows PuO_2(OH)_{(aq)} + H^+$	0.1	−9.73	≤−11.3 ± 1.5	Bennett *et al.* (1992) and Lemire *et al.* (2001)
$PuO_2^{2+} + H_2O \rightleftarrows PuO_2(OH)^+ + H^+$	0		−5.5 ± 0.5[a]	Guillaumont *et al.* (2003)
$PuO_2^{2+} + 2H_2O \rightleftarrows PuO_2(OH)_{2(aq)} + 2H^+$	0		−13.2 ± 0.5[a]	Guillaumont *et al.* (2003)
$2PuO_2^{2+} + 2H_2O \rightleftarrows (PuO_2)_2(OH)_2^{2+} + 2H^+$	0.1	−7.8	−7.5 ± 0.5[a]	Okajima and Reed (1993), Guillaumont *et al.* (2003), Reilly *et al.* (2000), and Madic *et al.* (1984)
$2PuO_2^{2+} + 4H_2O \rightleftarrows (PuO_2)_2(OH)_4 + 4H^+$	0.1	−19.3	–	Okajima and Reed (1993) and Reilly *et al.* (2000)

[a] Asymmetric uncertainties (+0.5, −1.5).

The Chemistry of the Actinide and Transactinide Elements, 2006

Comparison of Pu(IV) and Pu(V) Hydrolysis

- Data indicate first hydrolysis of Pu(V) and Np(V) does not occur until pH > 9
- Most databases report a log β_{11} value of -9.7 for Pu(V)

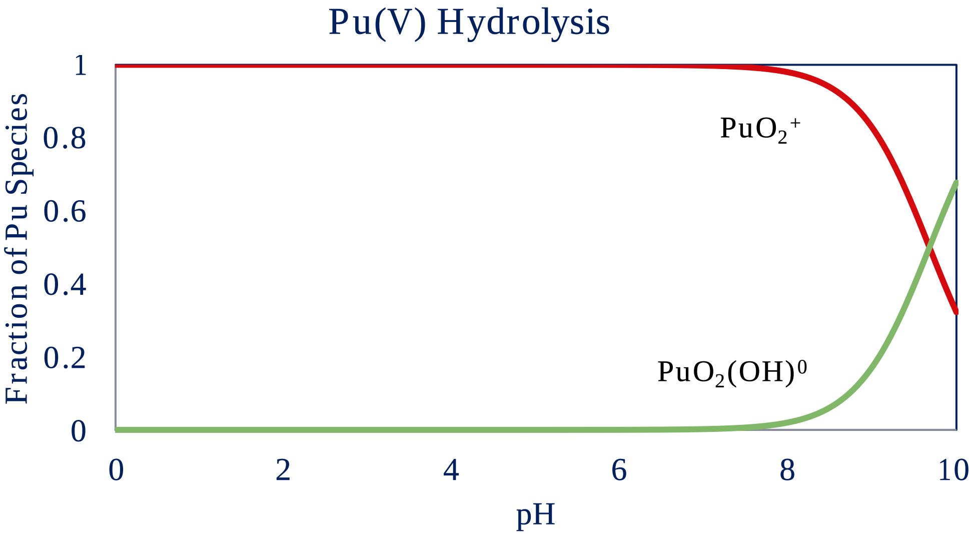


Hydrolysis of Pu(IV)

Modeled using Geochemist Workbench, LLNL database

Hydrolysis of Pu(V)

Modeled using Geochemist Workbench, LLNL database



Actinide Halide Complexes (F^-, Cl^-, Br^-, I^-)

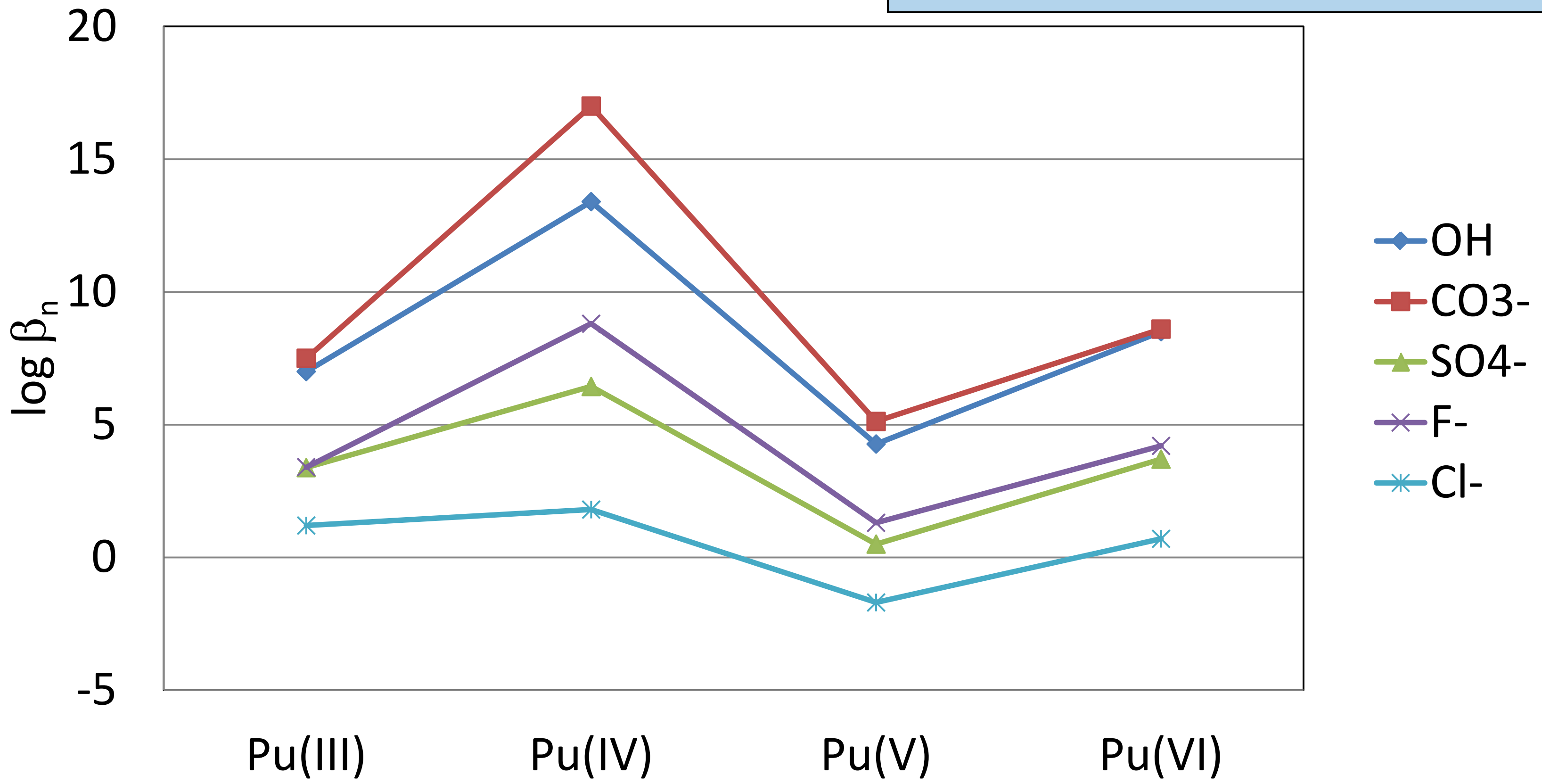
- With the exception of F^-, complexes are relatively weak
- Limited data because high ligand concentrations and acidic conditions are required
- Complexation strength
  - $F^- >>> Cl^- > Br^- > I^-$
- Believed F^- forms inner sphere complexes while Cl^-, Br^-, I^- form outer sphere complexes
- Note: In very strong acids, anionic species may form, such as $PuCl_6^{-2}$
- These and similar species are extremely important for separating actinides on ion exchange resins

Complexation with Common Inorganic Ions

General Trend:
Cl^-, NO_3^-< F^-, SO_4^{2-}, HPO_4^{2-} < CO_3^{2-}, OH^-

$$Pu^{x+} + nHL \Leftrightarrow PuL_n^{(x-n)} + nH^+$$

$$\beta_n = \frac{[PuL_n]^{(x-n)}[H^+]^n}{[Pu^{x+}][HL]^n}$$



Replotted from Silva and Nitsche, Radiochim. Acta, 70/71, 1995

Complexation with Oxo-ligands

- General trend: Cl^-, $NO_3^- < F^-$, SO_4^{2-}, $HPO_4^{2-} < CO_3^{2-}$, OH^-
- NO_3^- generally forms stronger complexes than Cl^-
- Primarily due to bidentate binding
- Complexation with other oxo-ligands extremely important for understanding environmental behavior
- Carbonate complexes are of particular importance

$CO_2(g) \text{ <-> } CO_2(aq)$ $\log K_H = -1.47$

$CO_2(aq) + H_2O \text{ <-> } H_2CO_3(aq)$ $\log K_{eq} = -2.70$

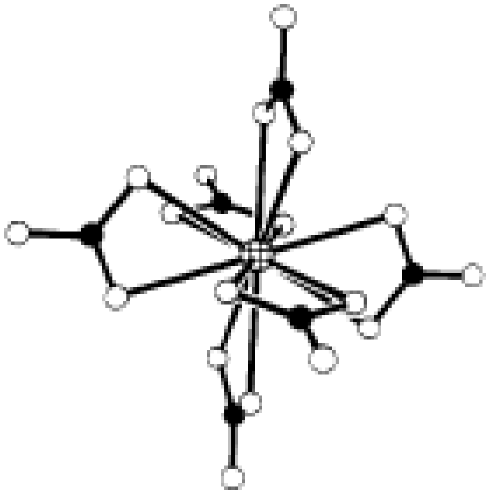
$H_2CO_3(aq) + H_2O \text{ <-> } H+ + HCO_3^-$ $\log K_1 = -6.35$

$HCO_3^- \text{ <-> } H^+ + CO_3^-$ $\log K_2 = -10.33$

Tetravalent Actinide-Carbonate Complexes

Clark et al., Chem. Rev. 95, 1995, 25-48

Reaction	Ionic Strength	log K
$Pu^{4+} + CO_3^{2-} <=> PuCO_3^{2+}$	0.3	17.0 +/- 0.7
$Pu^{4+} + 2CO_3^{2-} <=> Pu(CO_3)_2^0$	0.3	29.9 +/- 0.96
$Pu^{4+} + 3CO_3^{2-} <=> Pu(CO_3)_3^{2-}$	0.3	39.1 +/- 0.82
$Pu^{4+} + 4CO_3^{2-} <=> Pu(CO_3)_4^{4-}$	0.3	42.9 +/- 0.75
$Pu^{4+} + 5CO_3^{2-} <=> Pu(CO_3)_5^{6-}$	0.3	44.5 +/- 0.77
$Pu^{4+} + 2CO_3^{2-} + 4OH^- <=> Pu(OH)_4(CO_3)_2^{4-}$	0.1	46.4 +/- 0.70
$Th^{4+} + 5CO_3^{2-} <=> Th(CO_3)_5^{6-}$	1	26.2 +/- 0.2

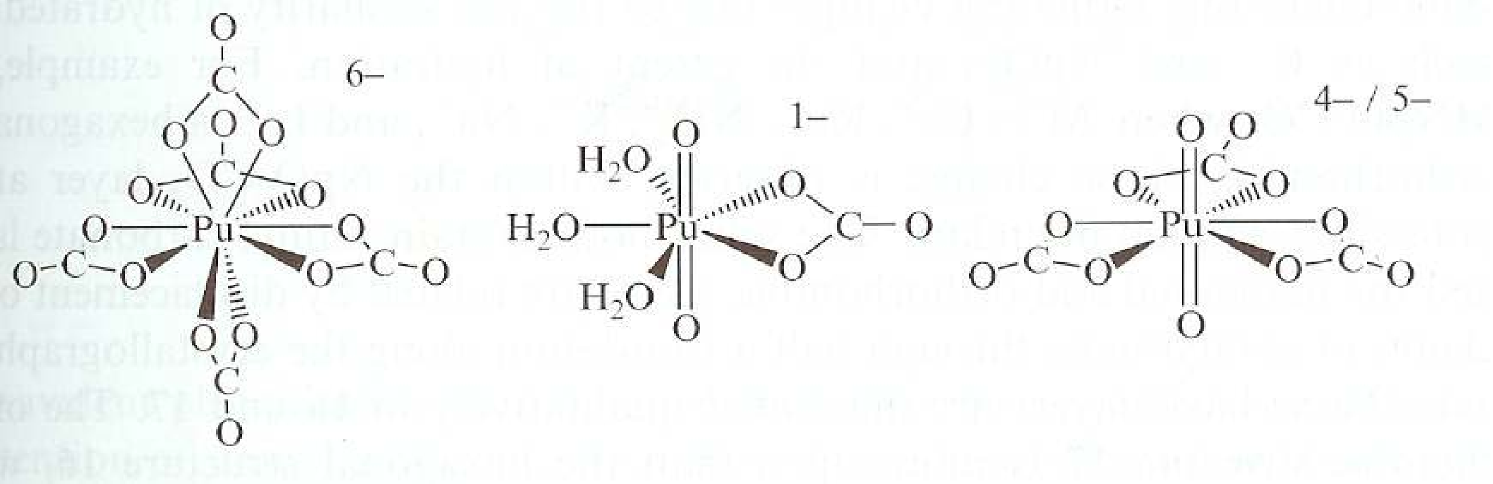


- Some uncertainty in these assignments
- Rai et al., 1999, and Zavarin et al., 2006, propose additional hydroxycarbonate species $Pu(OH)_2(CO_3)_2^{2-}$ and $Pu(OH)_4(CO3)_2^{4-}$
- Sorption data imply that Pu(IV) carbonate complexes do not significantly mobilize Pu(IV) (data discussed below)

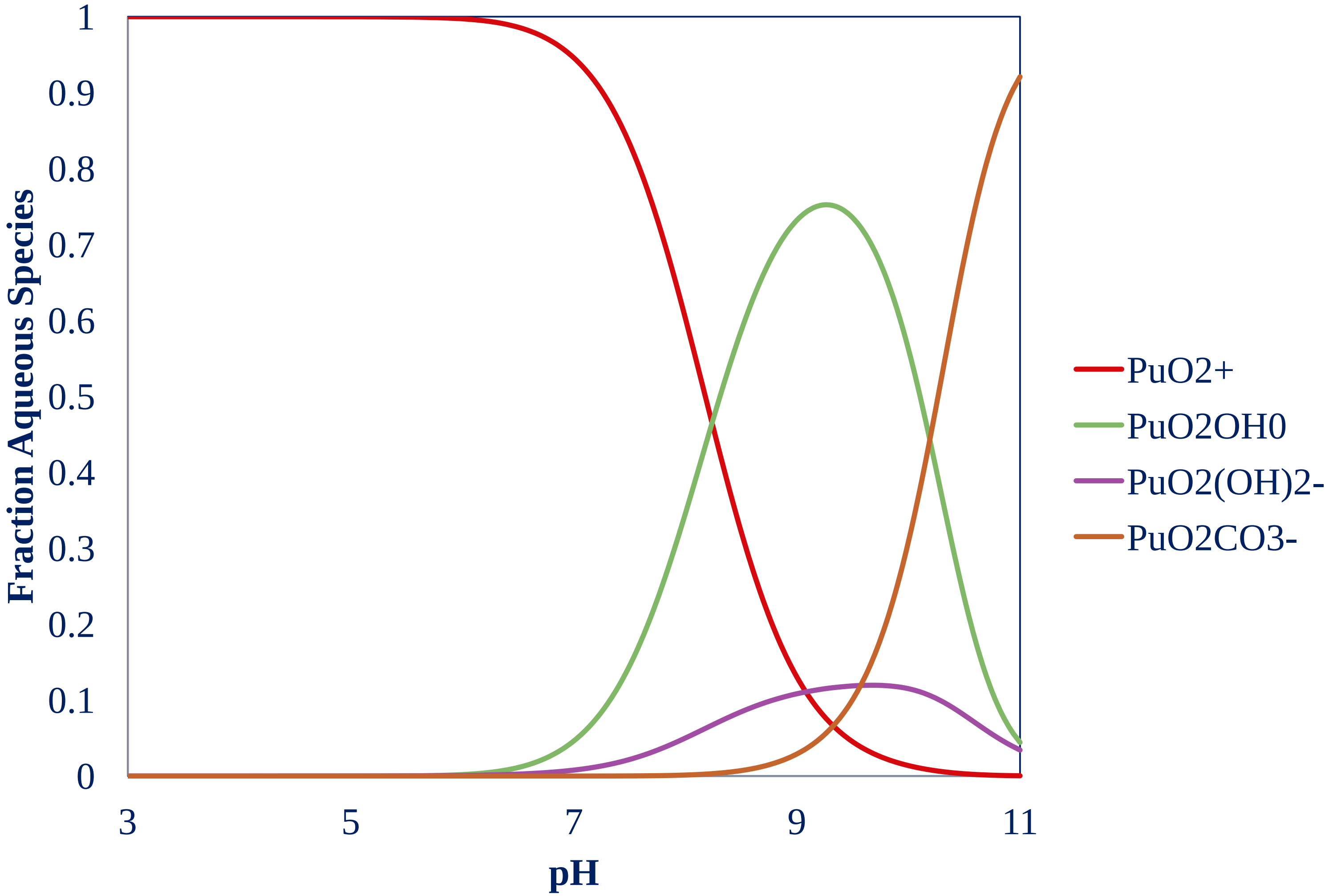
Pentavalent Actinide Carbonate Species

Clark et al., Chem. Rev. 95, 1995, 25-48

Reaction	Ionic Strength	log K
$NpO_2^+ + CO_3^{2-} <=> NpO_2CO_3^-$	0.5	4.2 +/- 0.1
$NpO_2^+ + 2CO_3^{2-} <=> NpO_2(CO_3)_2^{3-}$	0.5	6.4 +/- 0.2
$NpO_2^+ + 3CO_3^{2-} <=> NpO_2(CO_3)_3^{5-}$	0.5	7.8 +/- 0.3
$PuO_2^+ + CO_3^{2-} <=> PuO_2CO_3^{2-}$	0.5	4.6 +/- 0.04
$PuO_2^+ + 3CO_3^{2-} <=> PuO_2(CO_3)_3^{5-}$	1	10.0 +/- 2.1



Pu(V)-Carbonate Speciation



- Modeled using Geochemist workbench incorporating constants from Clark et al., 1995
- Conditions: [Pu(V)] = 10nM, [NaCl] = 10 mM, [CO_3^{2-}] = 1 mM

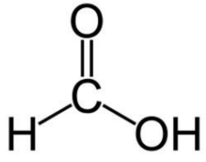
Naturally Occuring Ligands

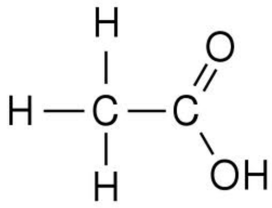
- Organic materials generated as exudates by organisms and plants and byproducts of decay of organic material
- Terminology
    - Dissolved organic matter (DOM)
    - Natural Organic Matter (NOM)

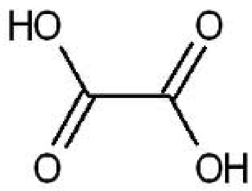
- Aliphatic organics
    - Formic acid (pKa 3.8)
    - Acetic acid (pKa 4.8)
    - Oxalic acid (pKa 1.3)

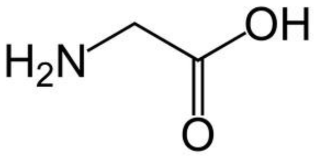
- Amino acids
    - Glycine
    - Aspartic acid
    - Common formula

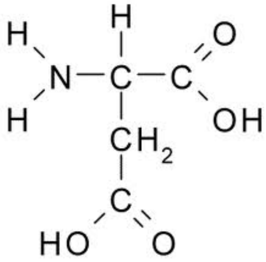
- Saccharides
    - Glucose, cellulose, lignin

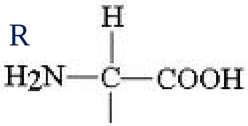












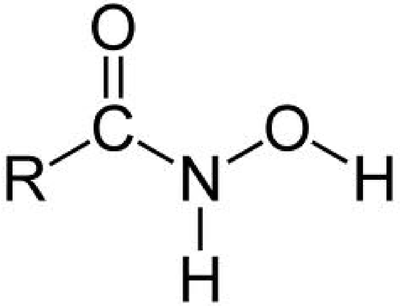
R

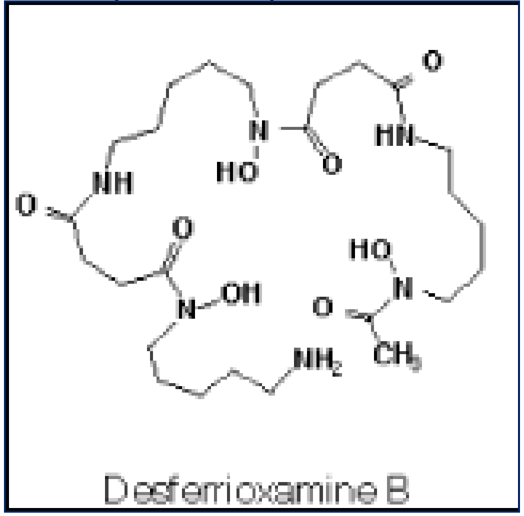
$H_2N-\overset{\overset{H}{|}}{\underset{|}{C}}-COOH$

