Plutonium Speciation in a Salt-Base Repository

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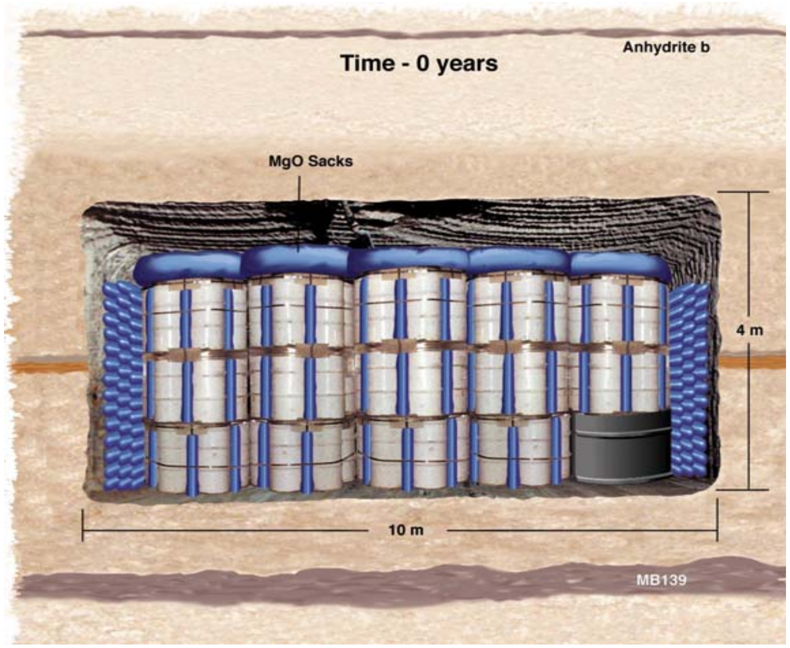
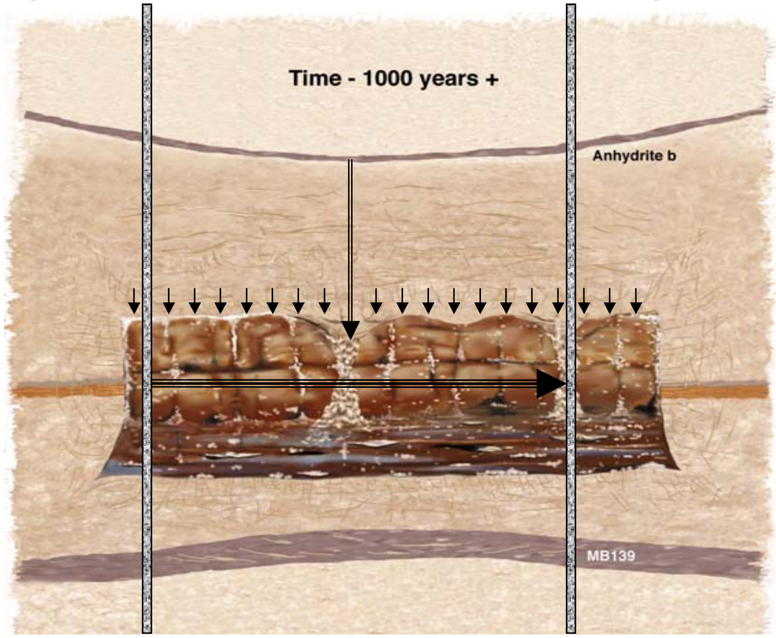
WIPP Disposal Room in a Time of Closure and 1000+ Years Later

View of the WIPP Disposal Room



Courtesy of Frank Hansen, SNL

Repository Inundation - Human Intrusion, DRZ and Anhydrite B



Total amount of key waste components and actinides present in WIPP

	Panel 1 (actual)	Panel 2 (actual)	WIPP (projected)
Radionuclide	**Amount (kg)**	**Amount (kg)**	**Amount (kg)**
Am-241	**34.6**	**9.2**	**143**
Pu total	**2 571**	**1 405**	**9 727**
Pu-239	**2 416**	**1 306**	**9 210**
U total	**22 323**	**6 850**	**647 000**
U-238	**22 170**	**6 808**	**645 000**
Np-237	**0.6**	**1.2**	**17**
Material			
Iron based metal, alloys	**3 327 871**	**4 922 035**	**51 416 440**
Aluminum based alloys	**5 459**	**17 730**	**2 234 176**
Other metals, alloys	**46 793**	**121 526**	**5 795 048**
MgO	**4 482 355**	**6 667 625**	**83 191 744**
Cellulosics	**706 141**	**477 213**	**10 174 884**
Plastic	**522 688**	**876 399**	**10 187 628**

Summary of Current WIPP Chemistry Model

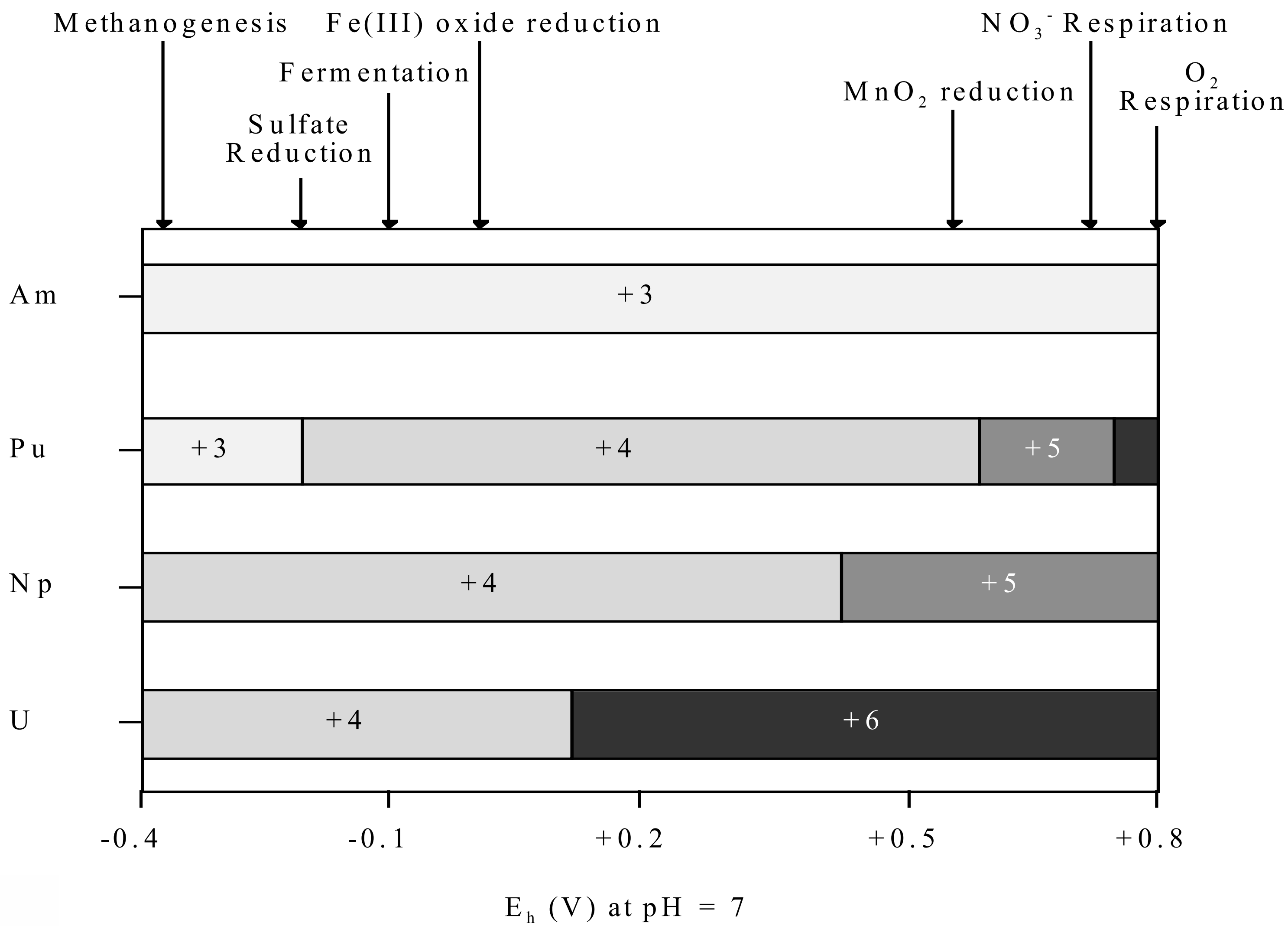
Geochemistry	Predominantly pure halite Salado formation salt with anhydrite interbeds
Temperature	Ambient is 28^{o}C, an increase of up to 3^{o}C is possible due to the emplacement of TRU waste, Humidity ~70% RH at the repository temperature
Water Content	Unsaturated for short period of time. Ambient brine inclusions in the salt range from 0.1 to 0.2 % by mass
Pressure	~15 MPa (147 atm) lithostatic, ~ 8 MPa (79.0 atm) hydrostatic in a borehole intrusion scenario
Gas Phase	Initially air at repository closure, but rapidly transitions to an anoxic atmosphere dominated by hydrogen and carbon dioxide with trace-levels of methane, H_2S and other microbial generated gasses at pressures up to lithostatic
Minimum brine volume for DBR	The calculated minimum volume of brine, from any source, needed for DBR release is 10,011 m^3 WIPP

Summary of Current WIPP Chemistry Model	
Brine	High ionic strength brine that is bracketed by GWB and ERDA-6 brine formulations; pH = 8.7; buffered by MgO
Engineered Barrier	MgO will sequester carbon dioxide and buffer pH by the precipitation of brucite, hydromagnesite, and magnesite.
Microbial Effects	Gas generation, primarily carbon dioxide also methane and hydrogen sulfide, due to the biodegradation of cellulosic, plastic and rubber (CPR) materials.
Corrosion	Container steel will react to remove oxygen and produce hydrogen.
Radiolysis	Localized oxidizing effects possible near high-activity actinides, but overall radiolytic processes will be overwhelmed by the reducing components.

Relevant Redox Half Reactions

Table 3-1. Redox Half Potentials for Key Fe, Pb, Pu and U Reactions		
Half Reaction	**E_o (Acidic) in V**	**E_o at pH = 8 in V**
$Pb^{4+} \rightarrow Pb^{2+}$	1.69	2.47
$PuO_2^{+} \rightarrow Pu^{4+}$	1.170	0.70
$PuO_2^{2+} \rightarrow PuO_2^{+}$	0.916	0.60
$Fe(OH)_3(s) \rightarrow Fe^{2+}$		0.1
$FeOOH(s) \rightarrow FeCO_3(s)$		-0.05
$UO_2^{2+} \rightarrow U^{4+}$	0.338	-0.07
$Pu^{4+} \rightarrow Pu^{3+}$	0.982	-0.39
$Pb^{2+} \rightarrow Pb$	-0.1251	-0.54
$Fe^{3+} \rightarrow Fe^{2+}$	0.77	-0.86
$Fe(II)(OH)_2 \rightarrow Fe(0)$	-0.44	-0.89
$U^{4+} \rightarrow U^{3+}$	-0.607	-1.95