Naturally Occuring Ligands - Siderophores

- Siderophore: small “iron-chelating” compound excreted by microorganisms, fungi, and grasses to assist with iron uptake
- Current literature shows that siderophores are not as selective as once thought
- Pu(IV) and Fe(III) have similar charge to radius ratios
- Therefore, many biological processes that utilize siderophores for metal uptake may intentionally or unintentionally influence actinides
- Most commonly studied siderophore is desferrioxamine B (DFOB) because it is the only one commercially available

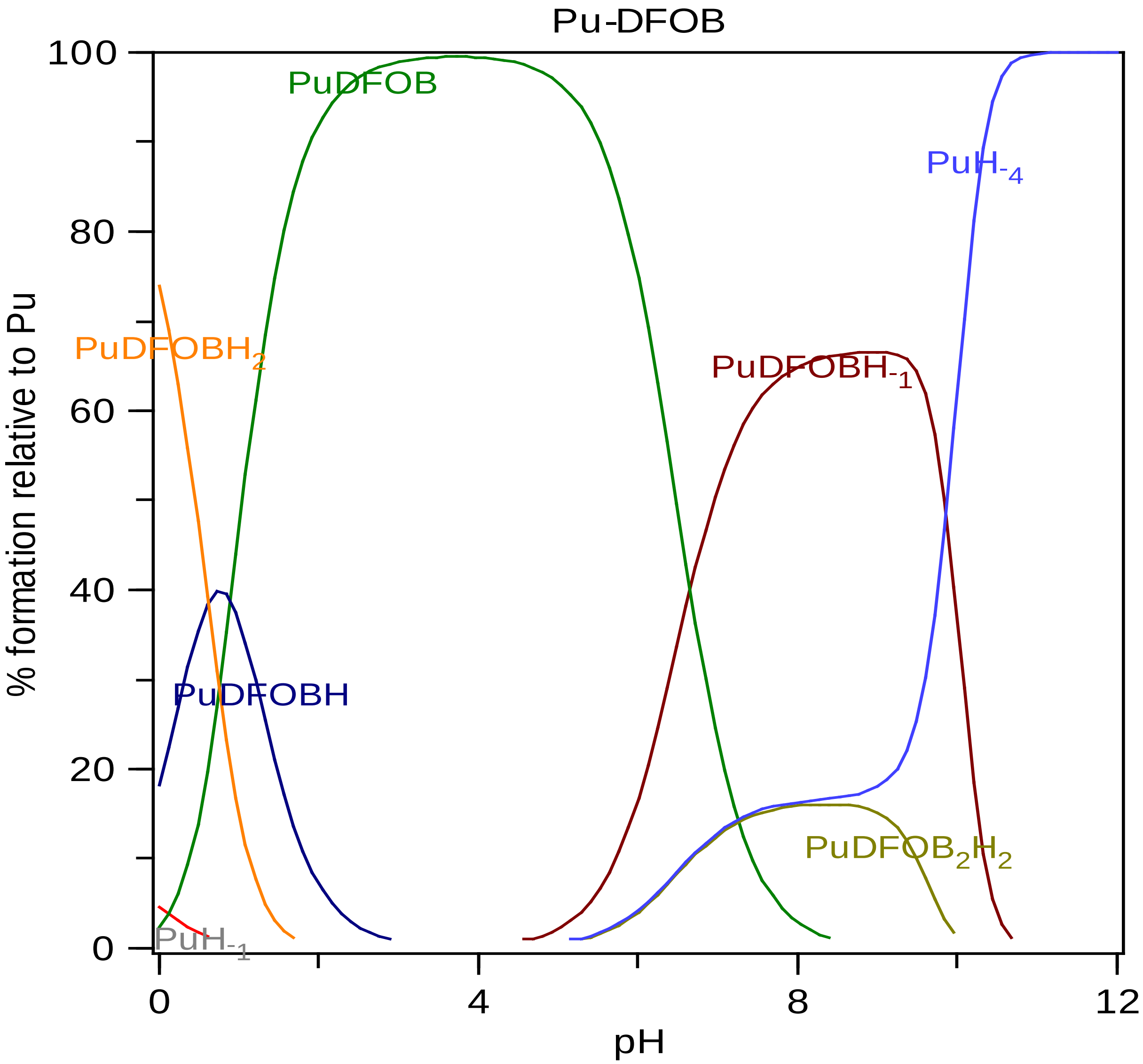
DFOB – polyhydroxamic acid ligand





Desferrioxamine B

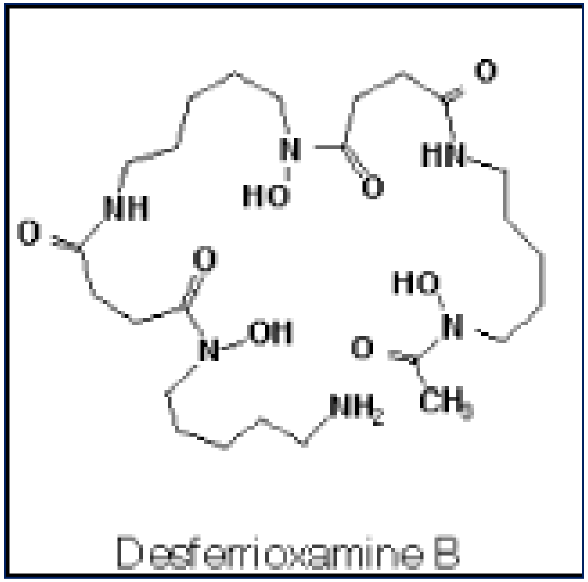
Pu-Desferrioxamine B Complexation



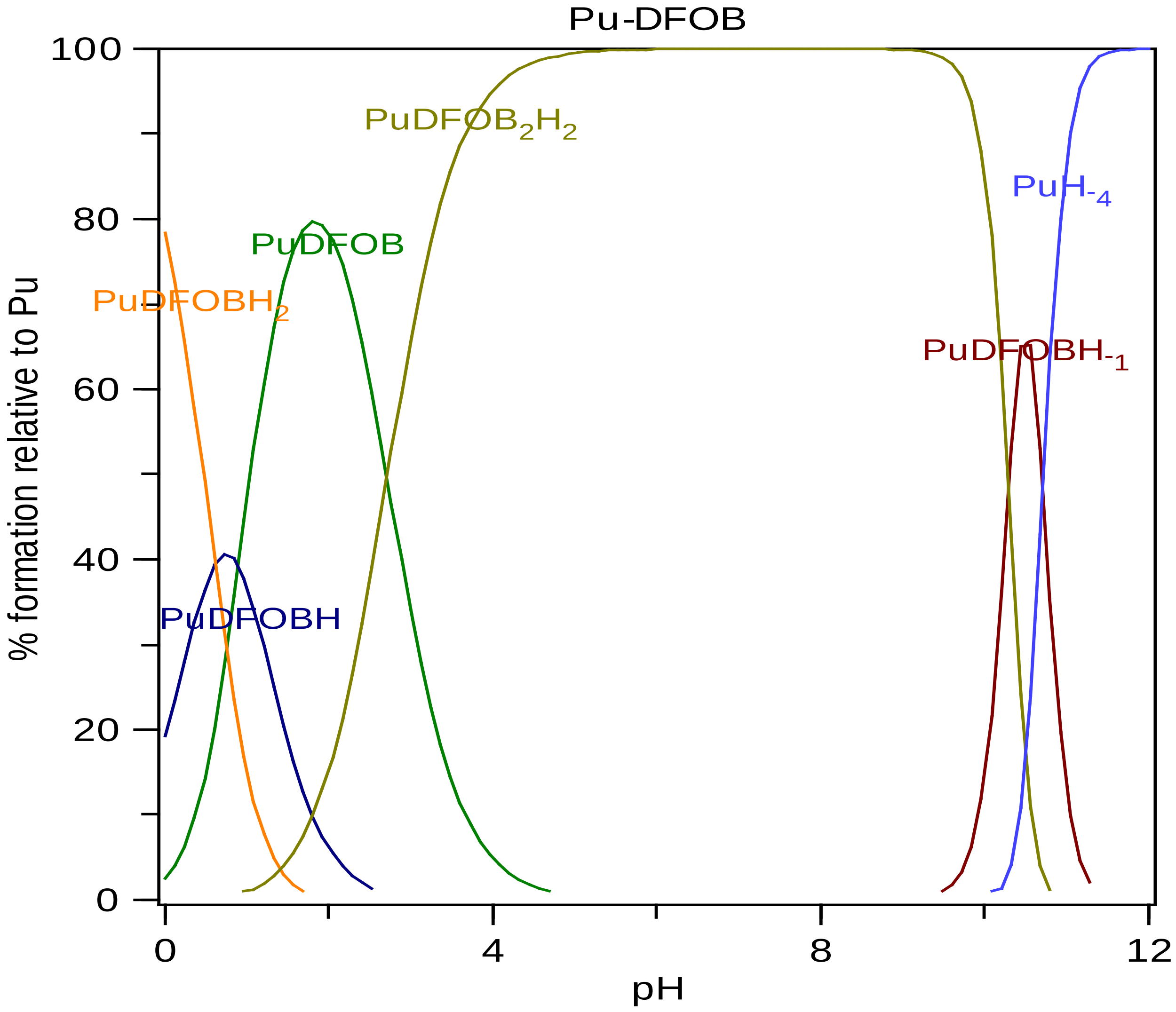
Modeled using HYSS

Constants from Boukhalfa et al., Inorg Chem., 2007, 46, 1018-1026

[Pu(IV)] = 1E-6 M
[DFOB] = 1E-6 M



Pu-Desferrioxamine B Complexation



Modeled using HYSS

Constants from Boukhalfa et al., Inorg Chem., 2007, 46, 1018-1026

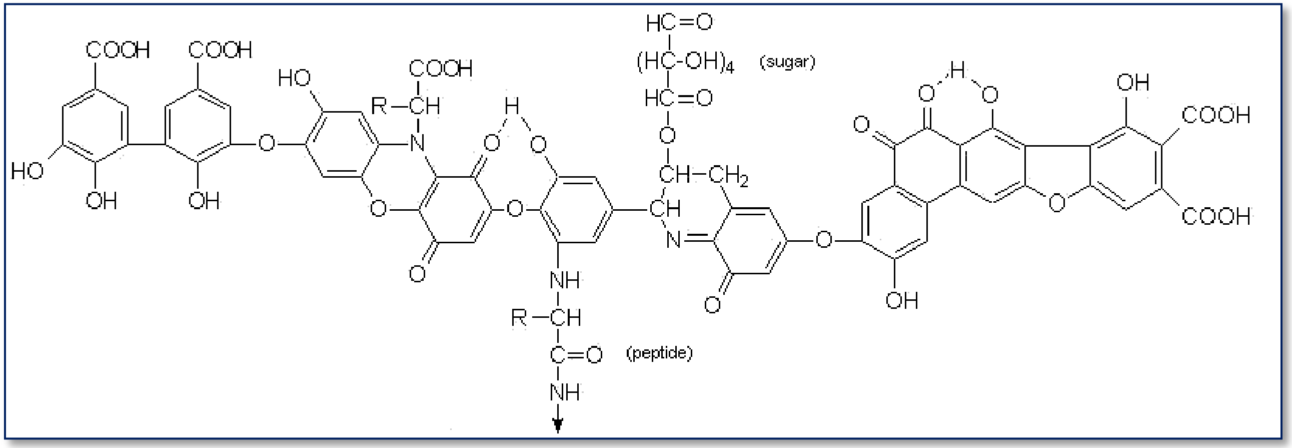
[Pu(IV)] = 1E-6 M
[DFOB] = 1E-3 M

Humic Substances

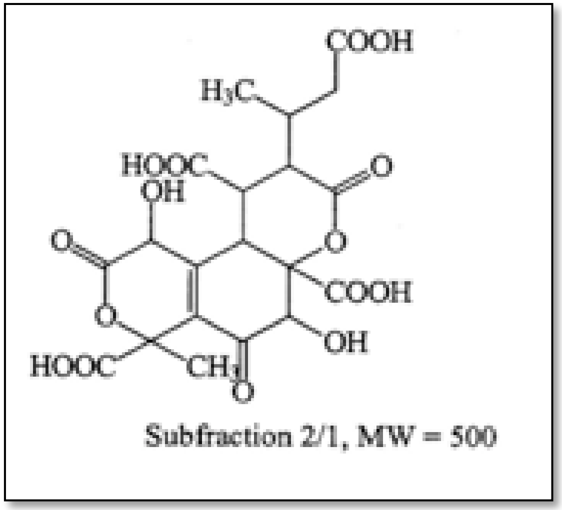
- See Sposito, *The Chemistry of Soils*, for more detail
- Humic substances
  - Humic acid: soluble above pH 2, 1000-10000 amu
  - Fulvic acid: soluble at all pH values, 500-2000 amu
  - Humin: Insoluble fraction
- Various complexing functional groups
  - Carboxylic – COOH
  - Phenolic – OH
  - Amino – NHR, $-NH_2$
  - Thiol – RS
- Model structures on following slides

Examples of Humic Substances

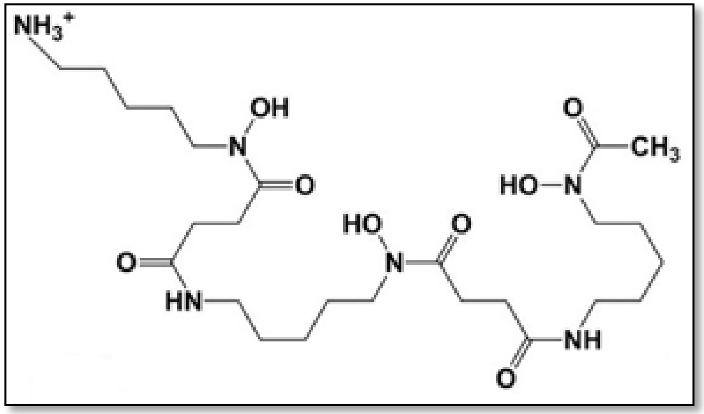
(DFOB and citric acid shown for comparison)



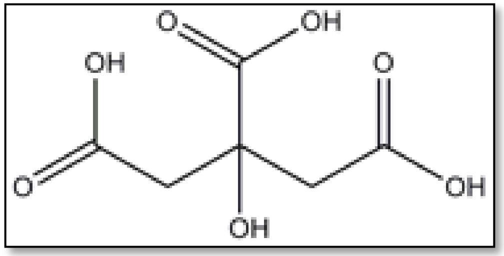
Humic acid (Stevenson 1982)



Fulvic acid



Desferrioxamine B



Citric acid

Modeling Actinide – NOM Binding

- Number of complexing groups and free binding sites is unknown
- Acid-base titrations can be used to calculate meq/gNOM values which can then be used to calculate protonation/deprotonation of available sites
  - Also calculate a degree of ionization
- Charge Neutralization Model (Kim and Czerwinski, 1996)
  - Uses an operational humic acid concentration and loading capacity

$$M^{z+} + HA(z) <=> MHA(z)$$

$$LC = \frac{[MHA(s)]_m}{[HA(z)]_{total}}$$

$$\beta = \frac{[MHA(z)]}{[M^{z+}]_{free}[HA(z)]_{free}}$$

$$\log\frac{[MHA(z)]}{[M^{z+}]_{free}} = \log[HA(z)]_{free} + \log\beta$$

$[MHA(s)]_m$ = maximum M^{z+} concentration permissible for complexation with functional sites

Humic Acid – Actinide Complexation

Silva and Nitsche, 1995, Radiochim. Acta

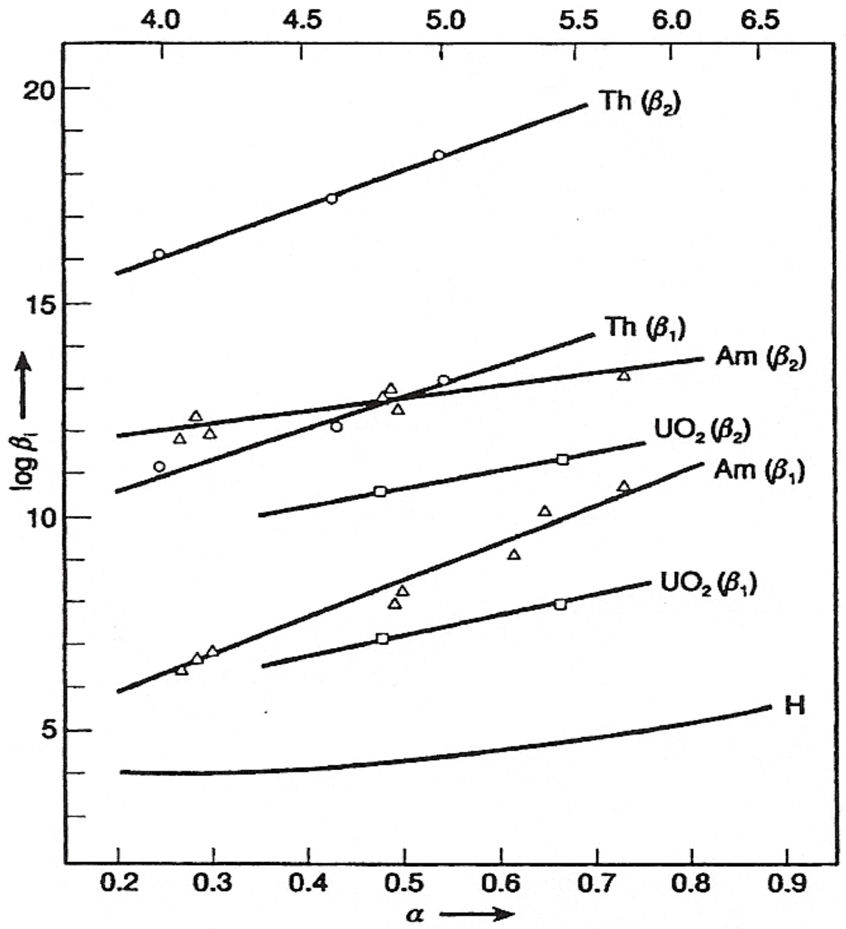
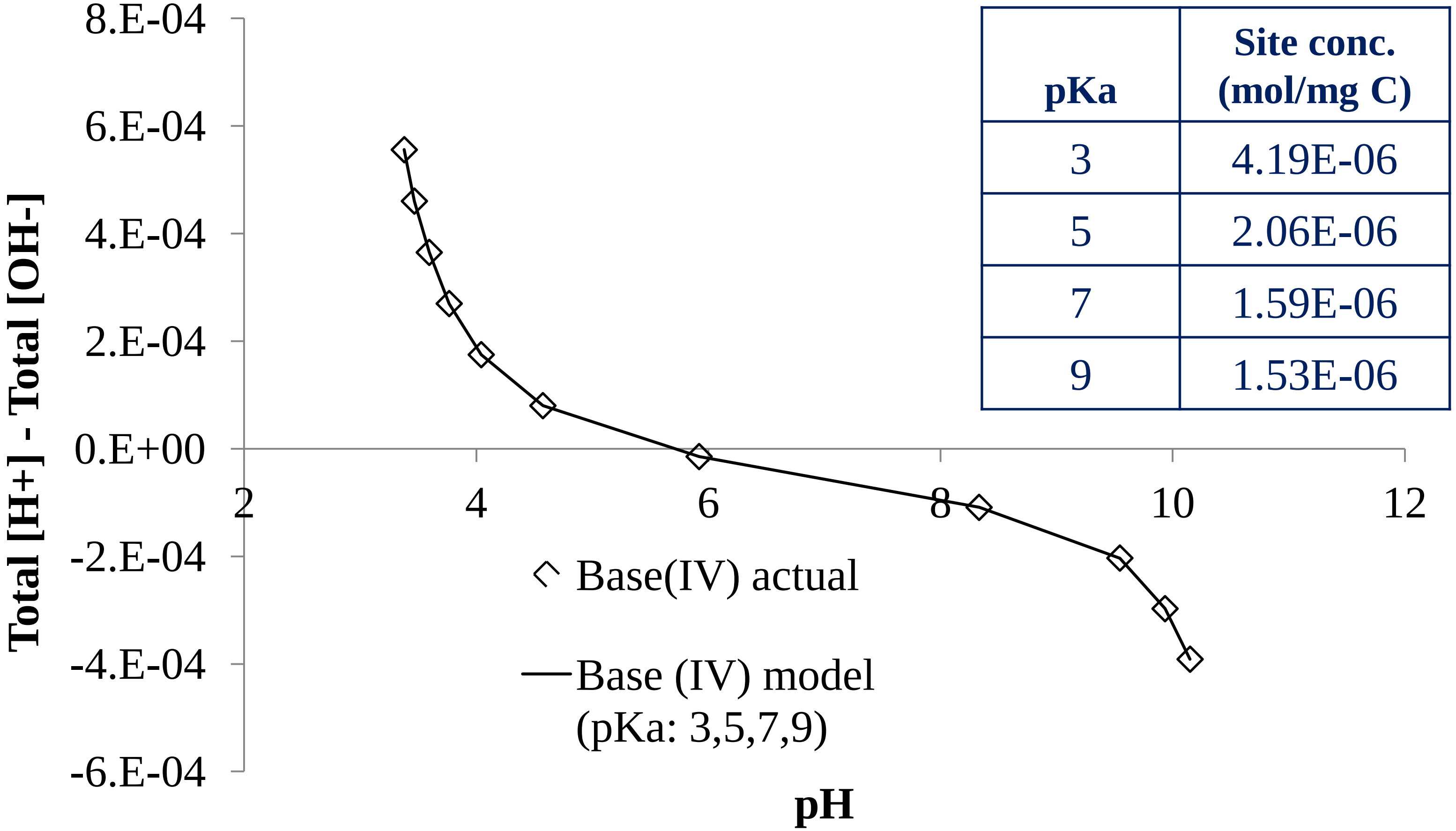


Figure 6.11 Complex formation constants of several actinides with humic acid as a function of the degree of ionization (α) and pH. (Reprinted from Ref. 75 with permission from the author.)

Modeling Actinide – NOM Interactions Discrete pKa Model

Acid-base titration of Leonardite Humic Acid

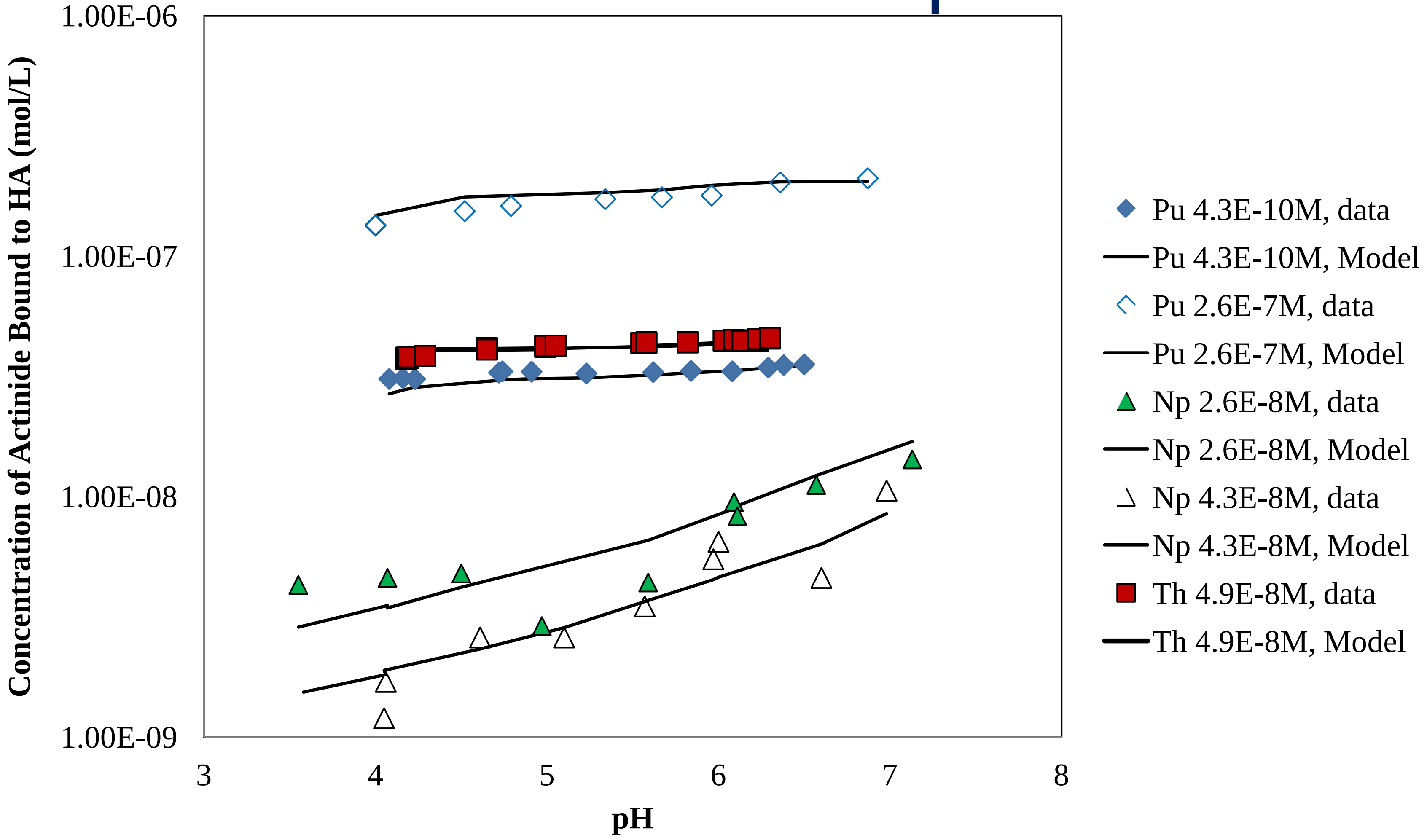


pKa	Site conc. (mol/mg C)
3	4.19E-06
5	2.06E-06
7	1.59E-06
9	1.53E-06

Zimmerman and Powell, Geochimica et Cosmochimica Acta, 2012, in review

Similar discrete pKa models for Pu complexation with extracellular polymeric substances (Harper *et al.*, 2008) and alginic acid (Kantar *et al.*, 2005)

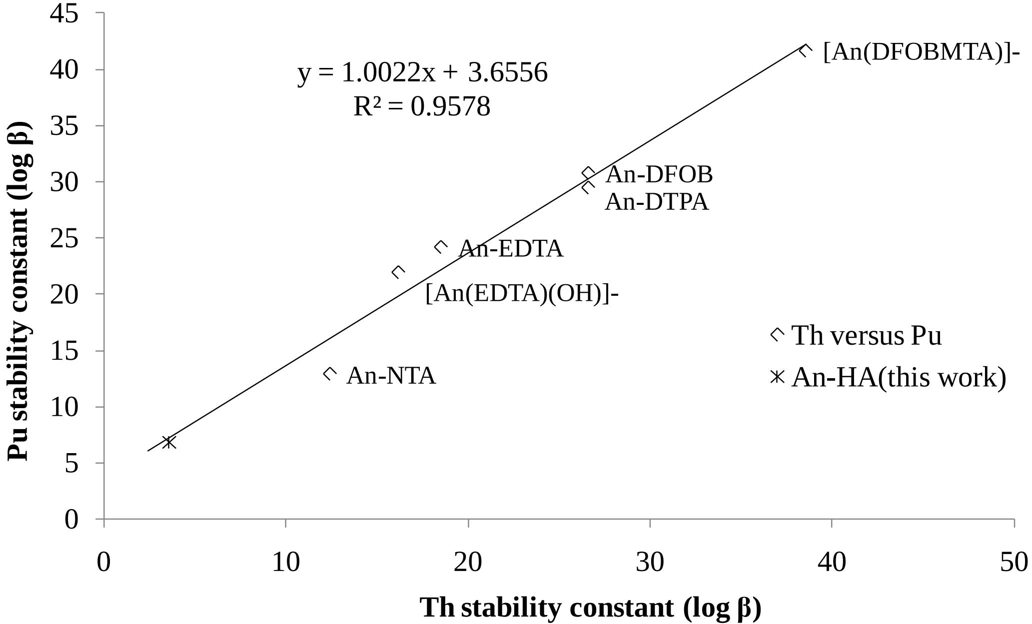
Discrete pKa Model
Actinide – Humic Acid Complexation



Zimmerman and Powell, Geochimica et Cosmochimica Acta, 2012, in review

Actinide – Leonardite Humic Acid Stability Constants

Reaction	Stability Constant
Four discrete pKa ligand binding sites	
$HL(x) \leftrightarrow H^+ + L(x)^-$	pKa = 3, 5,7, 9
$Pu^{4+} + HL3 + 2H_2O \leftrightarrow Pu(OH)_2L3^+ + 3H^+$	log K = 6.76
$Th^{4+} + HL3 + 2H_2O \leftrightarrow Th(OH)_2L3^+ + 3H^+$	log K = 3.58
$NpO_2^+ + HL1 <=> NpO_2L1 + H^+$	log K = 0.31
$NpO_2^+ + HL2 <=> NpO_2L2 + H^+$	log K = -1.35
$NpO_2^+ + HL3 <=> NpO_2L3 + H^+$	log K = -2.28



Zimmerman and Powell, Geochimica et Cosmochimica Acta, 2012, in review

Oxidation/Reduction – Outline

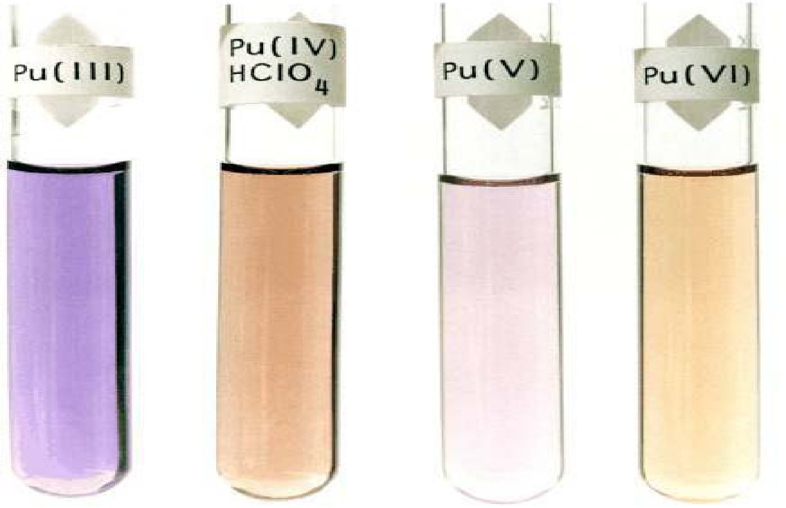
- Common oxidation states
- Redox speciation in natural waters

Plutonium Oxidation/Reduction

- Oxidation state has profound influence on Pu mobility
  - $Pu(IV)^{4+} << Pu(VI)O_2^{2+} \approx Pu(III)^{3+} < Pu(V)O_2^{+}$

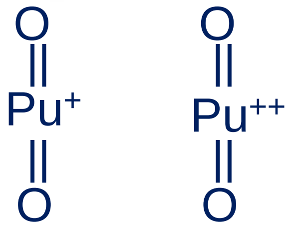
Formal electrochemical potentials versus standard hydrogen electrode (Clark et al., in *The Chemistry of the Actinide Elements*, vol. 3, 2006, p. 1118)

	acidic	neutral	basic
Pu(IV)/Pu(III)	0.98	-0.39	-0.96
Pu(V)/Pu(IV)	1.17	0.70	-0.67
Pu(VI)/Pu(V)	0.91	0.60	0.12
Pu(VI)/Pu(IV)	1.04	0.65	0.34