Relationship Between Redox, Oxidation State and Microbial Ecology



Bioreduction of Pu(V) by Shewanella Alga

- **Pu(V) reduction expected by metal-reducing bacteria – Pu(III) can be formed**

- **Pu(IV) – Pu(III) reduction reported by Boukhalfa et. al., also noted Pu polymer solubilization and reduction noted**

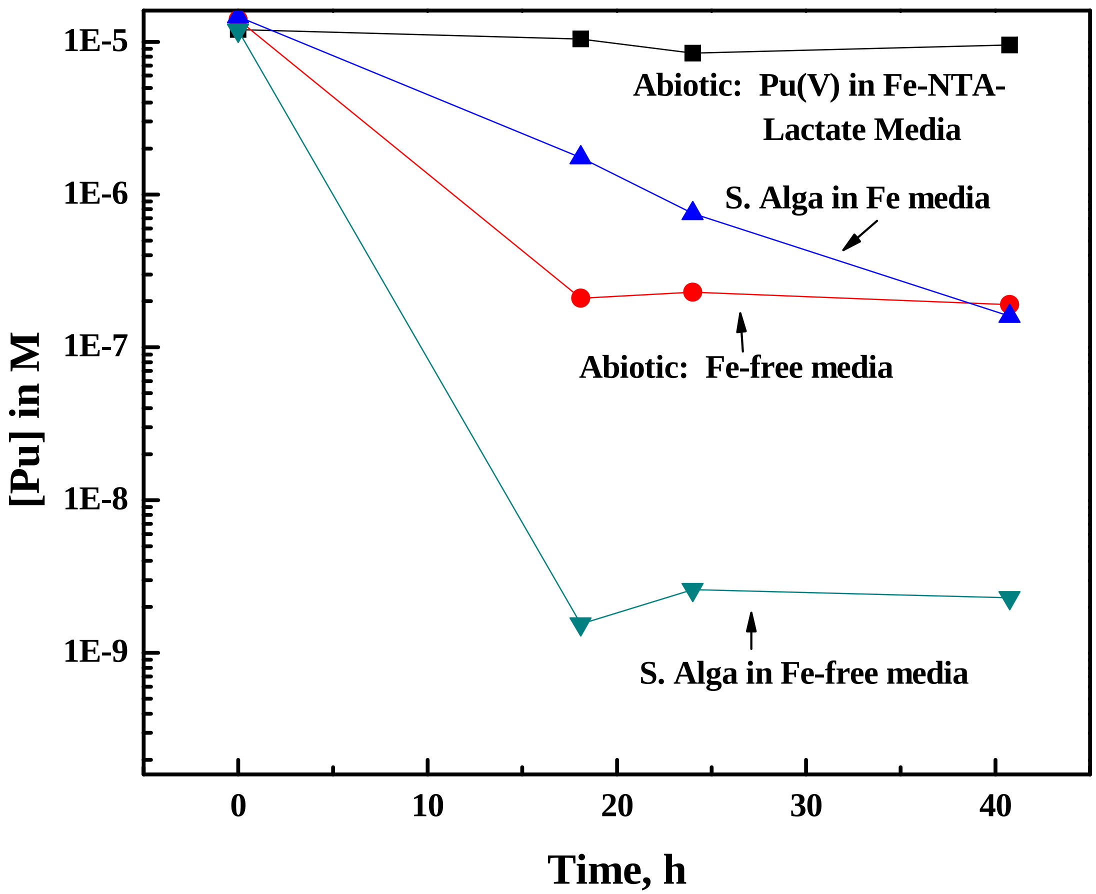


Figure 8. Bioreduction of higher-valent plutonium by *Shewanella alga BrY* under anaerobic conditions in the presence and absence of iron. Uncertainty in the plutonium concentration data is $\pm$ 10%.

ANL Experimental Matrix: Pu(VI) Reduction Studies

- pC_{H+} 5-10
- Pre-equilibrated systems, with and without carbonate
- G-SEEP and ERDA-6 brine
- Fe coupon, Fe^{2+} and MgO

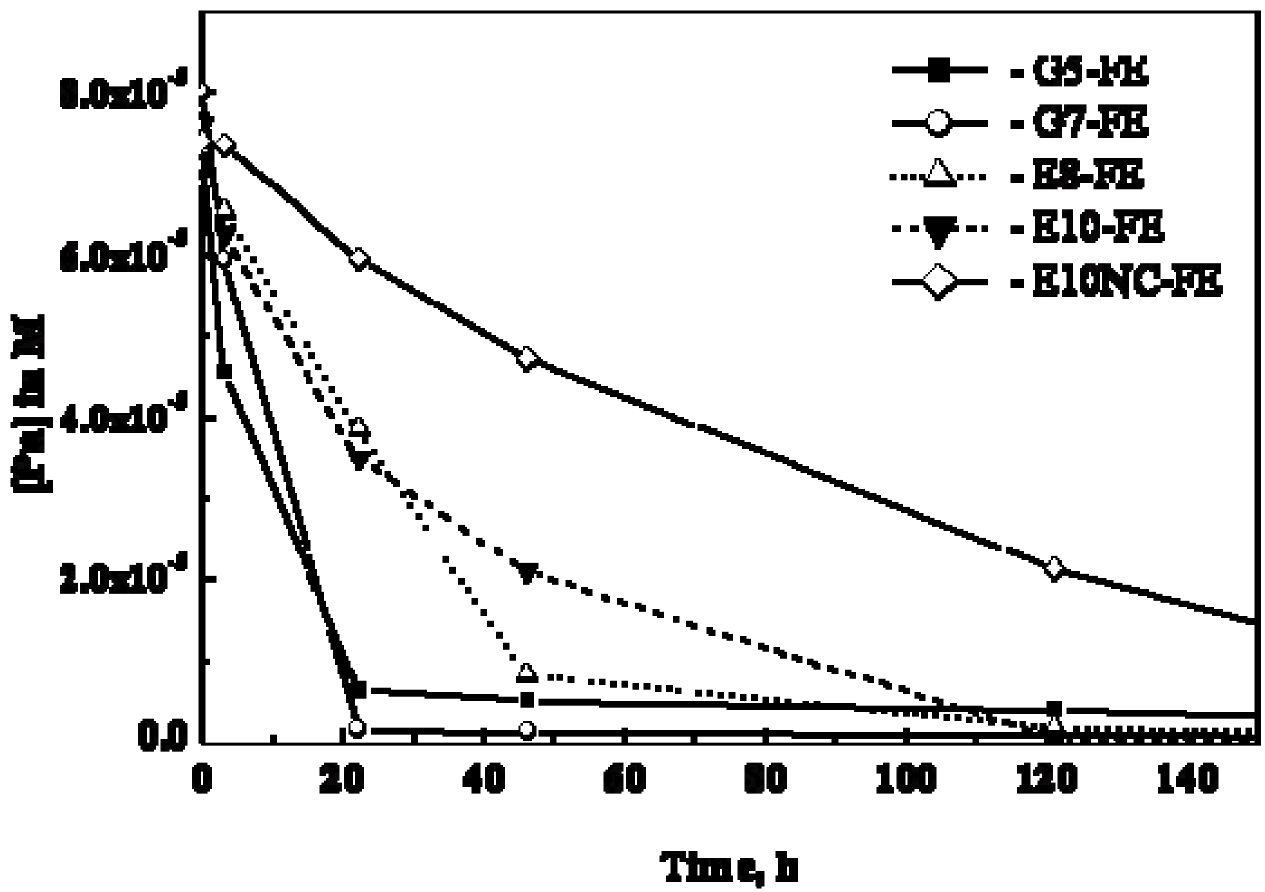
Table 4.1-1. Experimental Matrix to Determine the Stability of Pu (VI) in Brine[a]

Pu(VI) Stability Experiments		Pu(VI) Interaction Studies	
Experiment Designation	Description[b]	Experiment Designation	Description
PU-G5	10^{-4} M Pu(VI) in G-Seep brine at pC_{H+} 5	G5-B	PU-G5 Blank
		G5-FE	PU-G5 with low carbon steel coupon
		G5-FE2	PU-G5 with added Fe^{2+}
PU-G7 and PU-G7-NC	10^{-4} M Pu(VI) in G-Seep brine at pC_{H+} 7	G7-B	PU-G7 Blank
		G7-FE	PU-G7 with low carbon steel coupon
		G7-FE2	PU-G7 with added Fe^{2+}
PU-E8	10^{-4} M Pu(VI) in ERDA-6 brine at pC_{H+} 8 and 10^{-3} M Carbonate	E8-B	PU-E8 Blank
		E8-FE	PU-E8 with low carbon steel coupon
		E8-FE2	PU-E8 with added Fe^{2+}
		E8-MGO	PU-E8 with added MgO powder
PU-E10	10^{-4} M Pu(VI) in ERDA-6 brine at pC_{H+} 10 and 10^{-3} M Carbonate	E10-B	PU-E10 Blank
		E10-FE	PU-E10 with low carbon steel coupon
		E10-FE2	PU-E10 with added Fe^{2+}
		E10-MGO	PU-E10 with added MgO powder
PU-E10-NC	10^{-4} M Pu(VI) in ERDA-6 brine at pC_{H+} 10 with no added Carbonate	E10NC-B	PU-E10-NC Blank
		E10NC-FE	PU-E10-NC with low carbon steel coupon
		E10NC-FE2	PU-E10-NC with added Fe^{2+}

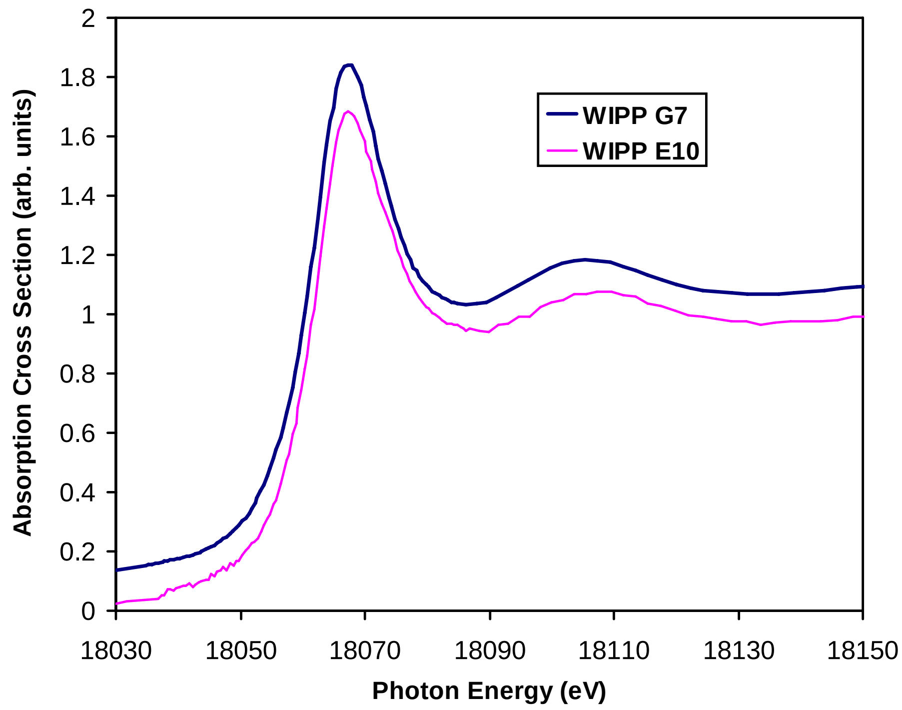
a All experiments were performed at 30 $\pm$ 2 °C, with Pu-239, in a once-through nitrogen glovebox