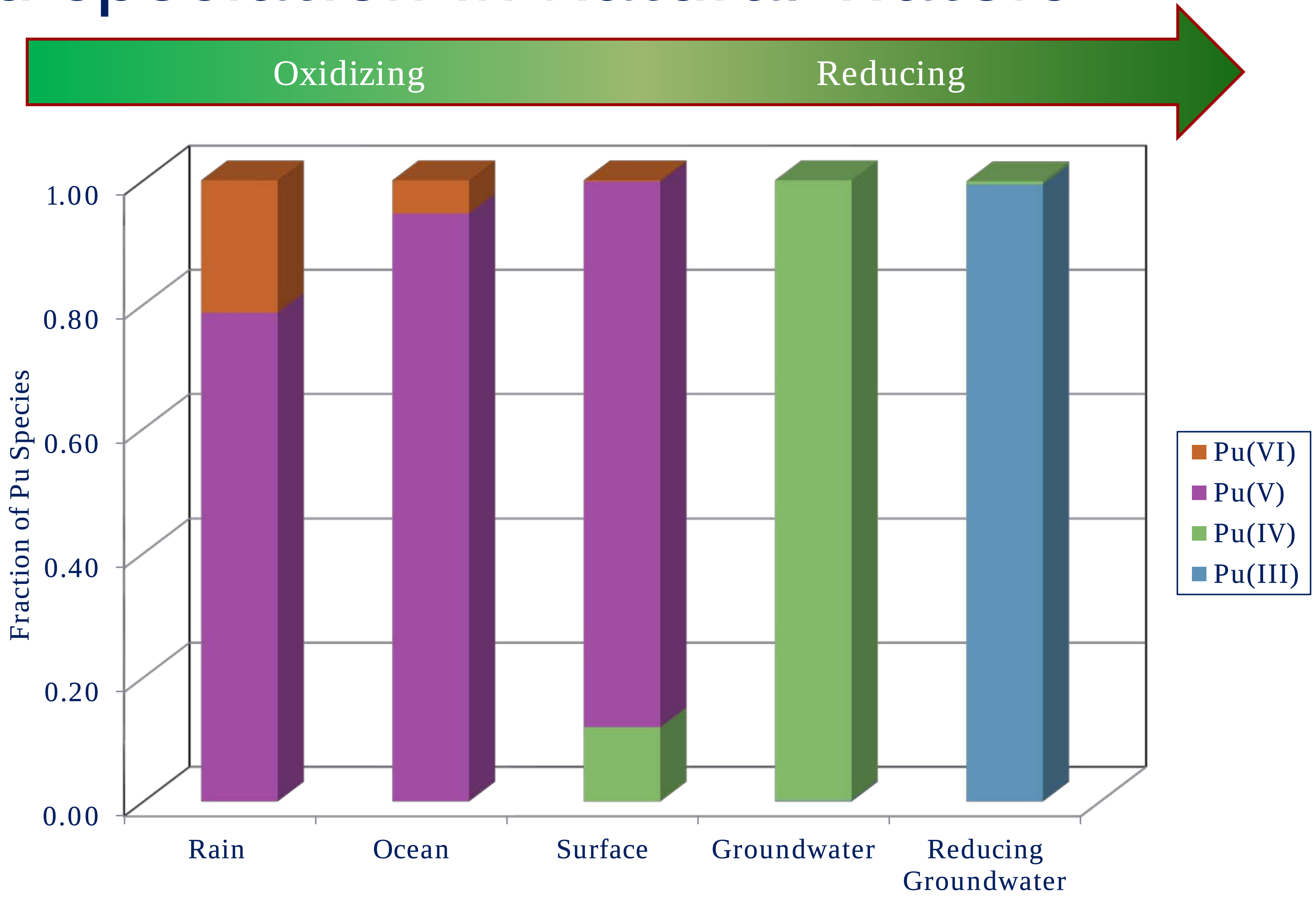
$Pu(OH)_x^{(4-x)}$

$Pu(OH)_x^{(3-x)}$

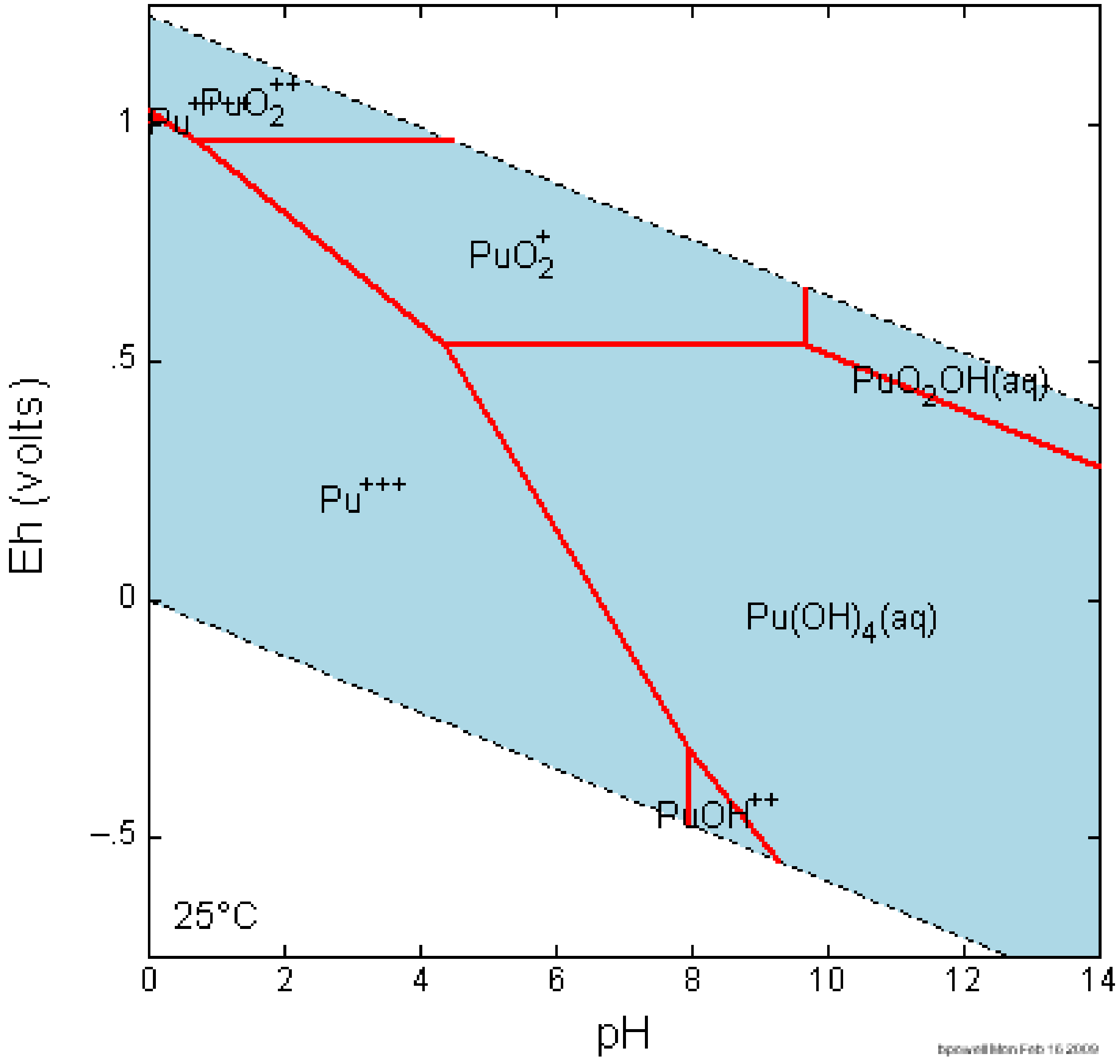


$O{=}Pu^{+}{=}O$ $\quad$ $O{=}Pu^{++}{=}O$

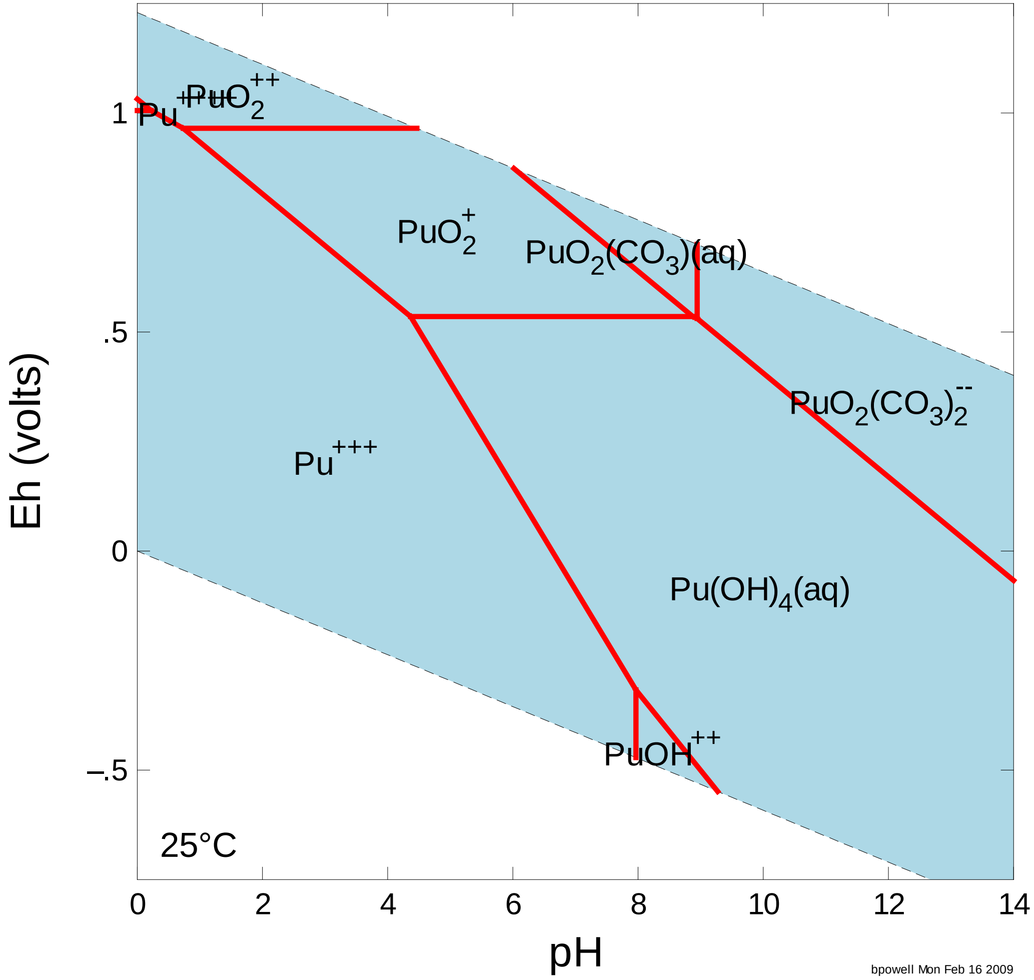
Pu Speciation in Natural Waters



Pu E_H – pH Diagram *GWB Modeling LLNL Database*



Pu E_H – pH Diagram Open to Atmosphere *GWB Modeling LLNL Database*



Actinide Speciation in J-13 Well Water

Nitsche and Edelstein, RCA, 39, 23-33, 1985

J-13 Well Water Composition

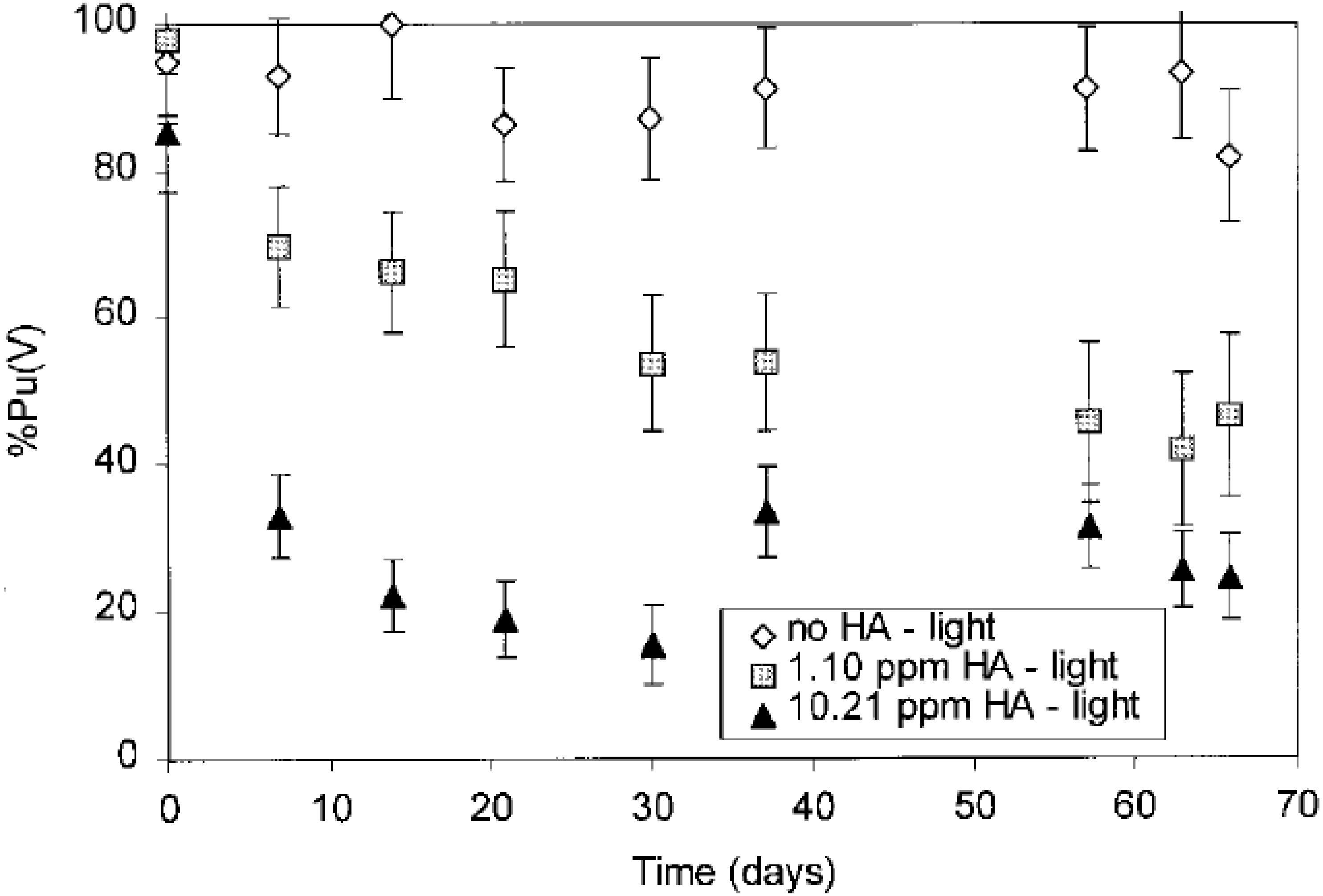
Species	Conc. (mM)
Ca^{2+}	0.29
Mg^{2+}	0.072
Na^{+}	1.96
K^{+}	0.136
Li^{+}	0.009
Fe	0.0008
Mn	0.00002
F^{-}	0.11
Cl^{-}	0.18
SO_4^{2-}	0.19
NO_3^{-}	0.16
Alkalinity	2.34 meq/L
pH	7
E_H	700mV

Solubility and Redox speciation of Pu added to J-13 well water using different initial oxidation states

Initial Species Added	Solubility in J-13 Water (M)	Final Oxidation State of soluble Species	Solid
Pu4+	$1.6 \pm 0.2 \times 10^{-6}$	Pu(III) + Pu(IV) = 2 +/-3% Pu(V) + Pu(VI) = 98 +/- 3%	Amorphous
PuO2+	$8 \pm 3 \times 10^{-6}$	Pu(III) + Pu(IV) = 0 +/-2% Pu(V) + Pu(VI) = 100 +/- 2%	Crystalline solid
PuO22+	$3 \pm 2 \times 10^{-5}$	Pu(III) + Pu(IV) = 2 +/-2% Pu(V) + Pu(VI) = 98 +/- 2%	Crystalline Solid

Pu(V) Reduction by Humic Acid

Andre and Choppin, Radiochim. Acta, 88, 613, 2000



Pu Speciation in Gorleben Groundwater *Marquardt et al., RCA, 92, 617-623, 2004*

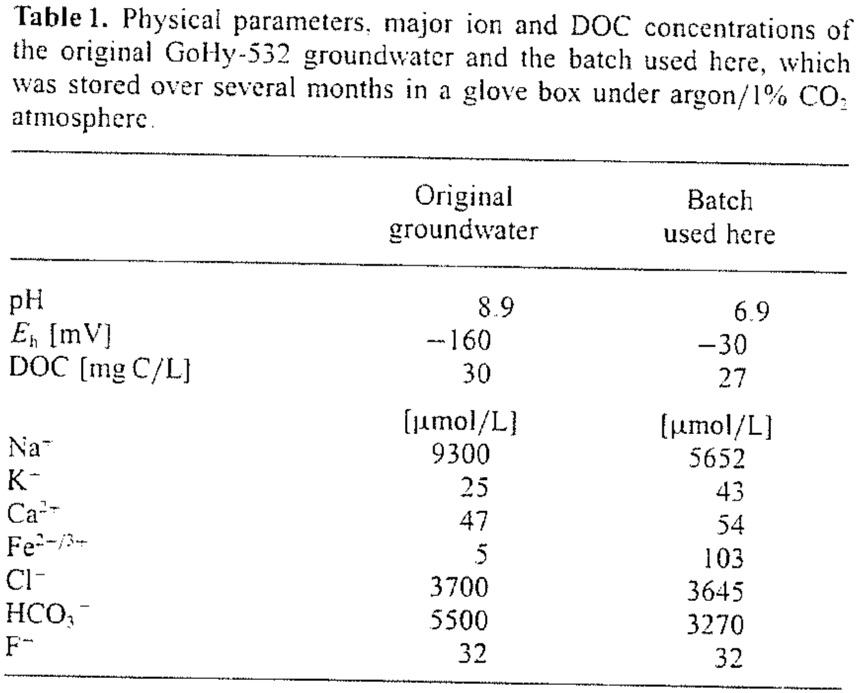


Table 1. Physical parameters, major ion and DOC concentrations of the original GoHy-532 groundwater and the batch used here, which was stored over several months in a glove box under argon/1% CO_2 atmosphere.

	Original groundwater	Batch used here
pH	8.9	6.9
E_h [mV]	−160	−30
DOC [mg C/L]	30	27
	[µmol/L]	[µmol/L]
Na^+	9300	5652
K^+	25	43
Ca^{2+}	47	54
$Fe^{2+/3+}$	5	103
Cl^-	3700	3645
HCO_3^-	5500	3270
F^-	32	32

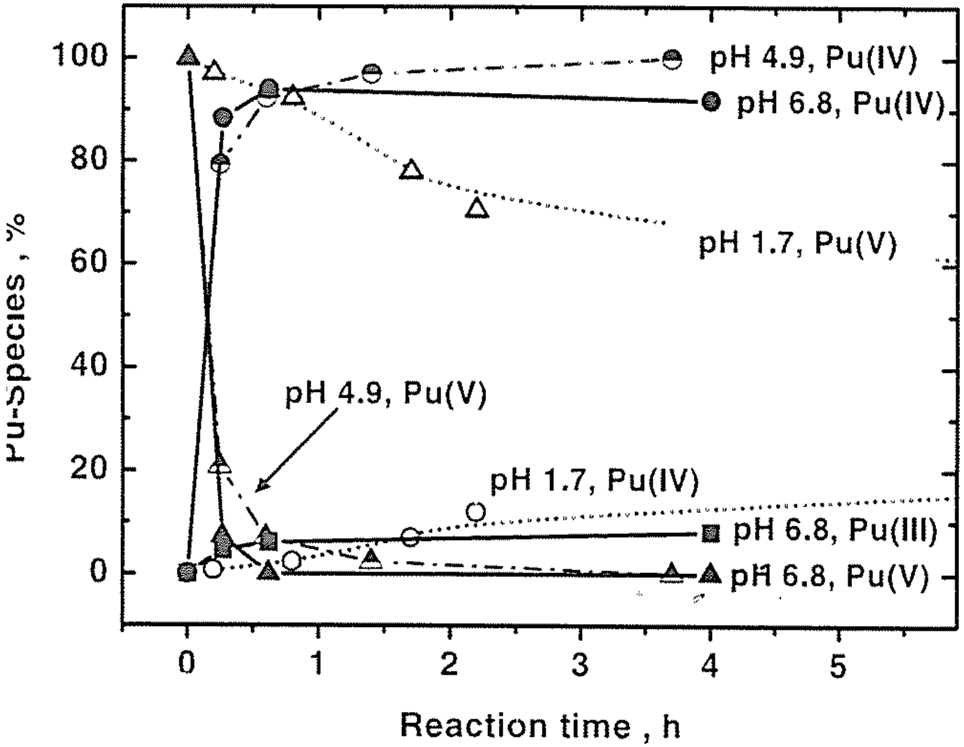


Fig. 3. Distribution of Pu(III), Pu(IV) and Pu(V) plotted versus the reaction time between Pu(V) and the GoHy-532 groundwater at different pH values obtained by CE-ICP-MS. The squares, circles and triangles represents Pu(III), Pu(IV) and Pu(V), respectively. [Pu] = 5×10^{-5} M.

Np Reduction by Quinonoid Enriched Humic Derivatives

Shcherbina et al., Env. Sci. Tech., 41, 7010-7015, 2007

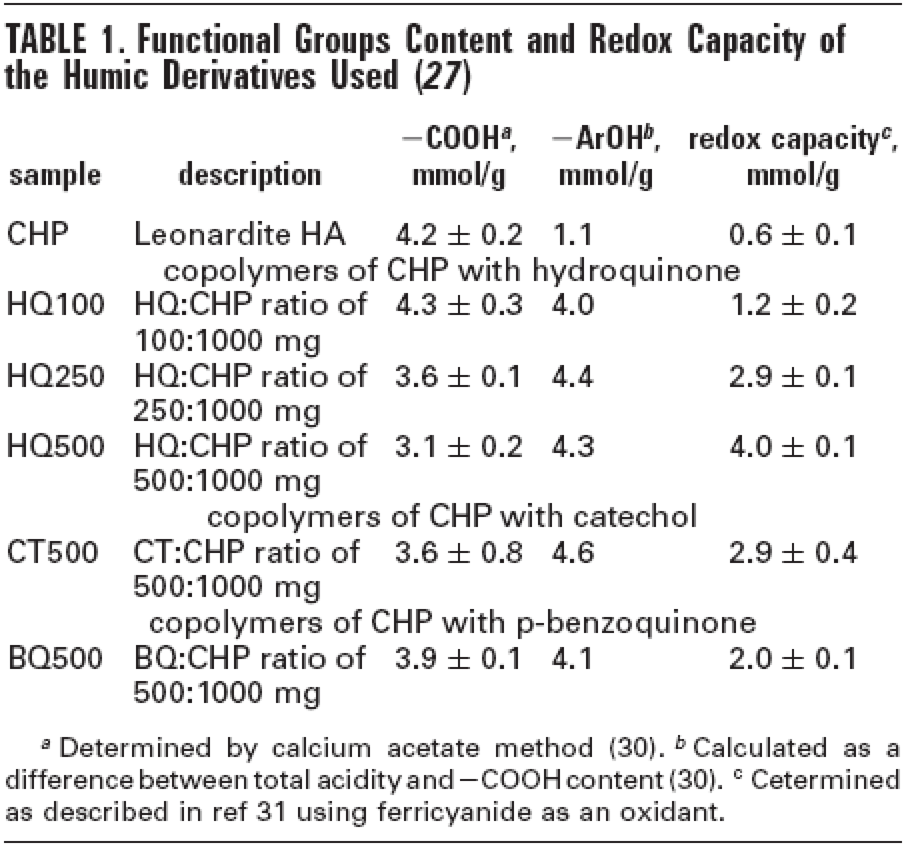


TABLE 1. Functional Groups Content and Redox Capacity of the Humic Derivatives Used (27)

sample	description	$-COOH^a$, mmol/g	$-ArOH^b$, mmol/g	redox capacity^c, mmol/g
CHP	Leonardite HA	4.2 ± 0.2	1.1	0.6 ± 0.1
	copolymers of CHP with hydroquinone			
HQ100	HQ:CHP ratio of 100:1000 mg	4.3 ± 0.3	4.0	1.2 ± 0.2
HQ250	HQ:CHP ratio of 250:1000 mg	3.6 ± 0.1	4.4	2.9 ± 0.1
HQ500	HQ:CHP ratio of 500:1000 mg	3.1 ± 0.2	4.3	4.0 ± 0.1
	copolymers of CHP with catechol			
CT500	CT:CHP ratio of 500:1000 mg	3.6 ± 0.8	4.6	2.9 ± 0.4
	copolymers of CHP with p-benzoquinone			
BQ500	BQ:CHP ratio of 500:1000 mg	3.9 ± 0.1	4.1	2.0 ± 0.1

[a] Determined by calcium acetate method (30). [b] Calculated as a difference between total acidity and –COOH content (30). [c] Determined as described in ref 31 using ferricyanide as an oxidant.

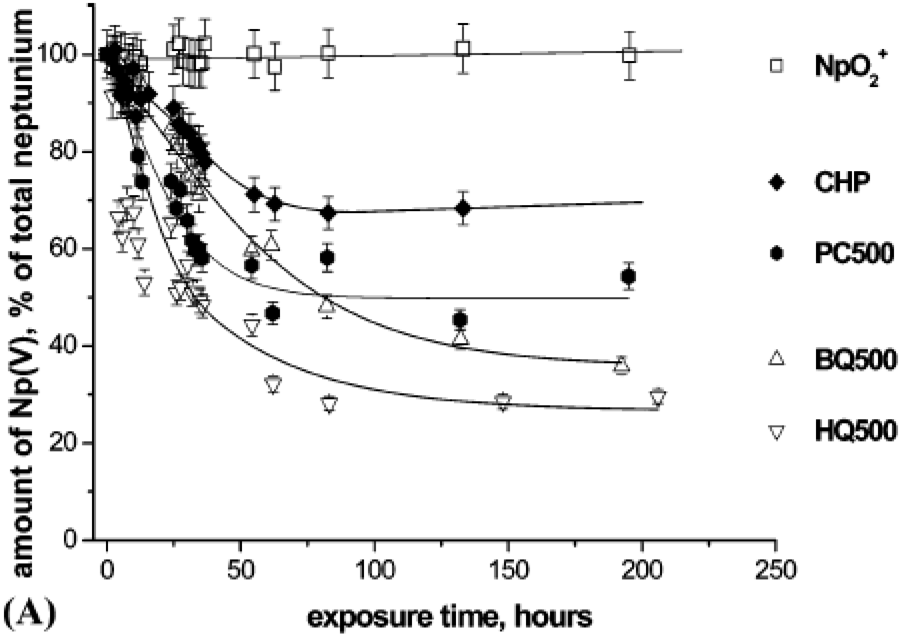
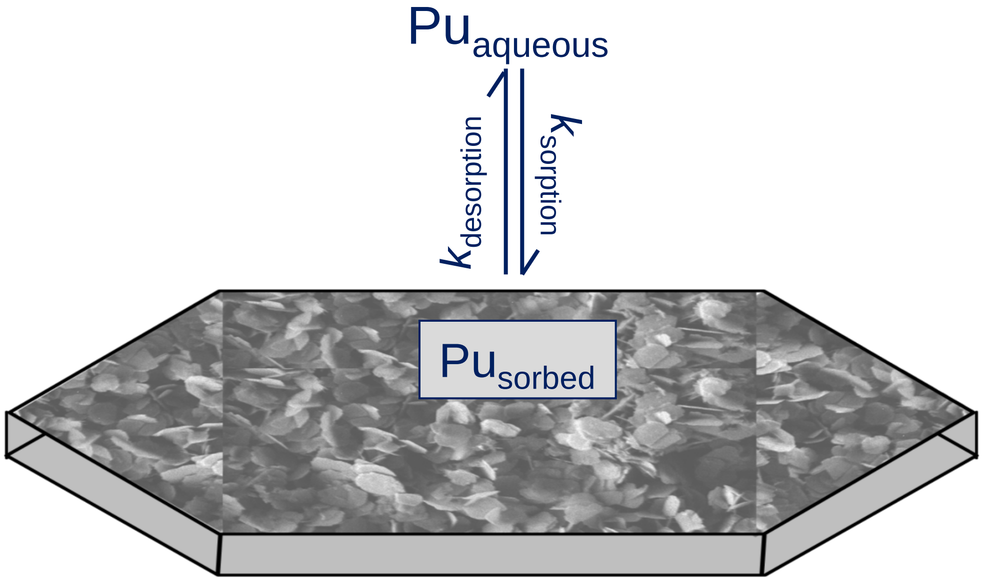


FIGURE 2. Reduction of Np(V) by humic derivatives under anoxic conditions and pH 4.7, $C_0(Np) = 5.4 \times 10^{-5}$ M, $C_0(HS) = 500$ mg/L, Np(V):HS ratio = 1:40. A, Effect of quinonoid monomer nature incorporated into humic structure; B, Effect of different parent HA-to-monomer ratio for HQ enriched derivatives.

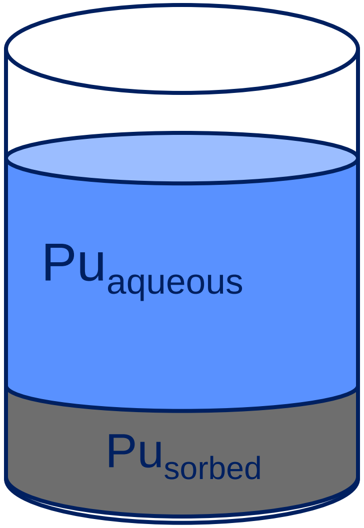
Sorption/Desorption

- Overview of mineral water interface chemistry
- Quantifying sorption processes
- Sorption in binary systems
- Influence of aqueous chemistry on sorption
  - Aqueous complexation with inorganic ions
  - Redox reactions complexation on sorption
  - Complexation with organic ions
- Colloidal transport of plutonium

Sorption Distribution Coefficients



$$K_D = \frac{\text{Pu Sorbed Conc.}}{\text{Pu Aqueous Conc.}}$$



Filter sample at time (t) and measure aqueous Pu concentration

$$K_D = \left[\frac{[\mathrm{Pu}]_o - [\mathrm{Pu}]_t}{[\mathrm{Pu}]_t}\right]\frac{V}{m}$$

$[\mathrm{Pu}]_o$ = initial aqueous Pu conc.
$[\mathrm{Pu}]_t$ = aqueous Pu conc. at time t
V = solution volume
m = mass of solid phase

Empirically Quantifying Sorption Processes

- Linear Distribution Coefficient, K_d

$$K_d = \frac{[Pu(t)]_{solid}}{[Pu(t)]_{aqu}}$$

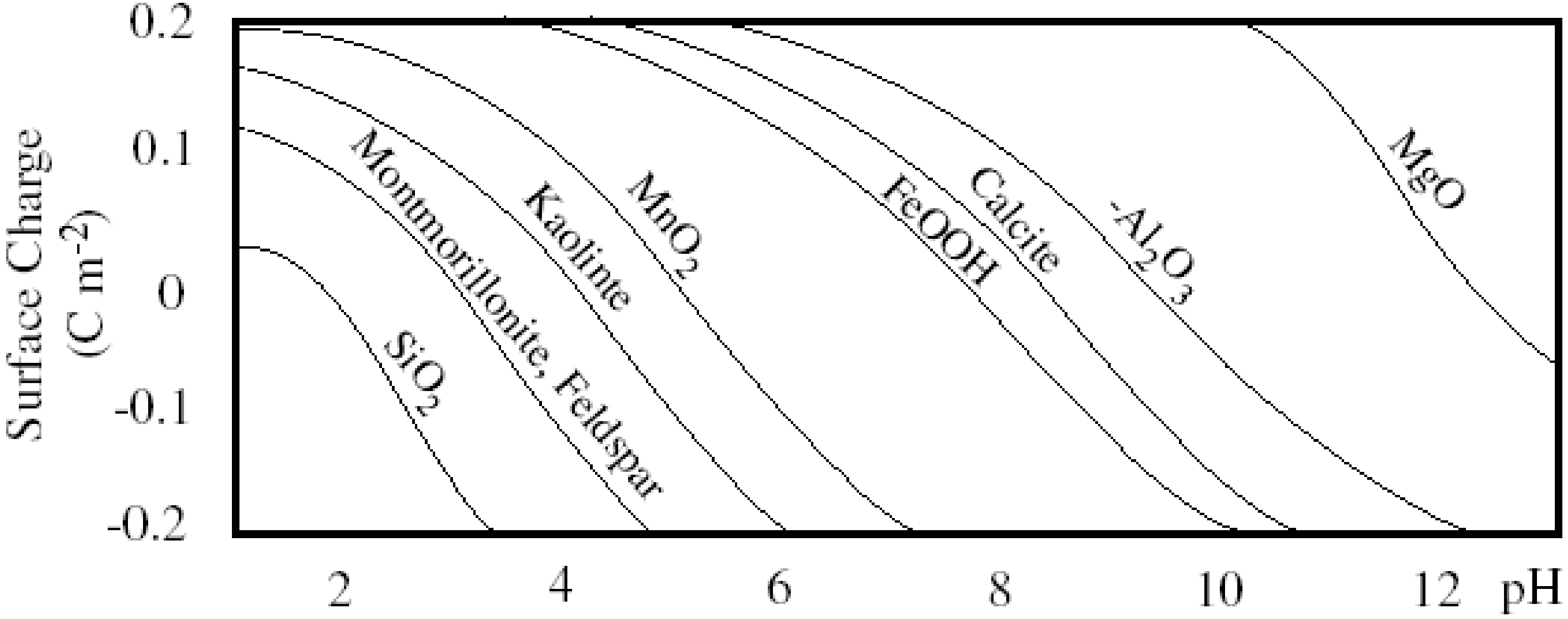
  - Typically determine $[An(t)]_{solid}$ by difference during sorption tests

$$[Pu(t)]_{solid} = ([Pu]_{total} - [Pu(t)]_{aqu}) * \frac{Volume_{aqu}}{mass_{solids}}$$

- Empirical Isotherms
  - Freundlich $$[Pu(t)]_{solid} = K_f [Pu(t)]_{aqu}^n$$
  - Langmuir $$[Pu(t)]_{solid} = \frac{[Pu(\max)]_{solid} K_l [Pu(t)]_{aqu}}{1 + K_l [Pu(t)]_{aqu}}$$

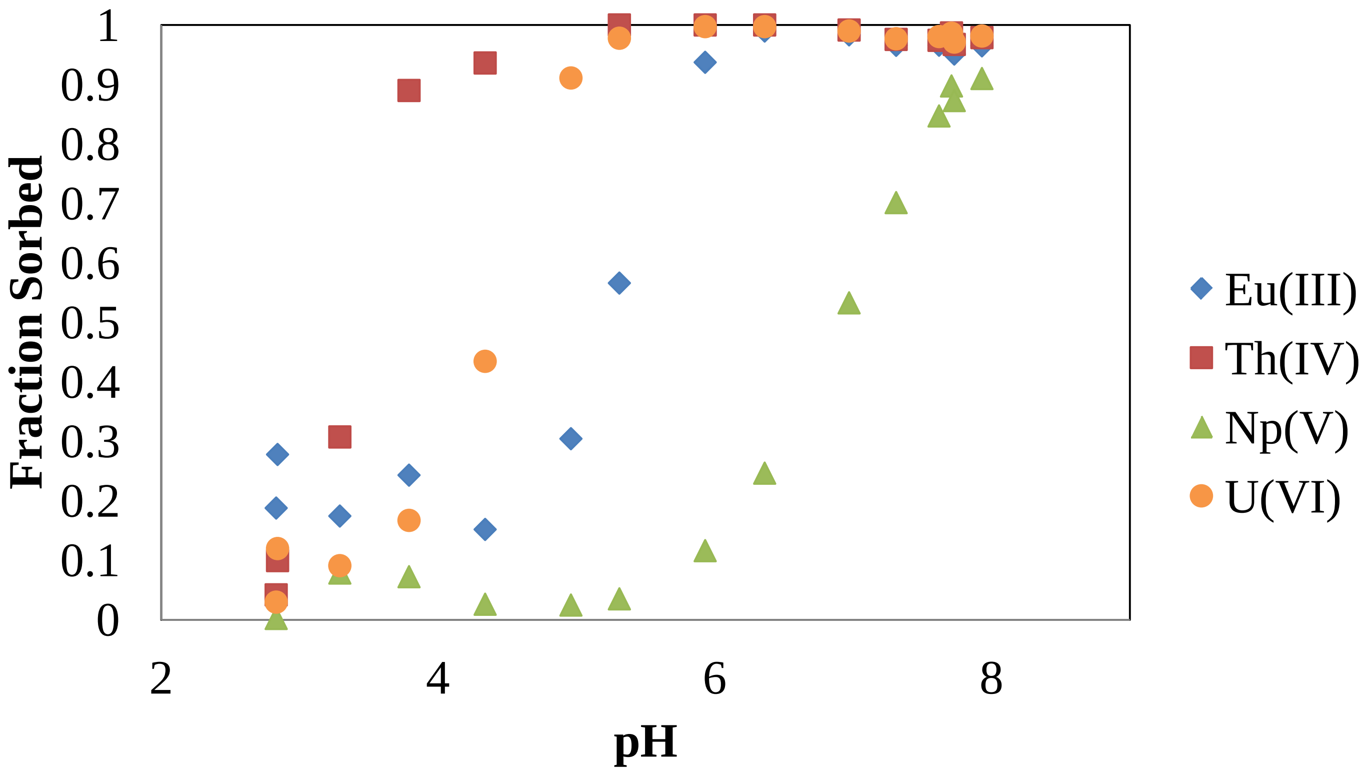
See second lecture in this series for a discussion of sorption models, including surface complexation modeling approaches.

Surface Charge Versus pH



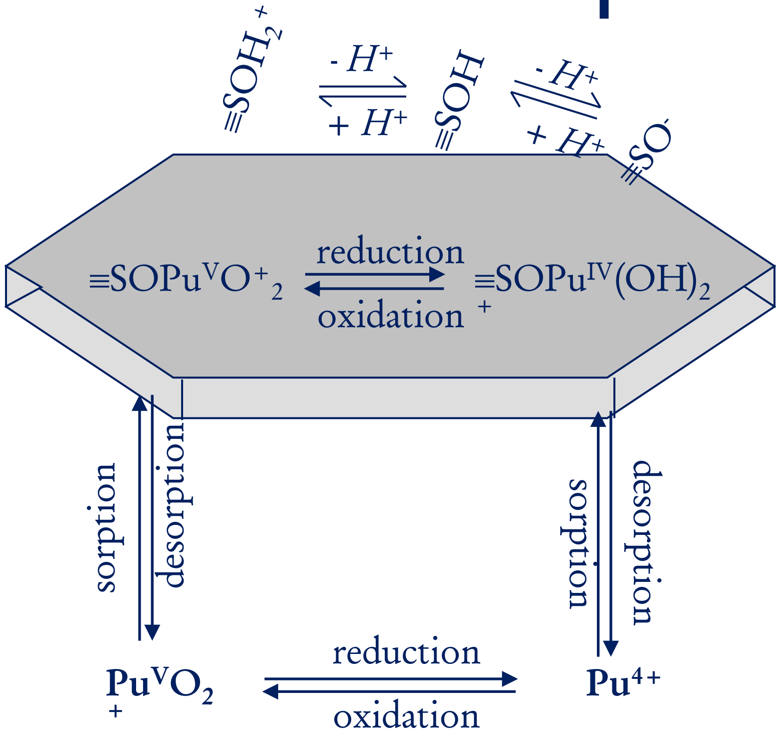
Modified from Stumm and Morgan, 1996

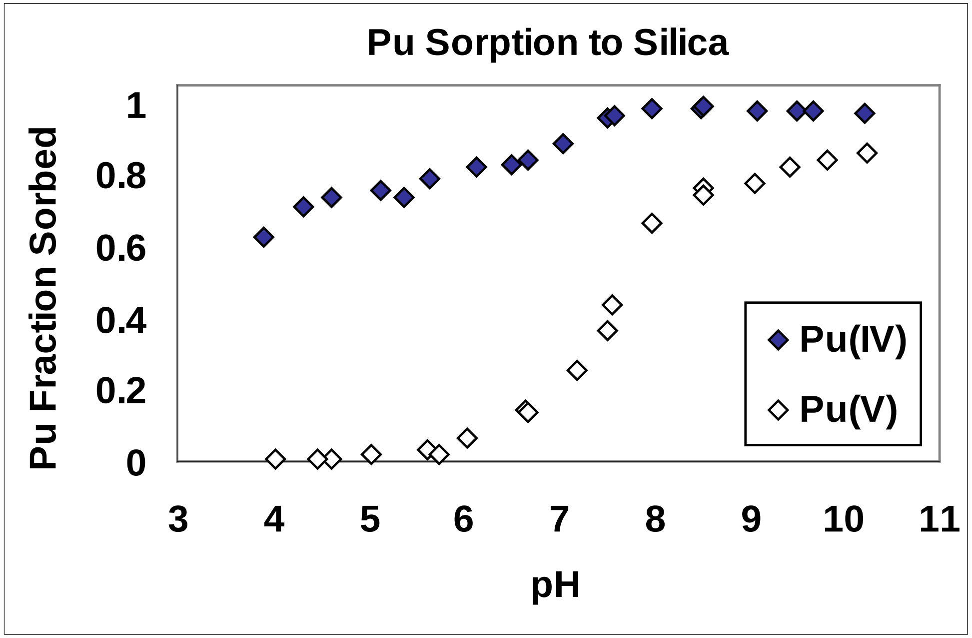
Cation Sorption: Actinide Sorption Trends

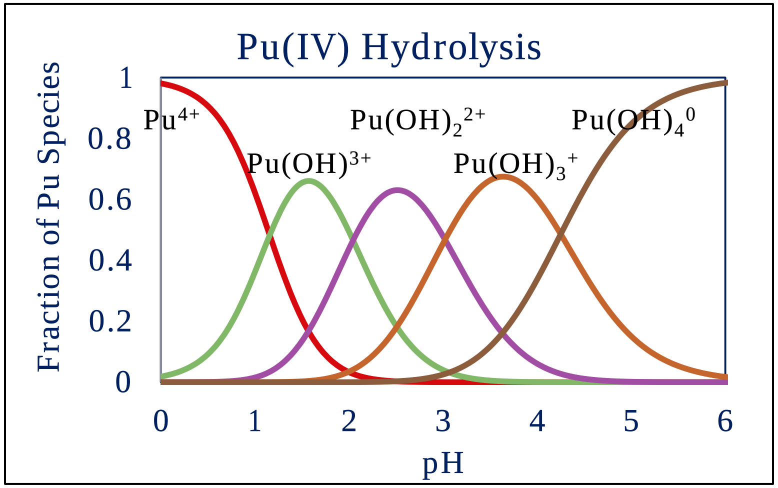


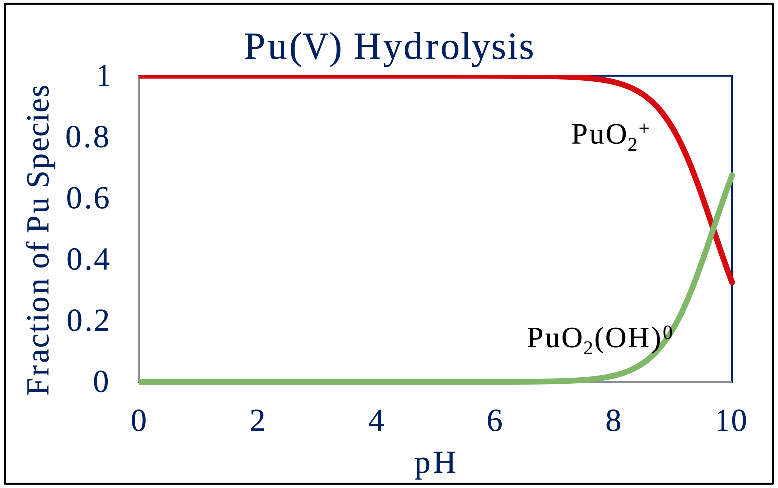
- Sorption of actinides to goethite versus pH
  - Unpublished data from Shanna Estes, Clemson University, 2011
- Sorption affinity follows expected trend
- An(IV) > An(VI) > An(III) > An(V)

Plutonium Sorption/Desorption



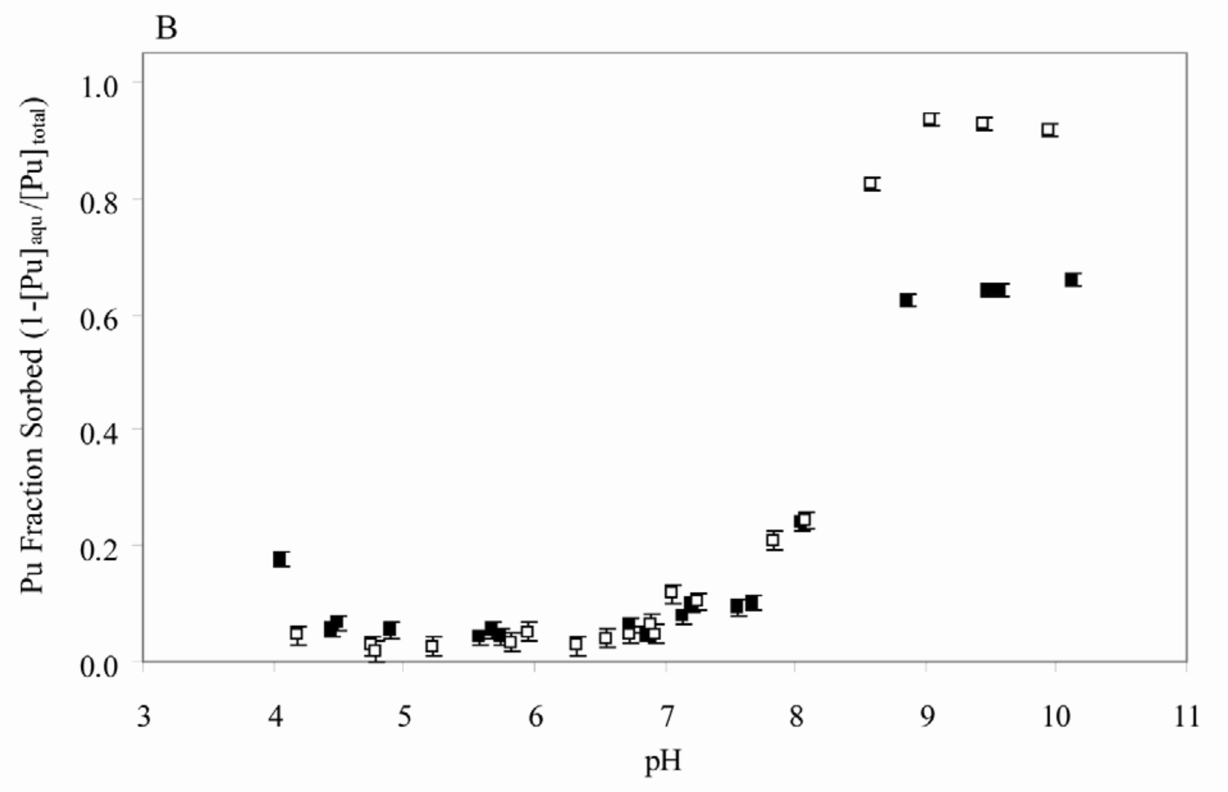






Effect of Carbonate on Pu(V) Sorption

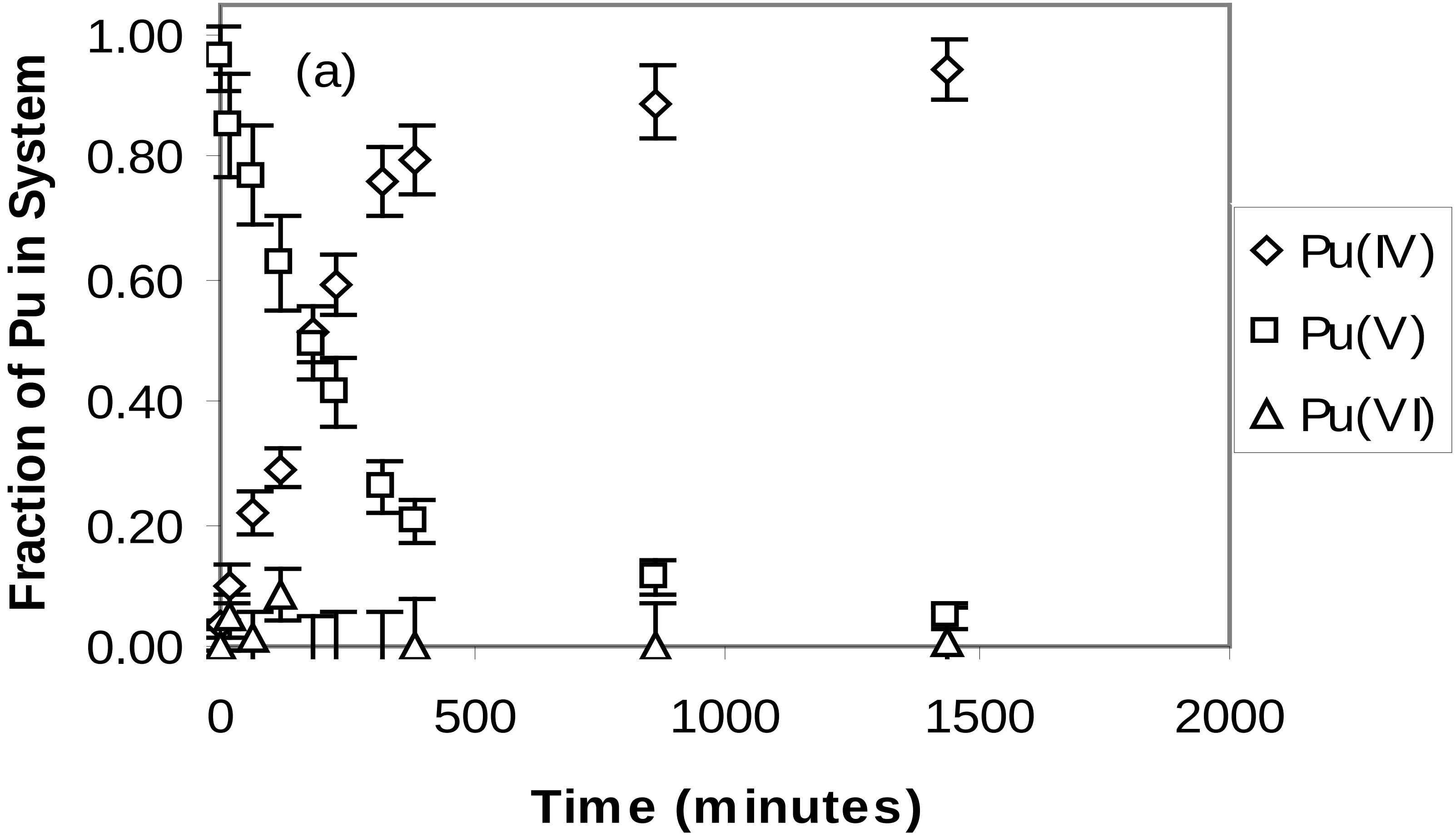
Powell et al., LLNL-TR- 408276, 2008



- Sorption of Pu(V) to SWy-1 Na-montmorillonite after 24 hours
- Open symbols represent systems where atmospheric CO_2(g) was excluded
- System parameters: [montmorillonite] = 10 m^2 L^{-1} (0.17 g L^{-1}); [Pu] = 1.2 x 10^{-10} M, initially added as Pu(IV); [NaCl] = 0.01; $NaHCO_3/Na_2CO_3$ added to solutions exposed to atmospheric CO_2(g) to speed equilibration. Total [HCO_3^-] at desired pH added based upon known K_{HCO3-} and $K_{CO3—}$values, but limited to a maximum concentration of 0.010 M at higher pH values.