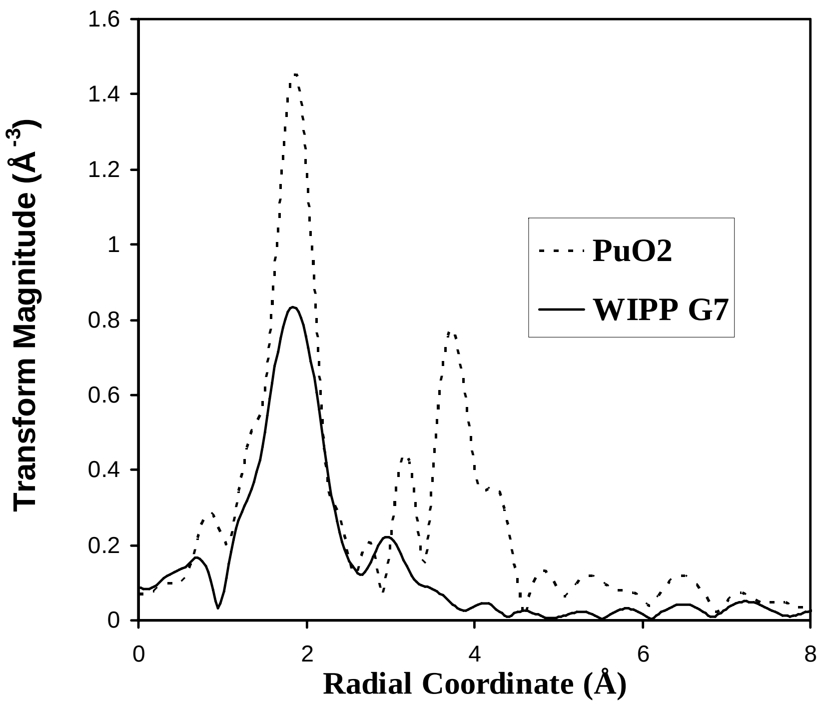
b pC_{H+}, is the measured pH corrected for ionic strength effects; $pC_{H+} = pH_{measured} + 0.9$