Plutonium Reduction by Magnetite (Fe_3O_4), pH 6.5

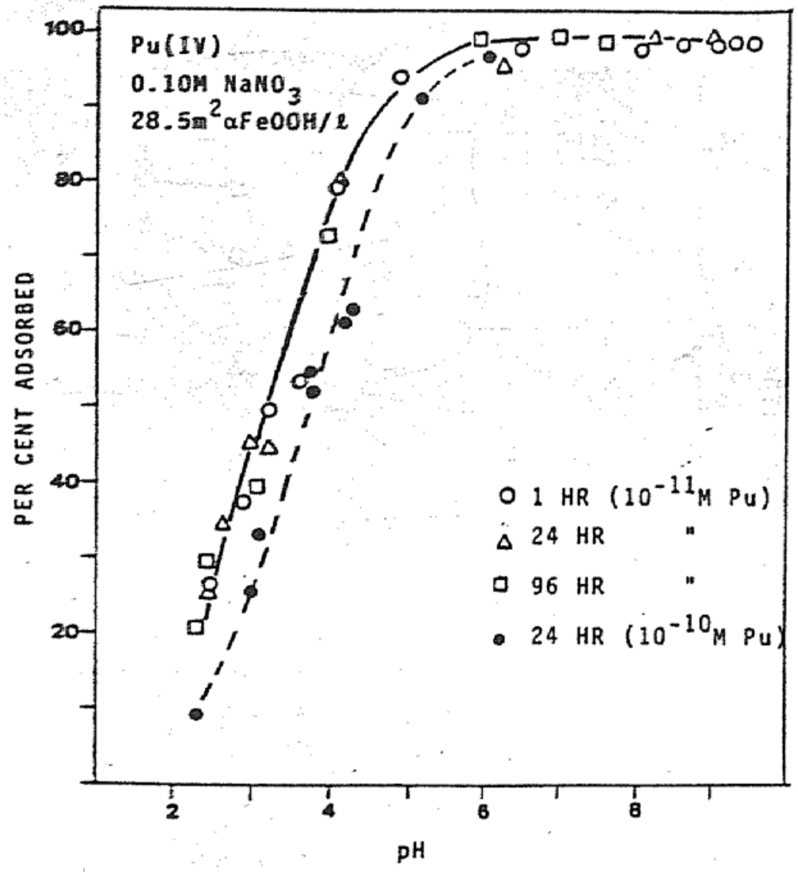
Powell et al., Environ. Sci. Tech., 38, 6016-6024, 2004

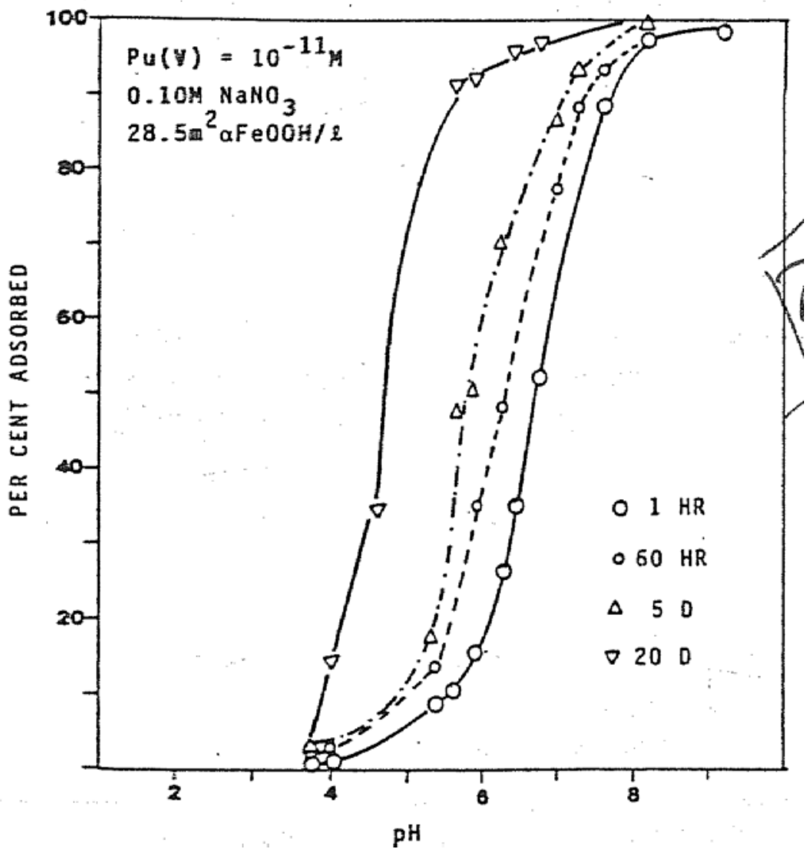


Apparent Surface Mediated Reduction of Pu(V)

Sanchez, Geochimica et Cosmochimica Acta, 1985

- The shift in the sorption edge to lower pH values over time is indicative of surface mediated reduction of Pu(V) to Pu(IV)
- Similar observations from Kenny-Kennicutt and Morse (1985) and Powell et al. (2005)





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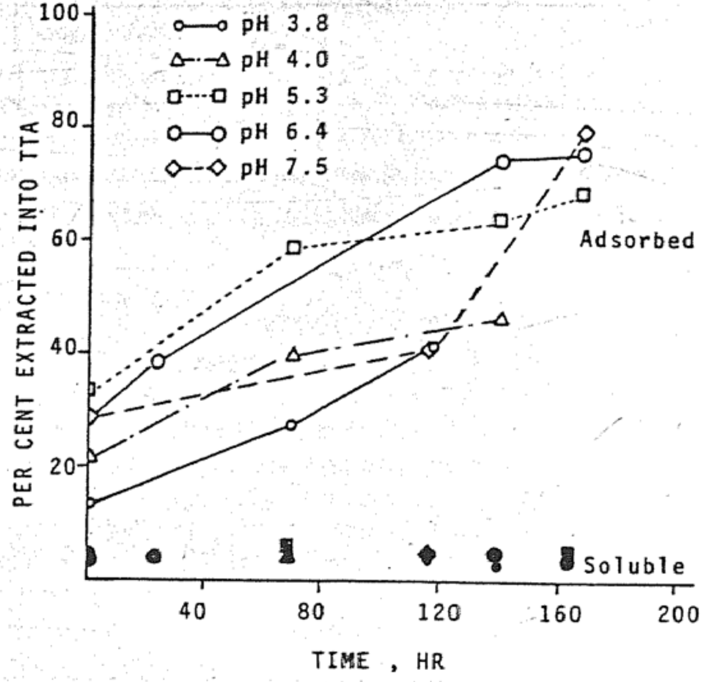
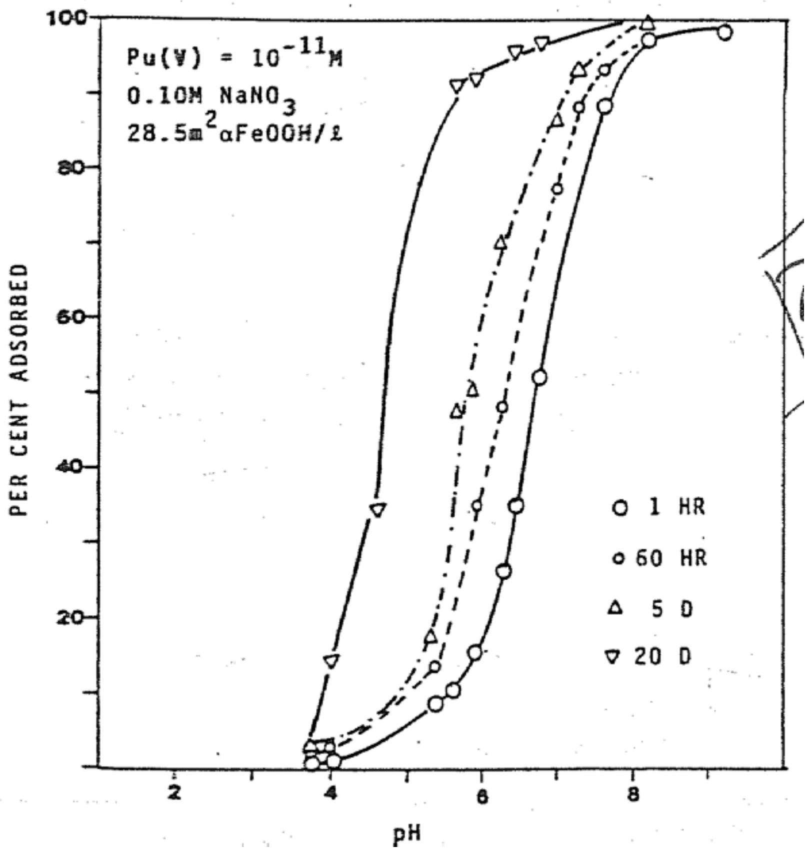


FIG. 2. The percent of total Pu(V) added that became TTA-extractable Pu(IV) as a function of time in the adsorbed and the dissolved fractions. Results from goethite experiments initially spiked with Pu(V). Initial data points are for 1 hour after adsorption started. Error for TTA extraction is ±5%.



Numerous Observations of Surface Mediated Redox Reactions

Plutonium Interactions with Synthetic Minerals and Sediments

Observed Reaction	Solid Phase
Pu(V) reduction to Pu(III/IV)	goethite (α-FeOOH)[1,2,3], hematite (α-Fe_2O_3) [3,4,5], magnetite(Fe_3O_4)[6], hausmannite (Mn_3O_4)[7], manganite (γ-MnOOH)[5], pyrolusite (β-MnO_2)[8], yucca mountain tuff[8], SRNL sediment[9]
Pu(IV)/Pu(V) oxidation to Pu(VI)	pyrolusite (β-MnO_2)[8], Other MnO_2-oxides[10]
Observed Pu(III) at steady state	SRS sediments exposed to field conditions for 2-12 years[11]

[1]Kenney-Kennicutt and Morse, 1985; [2]Sanchez et al., 1985; [3]Powell et al., 2005; [4]Khasanova et al., 2007; [5]Romanchuk et al., 2001; [6]Powell et al., 2004, [7]Shaughnessey et al., 2003; [8]Powell et al., 2006; [9]Kaplan et al., 2004 [10]Morgenstern and Choppin, 2002; [11]Kaplan et al., 2007

Comparison of Pu and Th Sorption

Banik et al., Radiochimica Acta, 95, 569-575, 2007

- Aqueous Pu at neutral pH region was found to be Pu(V) despite having added the Pu initially as Pu(IV)
- Implies a complicated equilibrium distribution of both Pu(IV) and Pu(V) in both aqueous and solid phases

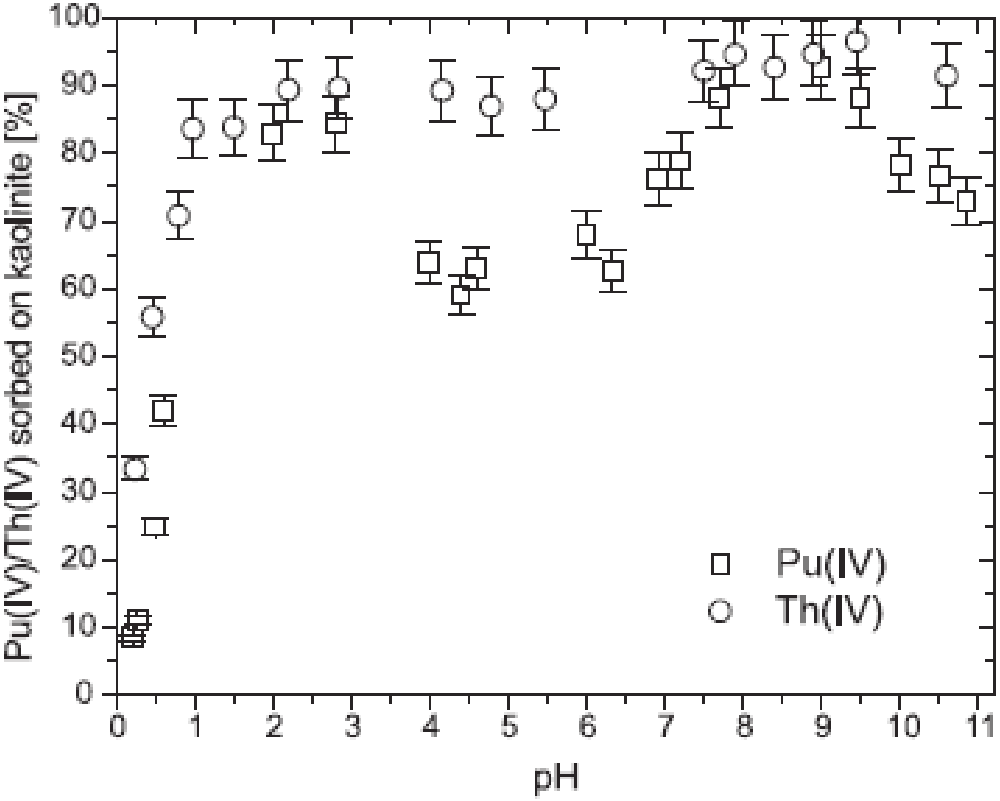
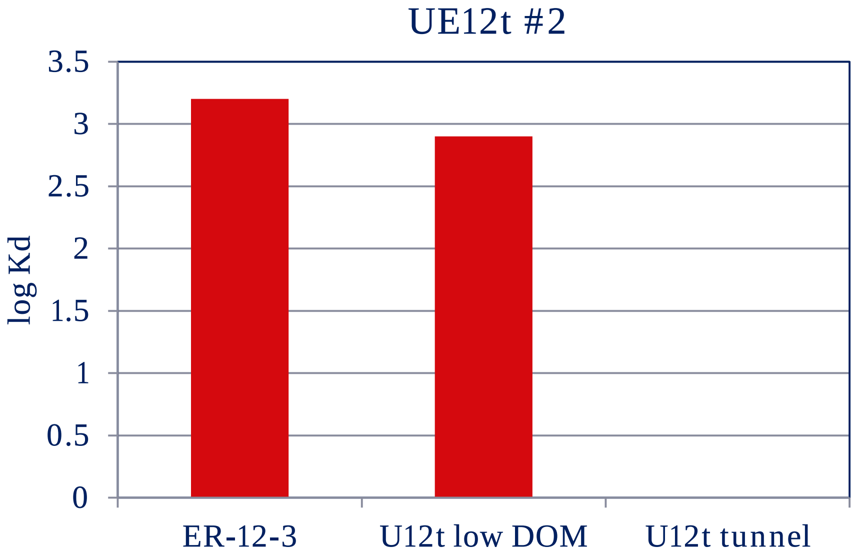
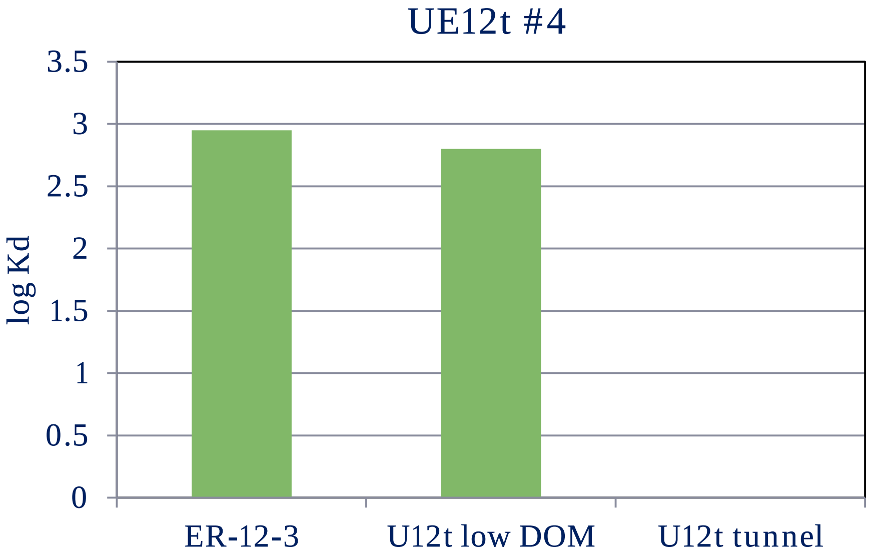


Fig. 4. Comparison of the sorption of tetravalent actinides (Pu, Th) onto kaolinite as a function of pH; pCO_2 = 10–3.5 atm, [KGa-1b] = 4 g/L, contact time = 120 h.

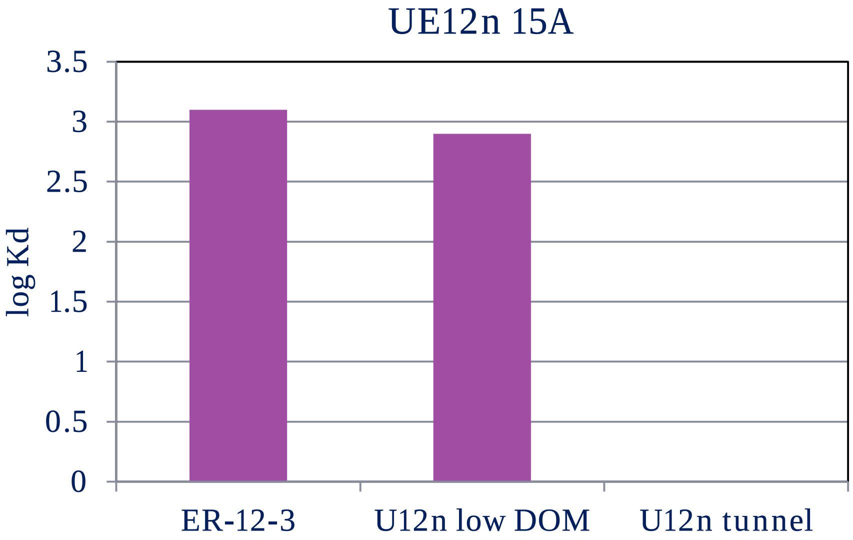
Pu Sorption to Nevada Test Site Tuff

Zhao et al., Applied Geochemistry, 26, 308-318, 2011


UE12t #2

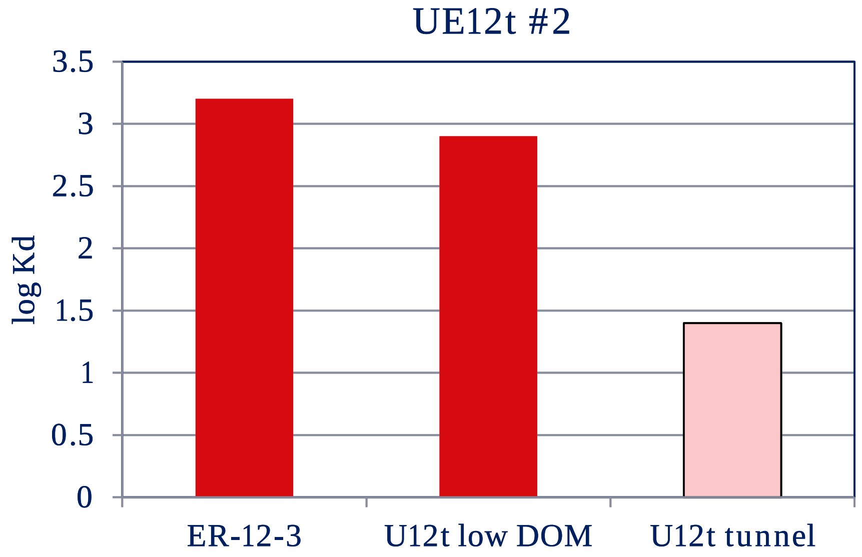

UE12t #4

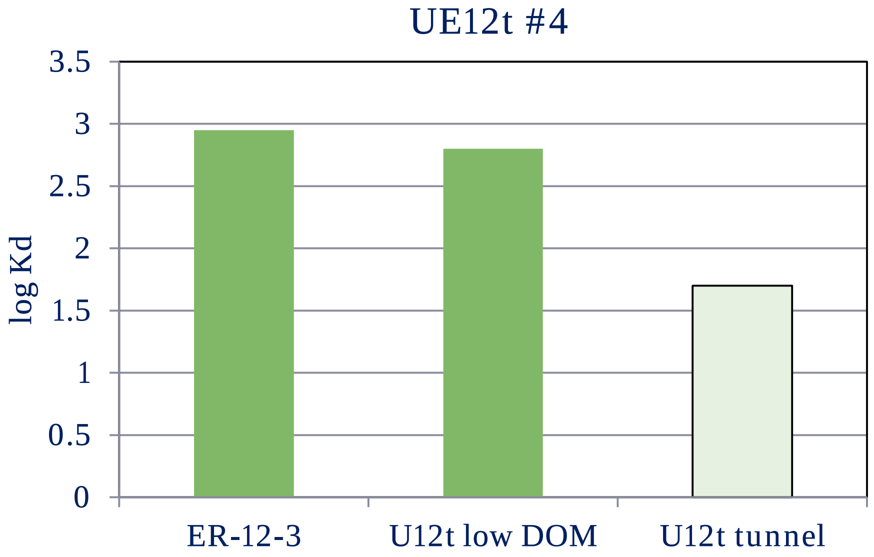
- ER-12-3 is a low-DOM water
- U12t tunnel has a high DOM concentration
- "U12t low DOM" is U12t water with the DOM removed


UE12n 15A

Pu Sorption to Nevada Test Site Tuff

Zhao et al., Applied Geochemistry, 26, 308-318, 2011





- ER-12-3 is a low-DOM water
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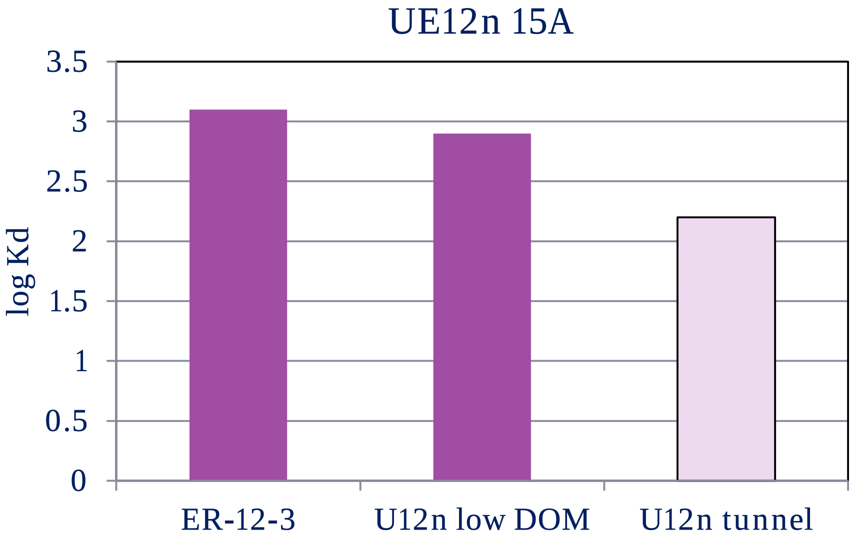
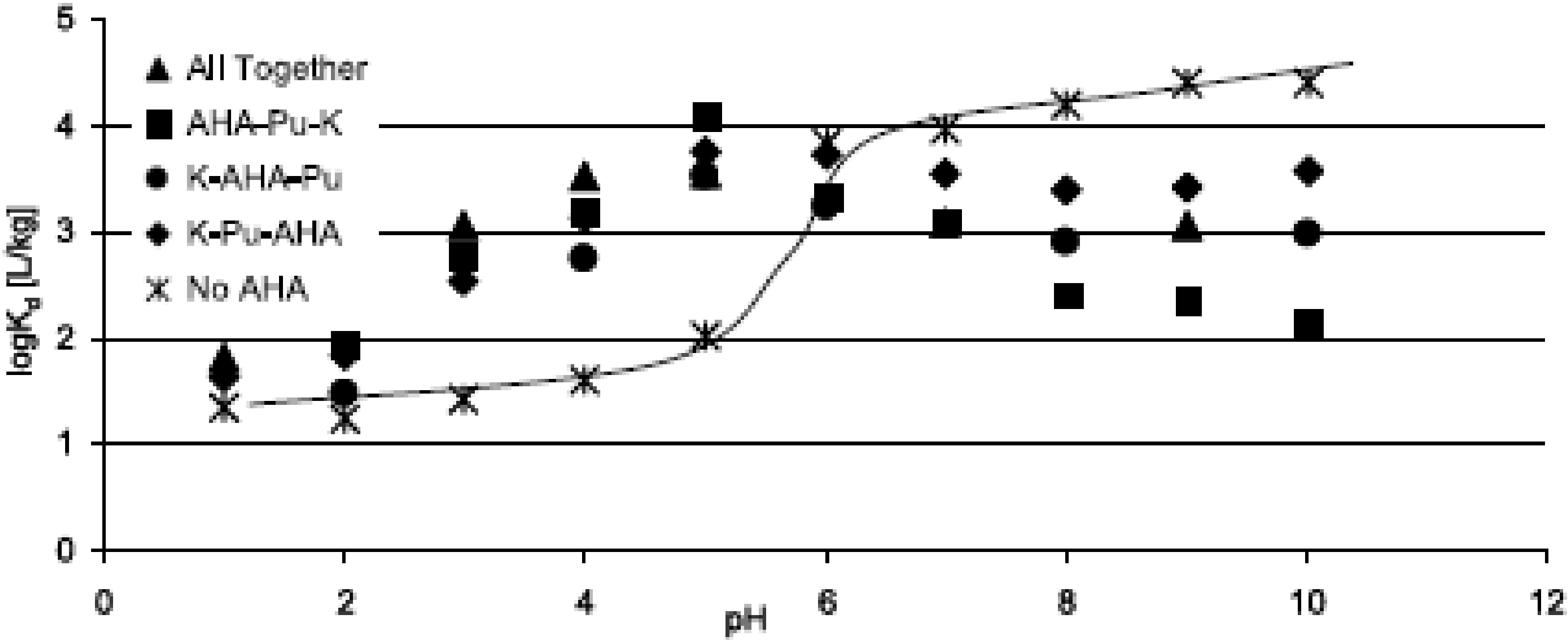