Concentration of Pu as a Function of Time, Brine Composition

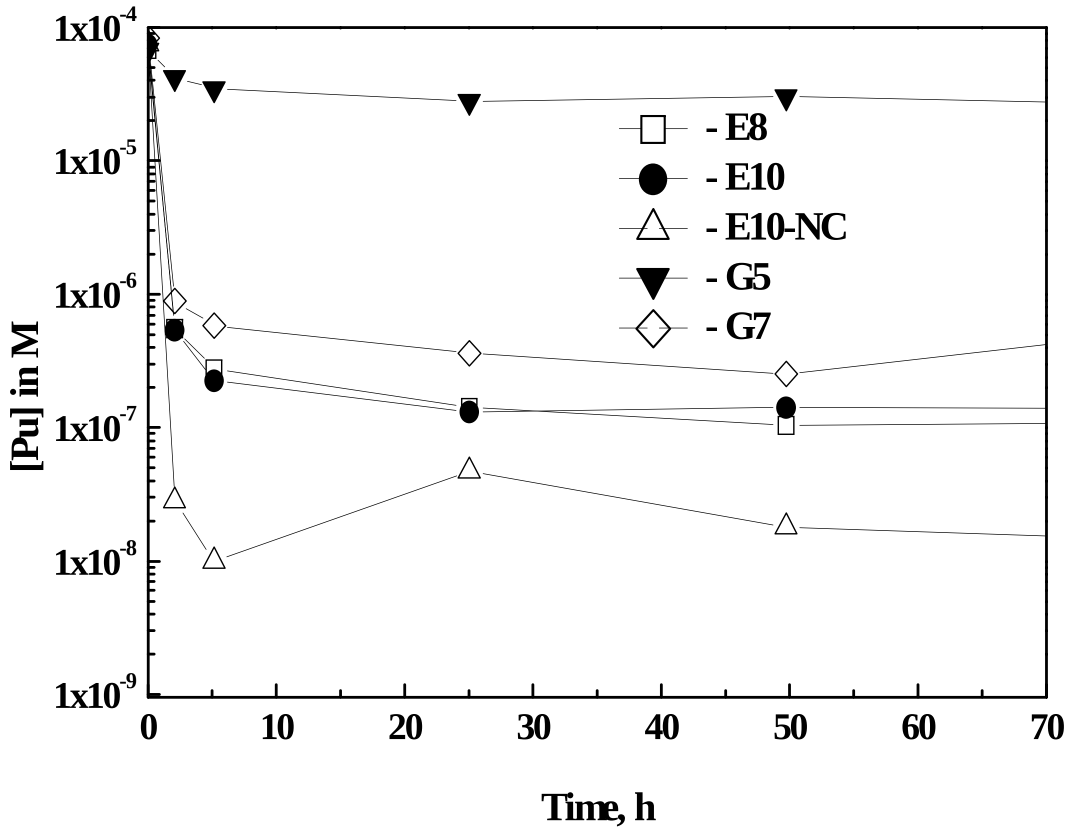


EXAFS/XANES of Reduced Pu Precipitates





Reduction of Plutonium (VI) by Fe^{2+}



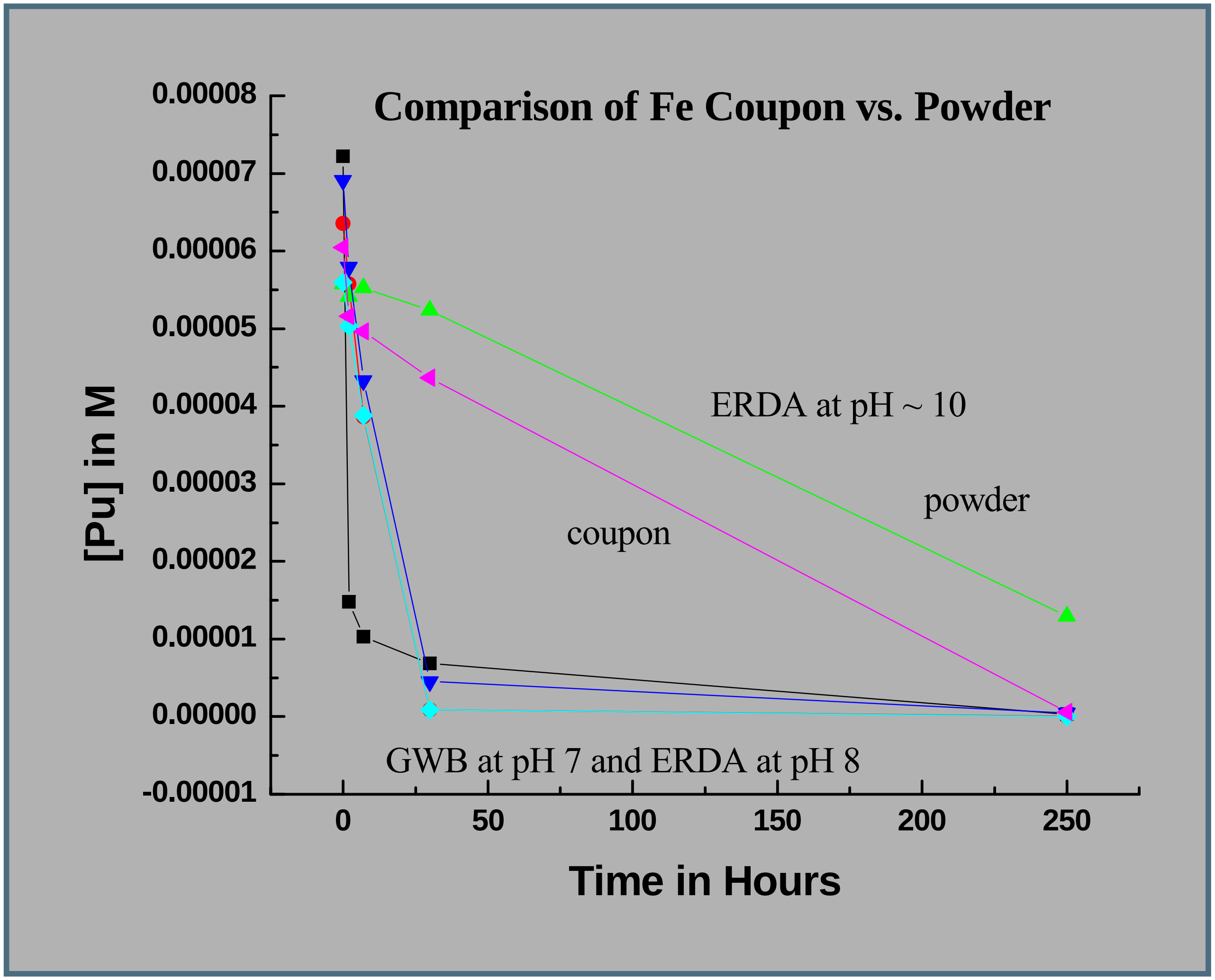
LANL/ACRSP Study of Pu Reduction by Iron(0,II)

- Very different appearances in iron reaction products were noted depending on pH, brine and initial iron phase
- Plutonium was associated with the Fe phases
- Green rust was often noted at the higher pH
- XANES established the green rust to be an Fe2/3 phase with a bromide center
- This green rust phase was linked to Pu as Pu(IV)

pC_{H+} = 10 for magnetite, ferric oxide, Fe powder and Fe coupon

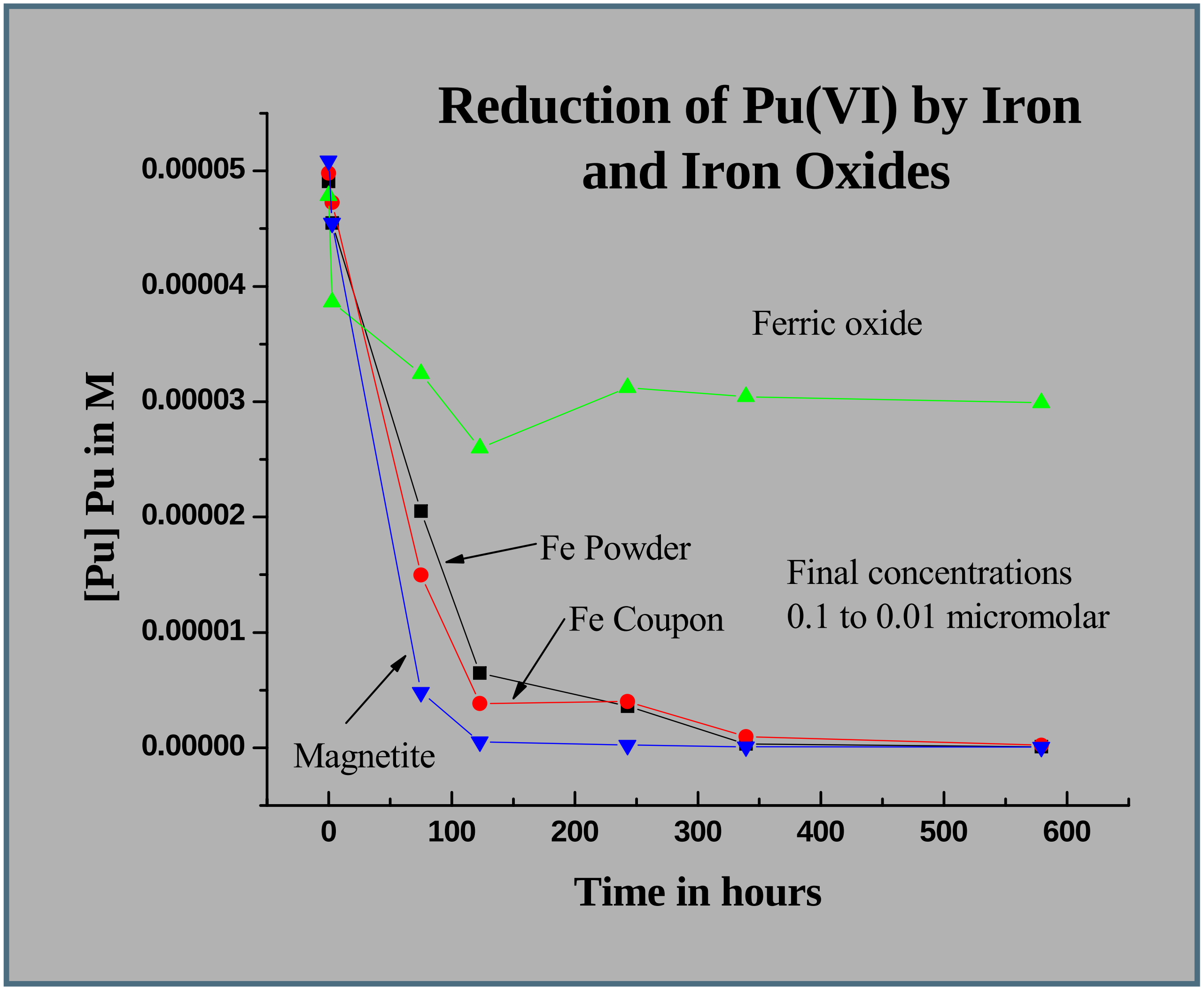
Reduction of Pu(VI) by Fe^0

- At pC_{H+}7, 8 and 10 Pu(VI) reduction was observed
- XANES analysis confirmed Pu(IV) phases
- Noticeably slower reduction was noted at higher pC_{H+} due to significantly lower reactivity of the iron