Influence of Humic Acid on Pu Sorption to Kaolinite

Buda et al., Radiochimica Acta, 96, 657-665, 2008



- Humic acid increases sorption at low pH likely due to ternary complex formation
- Humic acid decreases sorption at high pH likely due to aqueous complexation with humic acid
- Data also imply that order of addition of humic acid, Pu, and kaolinite influences the distribution

Colloidal Transport of Contaminants

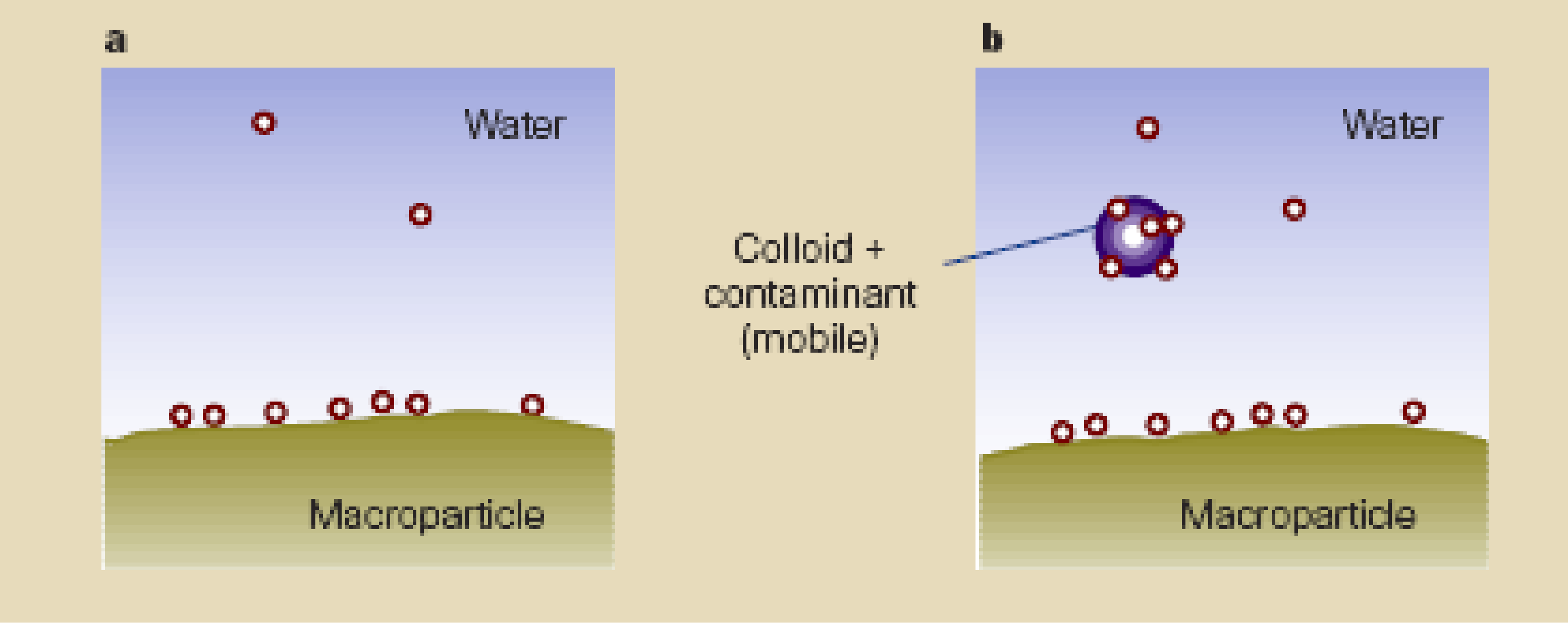


Figure 2 Comparison of generalized two- and three-phase groundwater systems. a, Two-phase; b, three-phase. The third phase in b is a colloid or microparticle, shown here with contaminant molecules sorbed to it, thus making them mobile. Colloidal material is usually chemically similar to the stationary macroparticle phase.

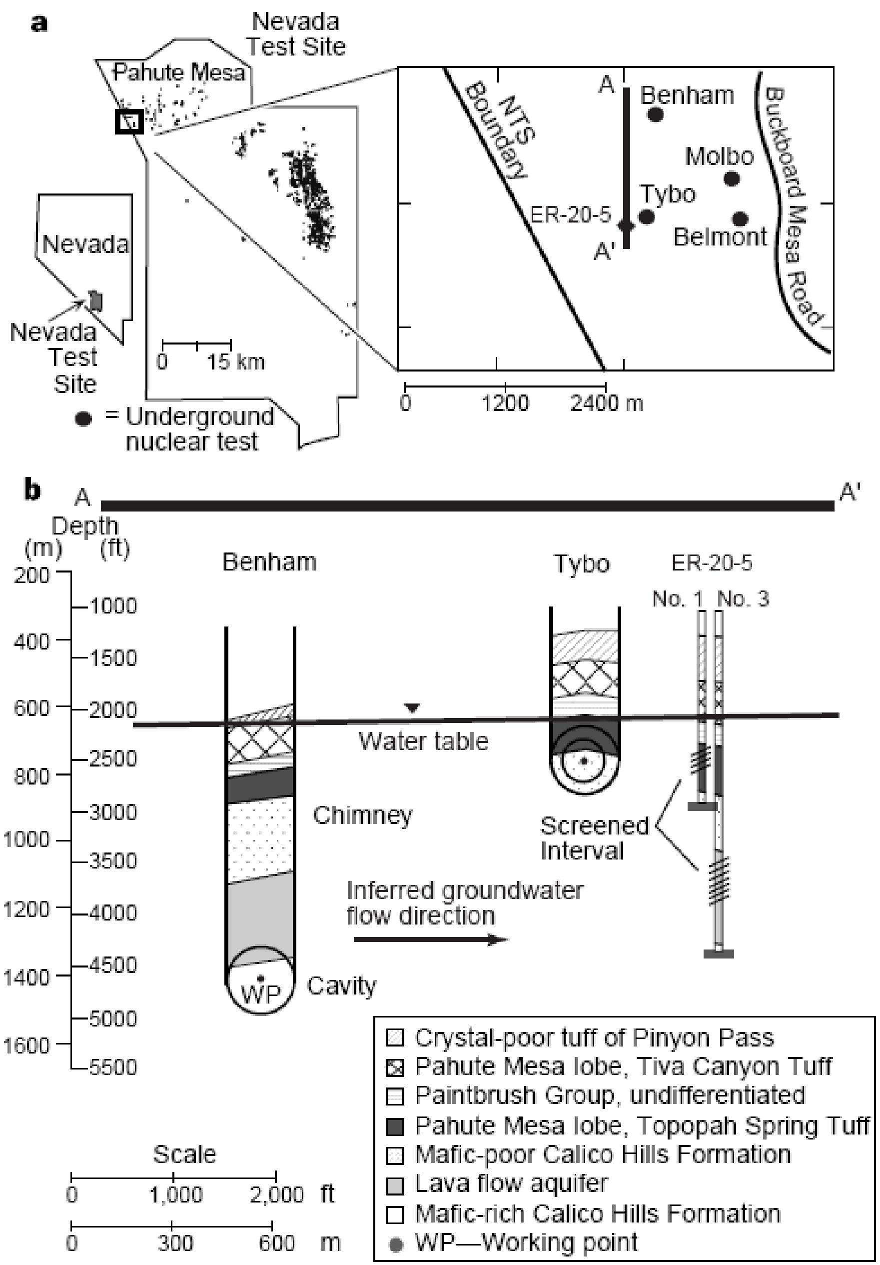
Nevada Test Site

- Over 900 nuclear detonations
- Approximately 2775 kg (8.3×10^5 Ci) of Pu (mostly ^{239}Pu by mass) remains in the subsurface as a byproduct of underground nuclear testing
- Kilometer scale movement of Pu observed in field measurements (Kersting et al., 1999)

Colloidal Pu Transport at the Nevada Test Site

Kersting et al., Nature, 397, 56-59, 1999

Figure 1 Location and geology of the study area. **a**, Map of the Nevada Test Site, showing the locations of all detonated underground nuclear tests. An enlarged map of the field area in Pahute Mesa is also shown, giving the location of the well cluster ER-20-5 and all other nearby underground nuclear tests. Molbo (1982) and Belmont (1986) have an announced yield between 20 and 150 kt. **b**, A–A′ is a north-south cross-section projecting the Benham and Tybo nuclear tests relative to the ER-20-5 well cluster. Well no. 3 is located ~30 m south of well no. 1. The Tybo test was detonated in moderately welded tuff on 14 May 1975 at a depth of 765 m and had an announced yield between 200 and 1,000 kt. Benham was denotated in zholitized bedded tuff on 19 December 1968 at a depth of 1,402 m with a nuclear yield of 1,150 kt. The working point (WP) denotes the location of the nuclear device before detonation. The radius of the cavity is a function of the nuclear yield, density of the rock type and depth of burial (distance from ground surface to WP)[31]. Benham has a calculated cavity radius of 98 m, and Tybo between 62 and 105 m based on the unclassified range in yield.



Colloidal Pu Transport at the Nevada Test Site

Kersting et al., Nature, 397, 56-59, 1999

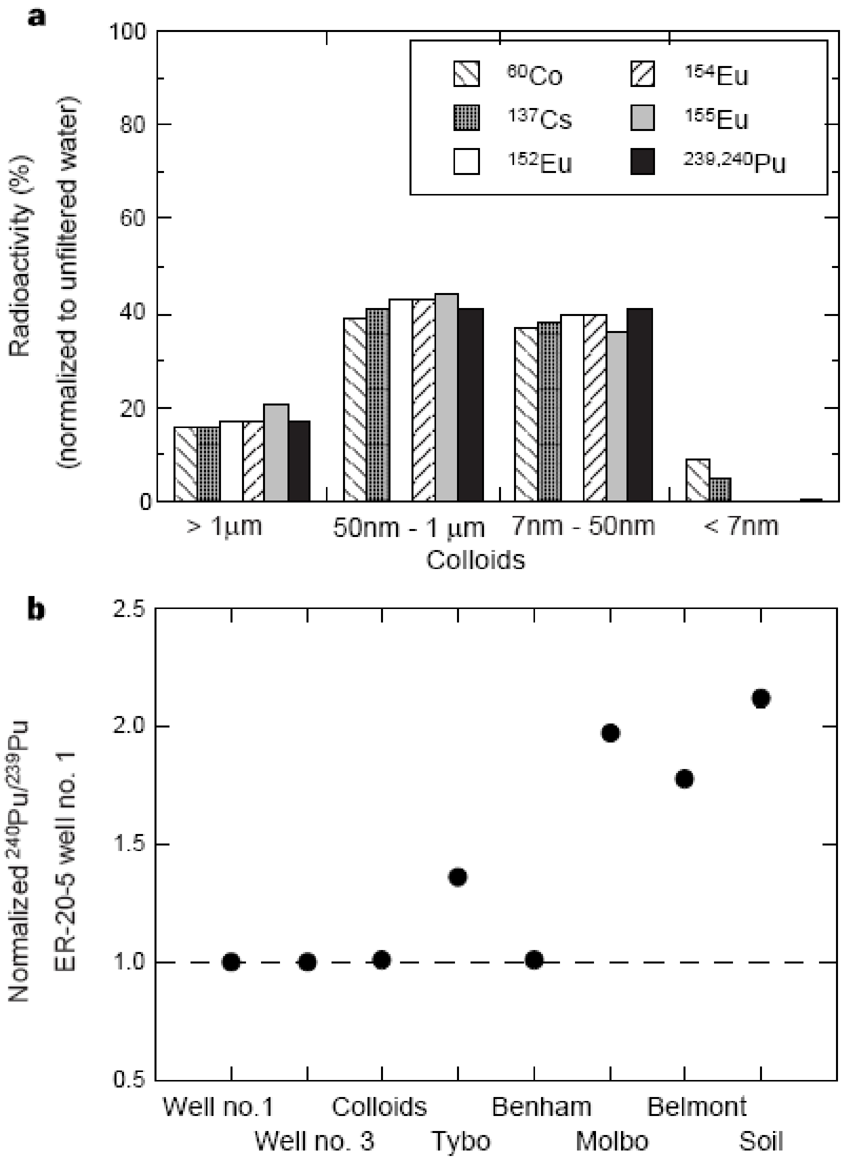


Figure 3 Radioactivity of the colloidal minerals and comparison of Pu isotope ratios from ER-20-5 ground waters to other nuclear tests. **a**, Comparison of the radioactivity of the colloids collected on the different filter sizes and the ultrafiltrate fraction. Data are normalized to the total radioactivity measured in the unfiltered water. The ultrafiltrate is the water that passed through all the filters (<~7 nm). Filtration occurred in series. A tangential filtration system was used for the 100,000 nominal molecular mass (~7nm) size filters. **b**, Comparison of the ^{240}Pu/^{239}Pu isotope ratios of different samples in this study normalized to the radioactivity measured in ER-20-5 no. 1. Precision is ± 1.5%. The errors plotted are smaller than the symbols used. Results of the Pu isotopic analyses of the archived melt glass material collected from the cavity region immediately after the detonation of Benham and Tybo from both laboratories agree to within 1.5% and also match the original values measured immediately following the nuclear tests. Total laboratory procedural blanks had <2 pg Pu, significantly below the concentrations analysed and did not contribute to the isotope ratio measured. The concentrations of Pu detected in the soil samples were extremely low (<4 pg Pu per g sample), and the isotopic ratios distinctly different from the ground water. Values plotted are averages: ER-20-5 no 1, $N = 3$; ER-20-5 no. 3, $N = 2$; Colloids, $N = 4$; Tybo, $N = 6$; Benham, $N = 12$; Molbo, $N = 7$; Belmont, $N = 4$; and soil, $N = 2$. Here N is the number of samples averaged.

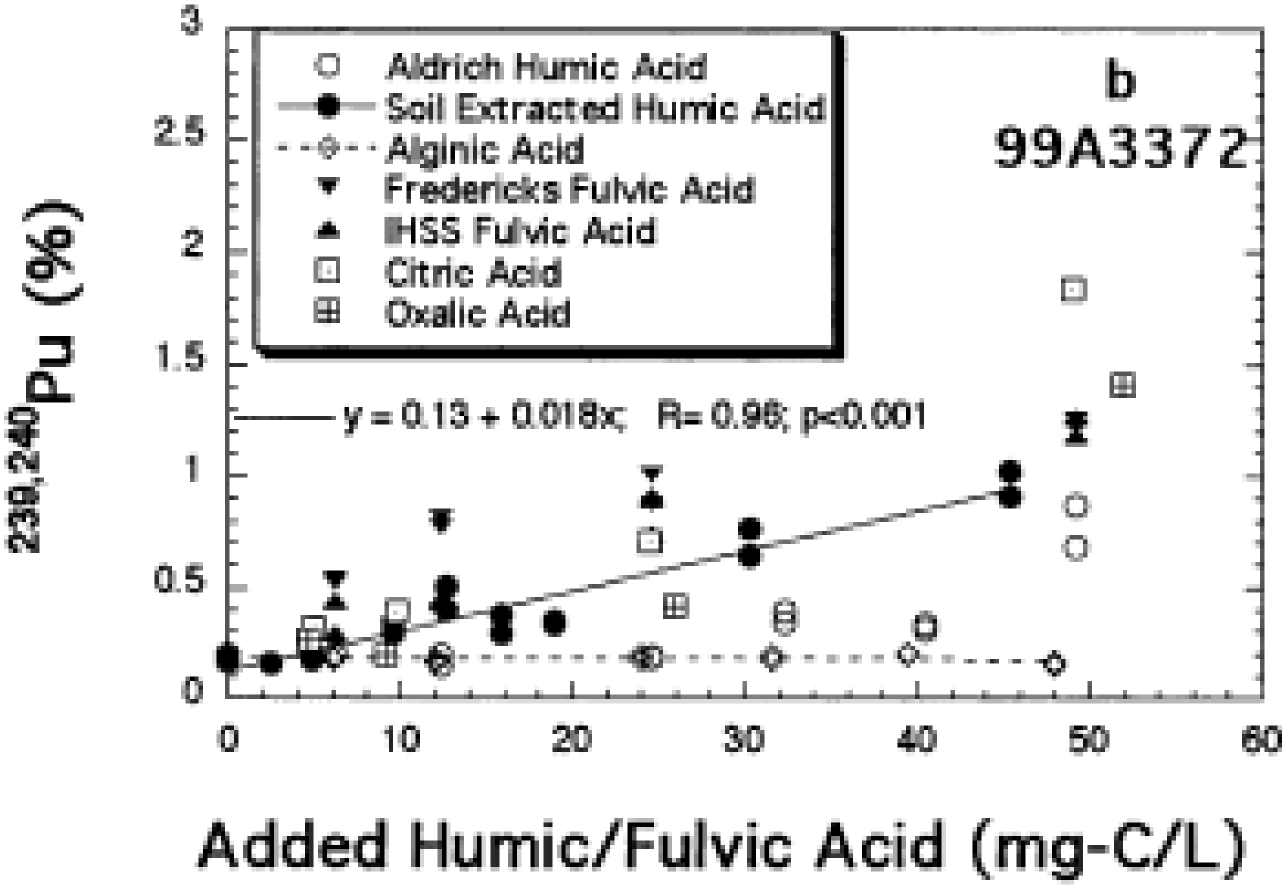
Organic Rich Colloids from Rocky Flats Environmental Technology Site

Santschi et al., Env. Sci. Tech., 36, 3711-3719, 2002; Roberts et al., Coll. Surf. A, 244, 105-111, 2004

Fig. 4. TEM image depicting cellulose-type "crystalline" colloids (3 kDa, 0.5 μm) from pond B4. Scale bar = 1 μm.

Organic Rich Colloids from Rocky Flats Environmental Technology Site

Santschi et al., Env. Sci. Tech., 36, 3711-3719, 2002; Roberts et al., Coll. Surf. A, 244, 105-111, 2004

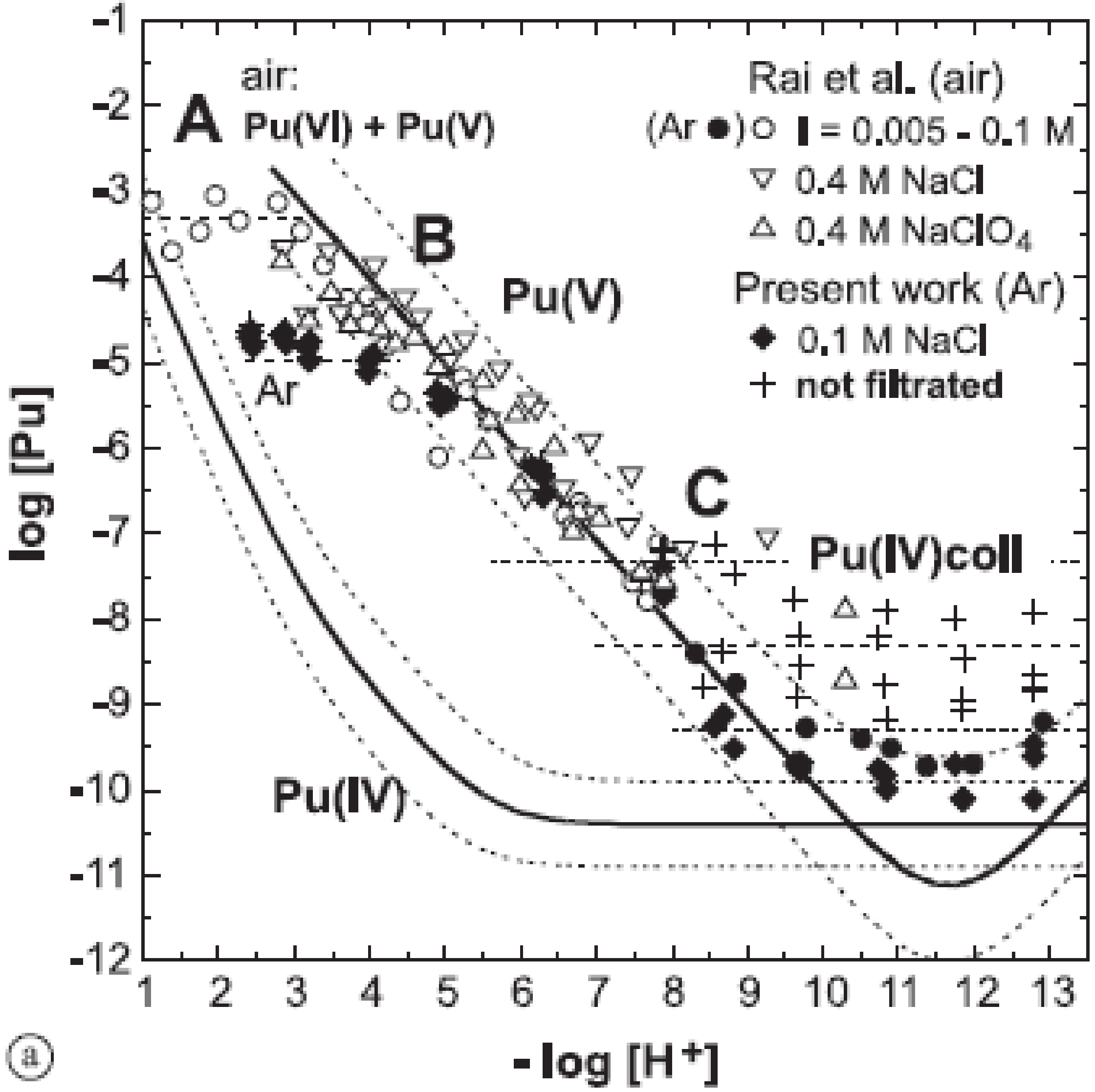


Precipitation/Dissolution

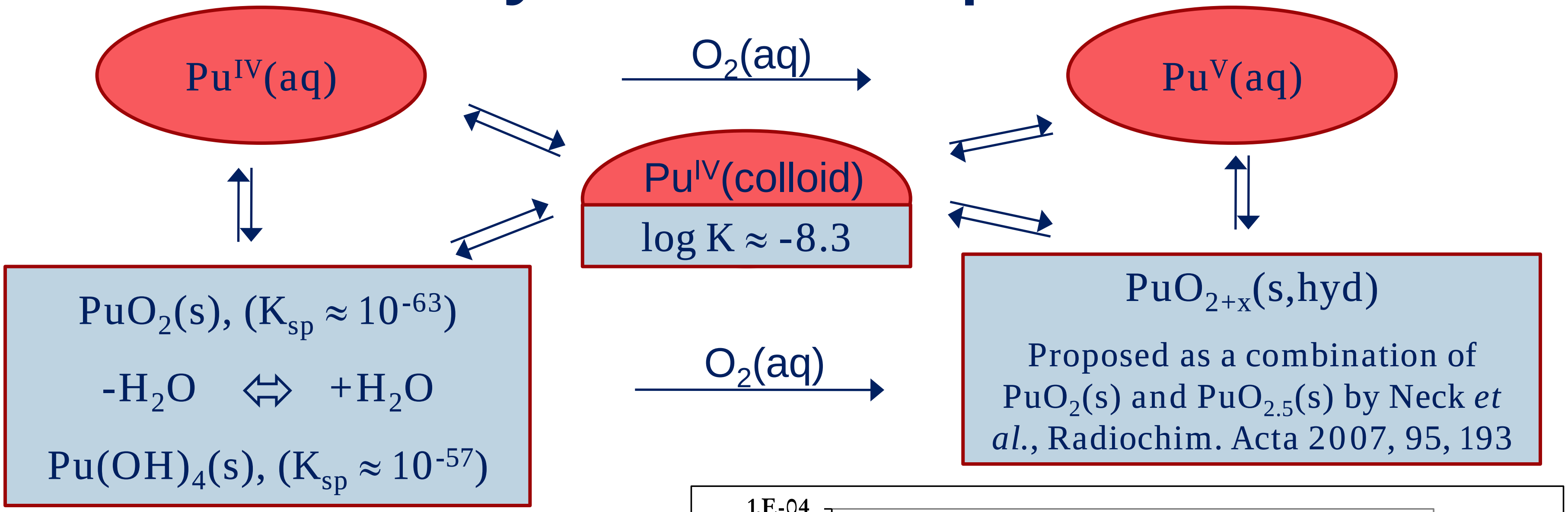
- Expected (nano) precipitates under environmental conditions
- See webinars on “Uranium Chemistry” and “Plutonium Chemistry” for detailed discussions of many solid phases

Modeling Pu Solubility

Neck et al., Radiochim. Acta, 2007, 95, 193-207



Pu Solubility and Precipitation



$Pu^{IV}(aq)$

$O_2(aq)$

$Pu^{V}(aq)$

$Pu^{IV}(colloid)$

log K ≈ -8.3

$PuO_2(s)$, ($K_{sp} \approx 10^{-63}$)

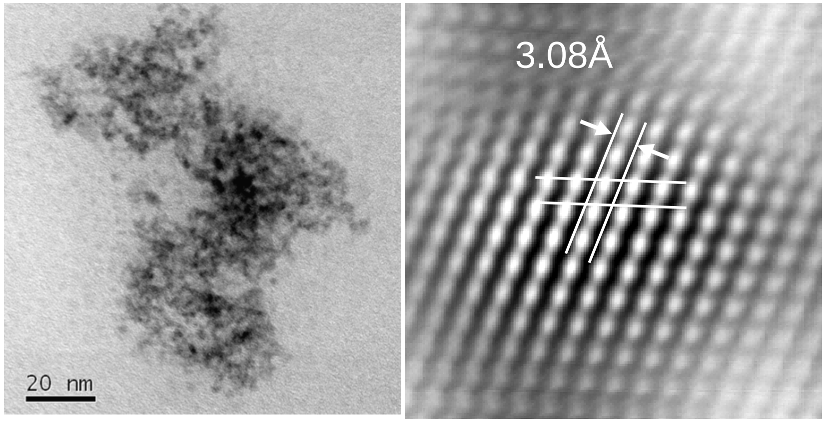
$-H_2O \Leftrightarrow +H_2O$

$Pu(OH)_4(s)$, ($K_{sp} \approx 10^{-57}$)

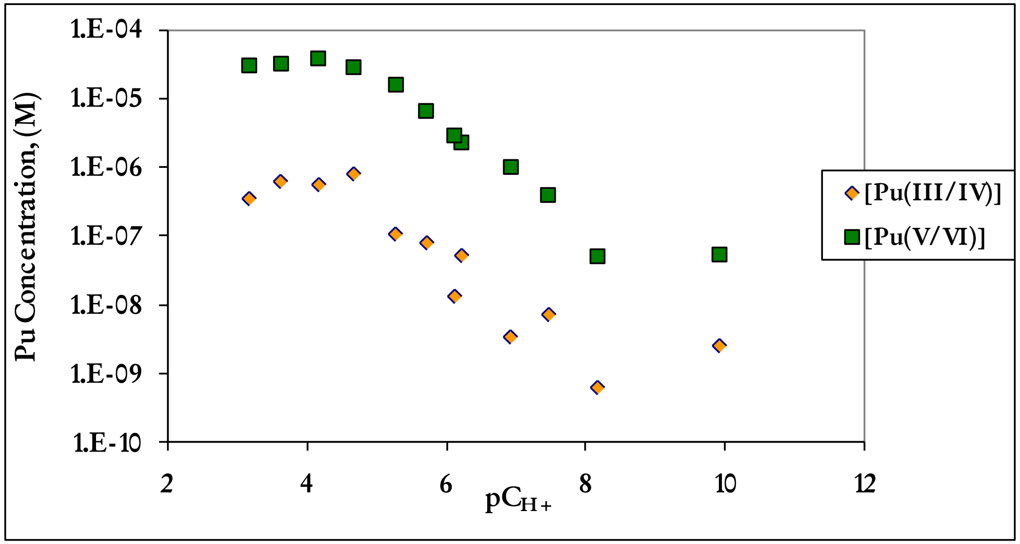
$O_2(aq)$

$PuO_{2+x}(s,hyd)$

Proposed as a combination of $PuO_2(s)$ and $PuO_{2.5}(s)$ by Neck *et al.*, Radiochim. Acta 2007, 95, 193

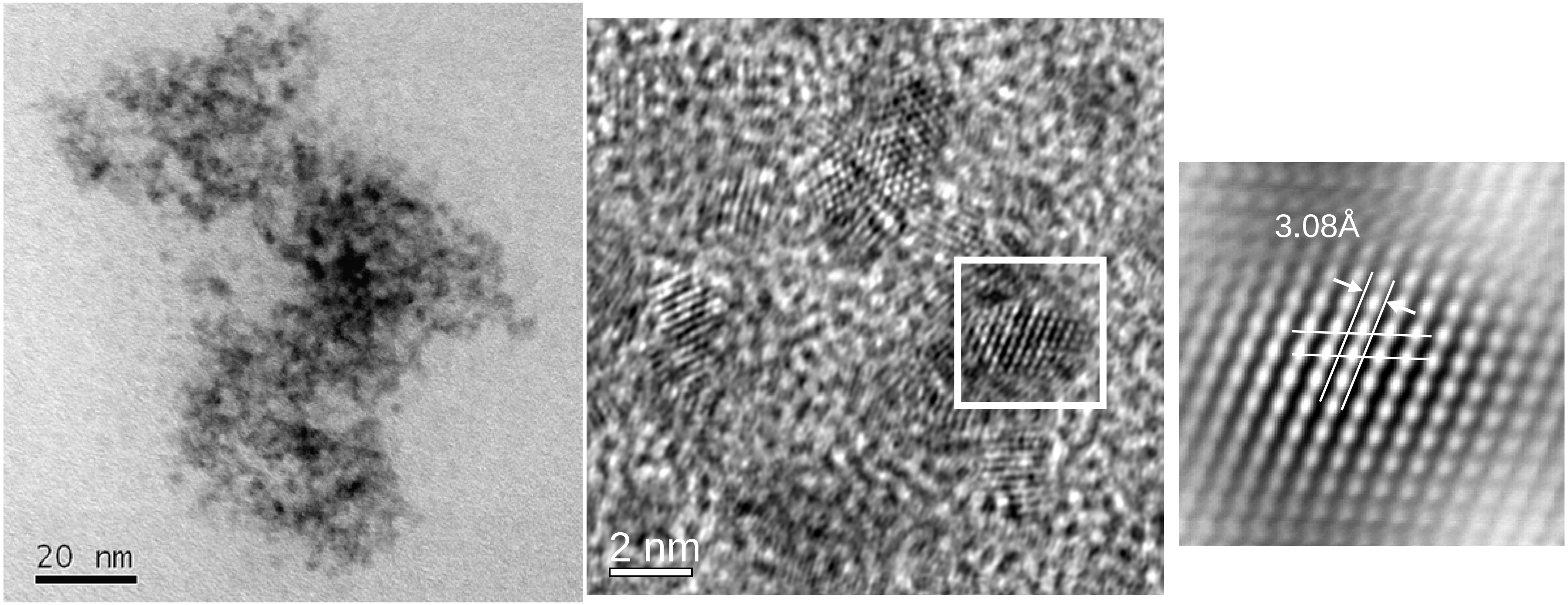


Pu(IV) nanocolloids, Powell et al., 2012



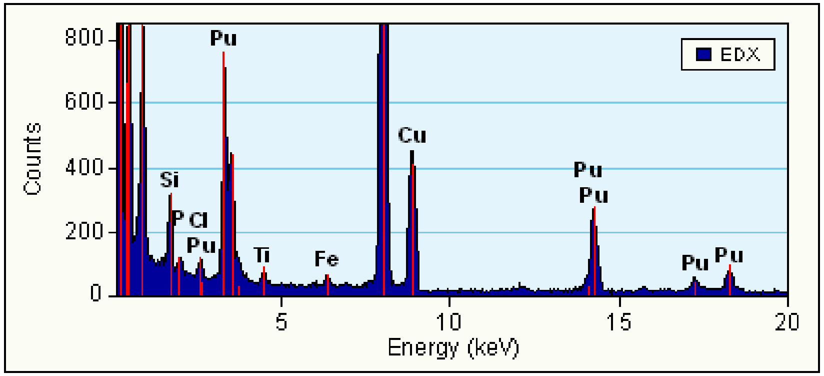
Pu Solubility in 0.4M NaCl
Rai *et al.*, Radiochim. Acta 2001, 89, 491

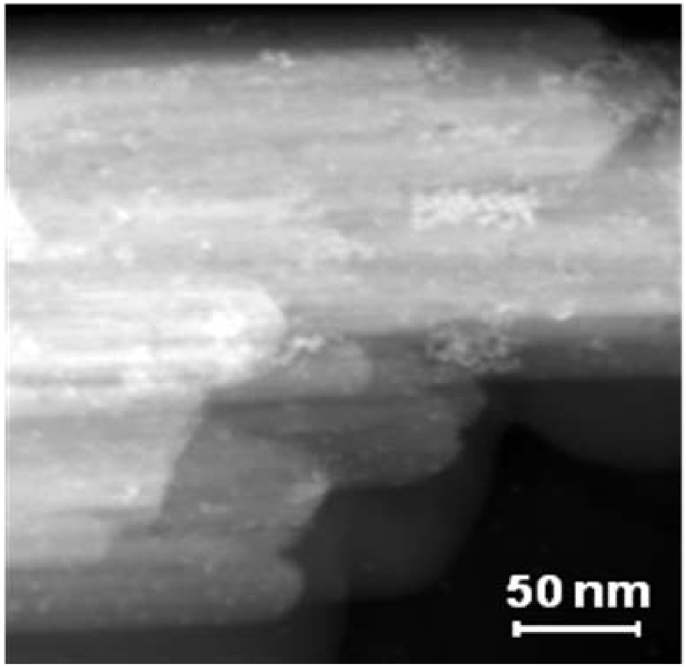
TEM Analysis of Plutonium Oxide Particles

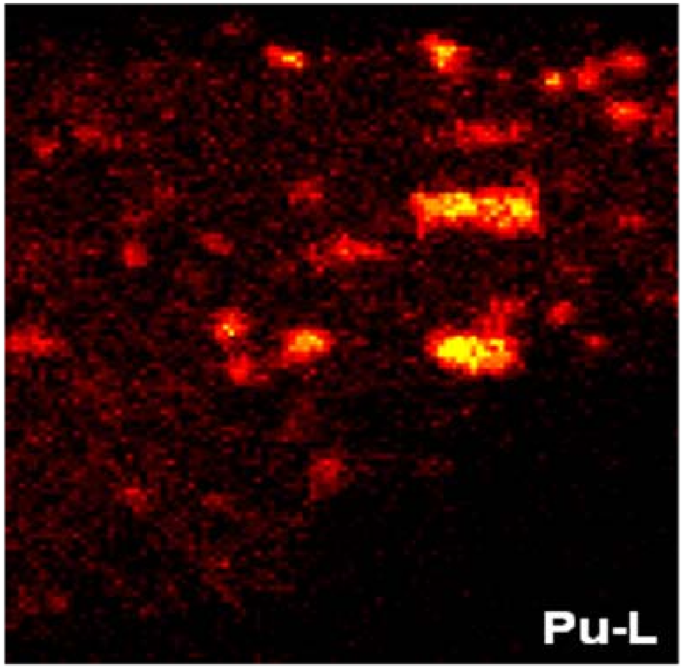


- Starting in 1950, observations of decreased solubility of Pu over time lead scientists to believe that $PuO_2(s)$ takes a polymeric form
- X-ray scattering data indicates nanoclusters of Pu may form from saturated LiCl solutions ($[Pu_{38}O_{56}Cl_{54}(H_2O)_8]^{14-}$, Soderholm et al., 2008)
- TEM data (above) indicate that PuO_2 is comprised of aggregated PuO_2 nanoparticles and does not take a polymeric form (Powell et al., 2011)
- Are these nanoparticles/nanocolloids mobile?

Pu Nanocolloids Associated with Goethite



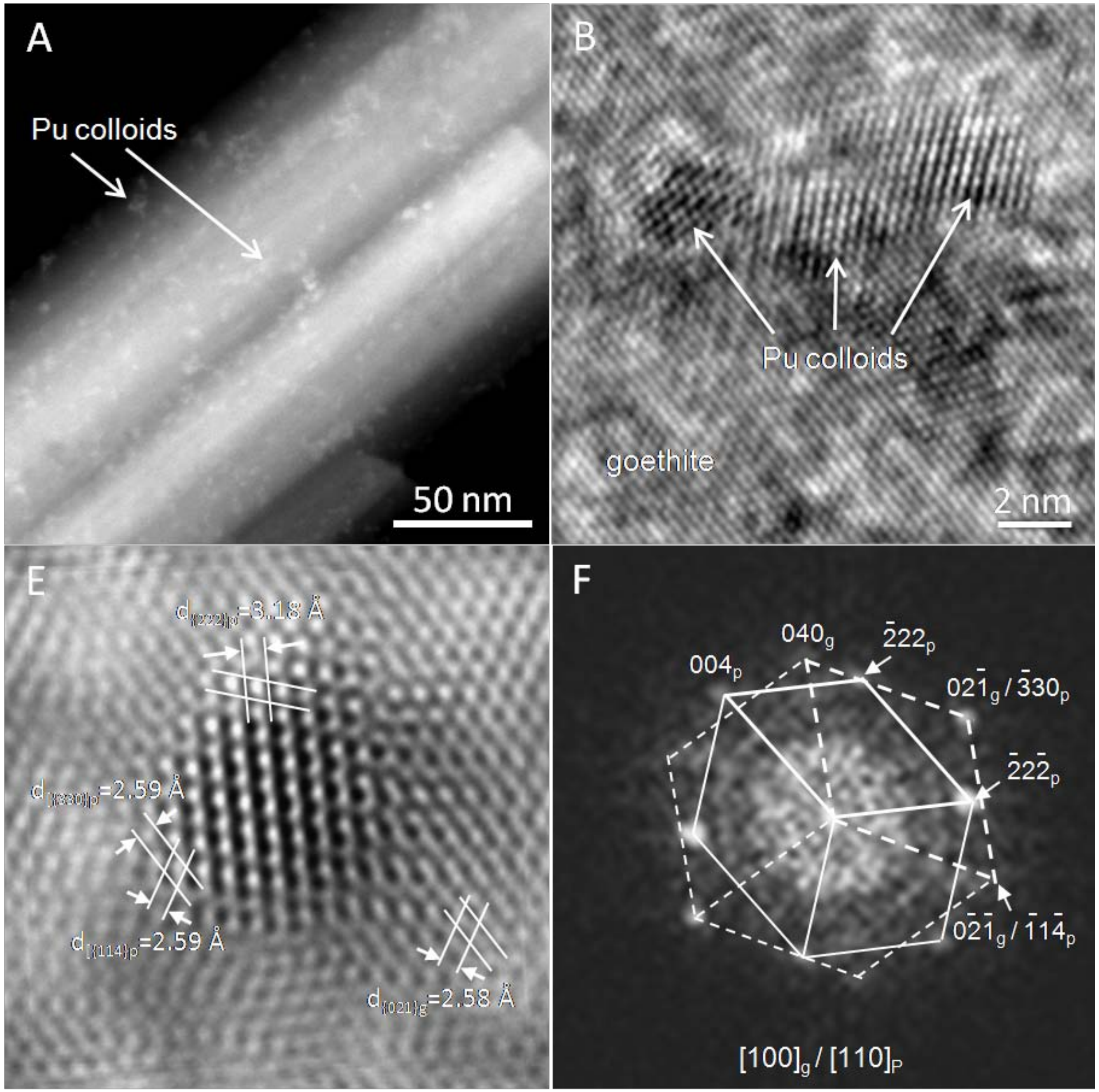




Powell et al., Environ. Sci. Tech, 2011

TEM Analysis of Plutonium Oxide Particles on Goethite

- Plutonium nanocolloids formed on goethite have undergone a lattice distortion relative to the ideal fluorite-type structure, fcc, PuO_2, resulting in the formation of a bcc, Pu_4O_7 structure.
- Distortion is a result of epitaxial growth of the PuO_2 nanocolloid on goethite
- Implication of strong bonding of Pu to goethite



Powell et al., Environ. Sci. Tech, 2011

Summary

- Plutonium exhibits remarkably complex chemistry owning to the sensitivity of Pu to undergo redox reactions

- Environmental mobility is influenced by a variety of factors
  - Transport of colloidal Pu(IV) associated with natural colloids and possibly as PuO_2 nanocolloids
  - Tranport of soluble Pu(V) or Pu(IV)-organic ligand complexes

- Sorption behavior and subsequent mobility is primarily controlled by complex aqueous speciation

- Understudied but significant microbial interactions are likely very important

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