Reduction of Pu(VI) by Iron Oxides

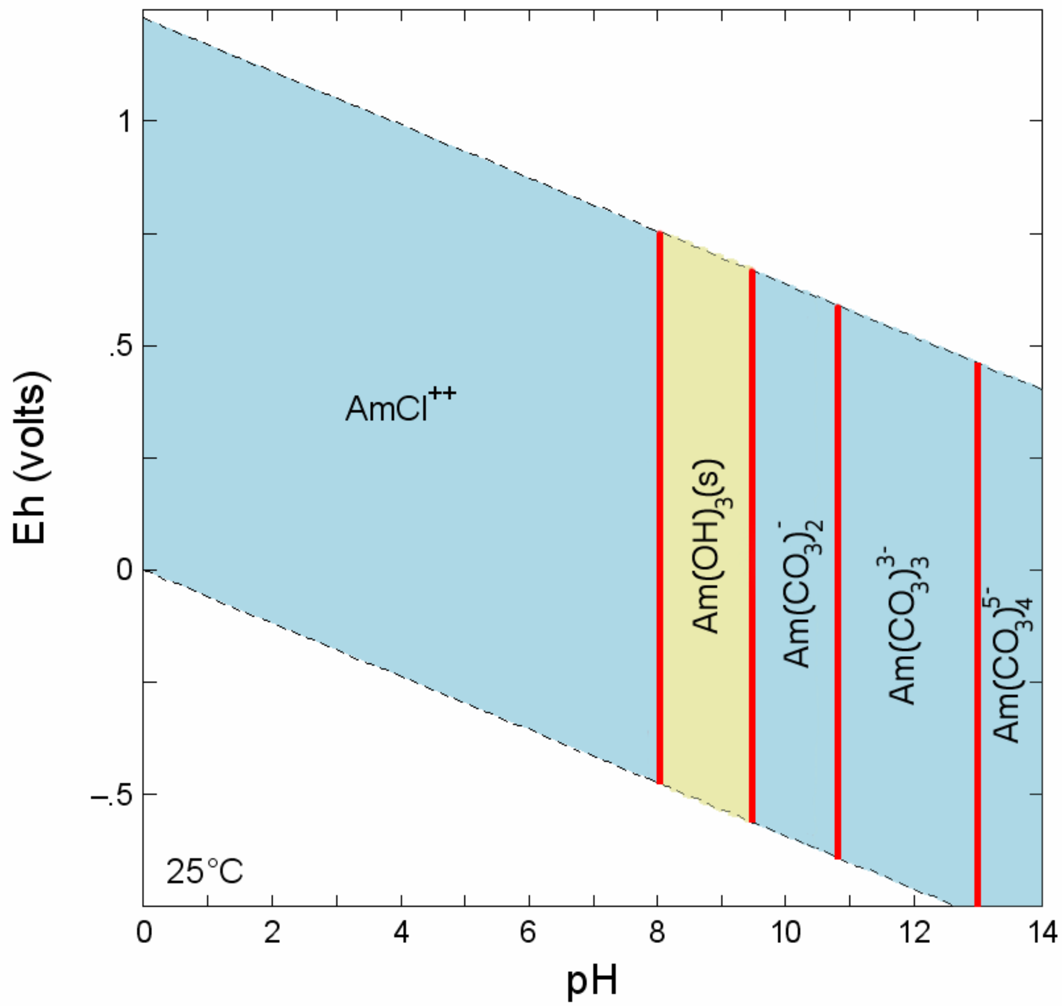
- Pu(VI) reduction was fastest when there was available Fe(II)
- ~ no reactivity noted with Fe(III) phases (as expected)



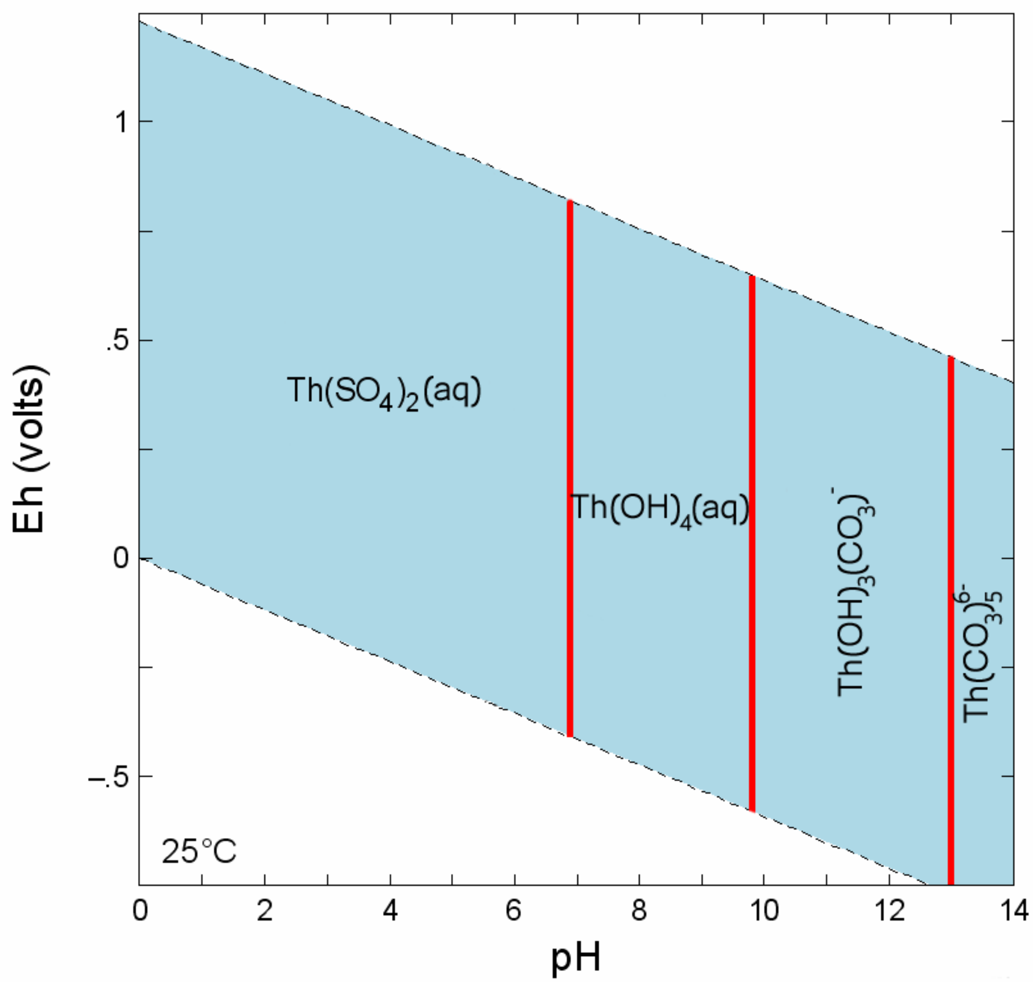
Pu Solubility and Speciation in WIPP

- Pitzer formalism
- Redox Assumption
- Use of oxidation state analogs
  - Nd(III) for Pu(III) or Am(III)
  - Th(IV) for Pu(IV)
- Pu solubility
- Pu species in WIPP

Predominant Species of An(III) in WIPP Brine Calculated for Am(III)



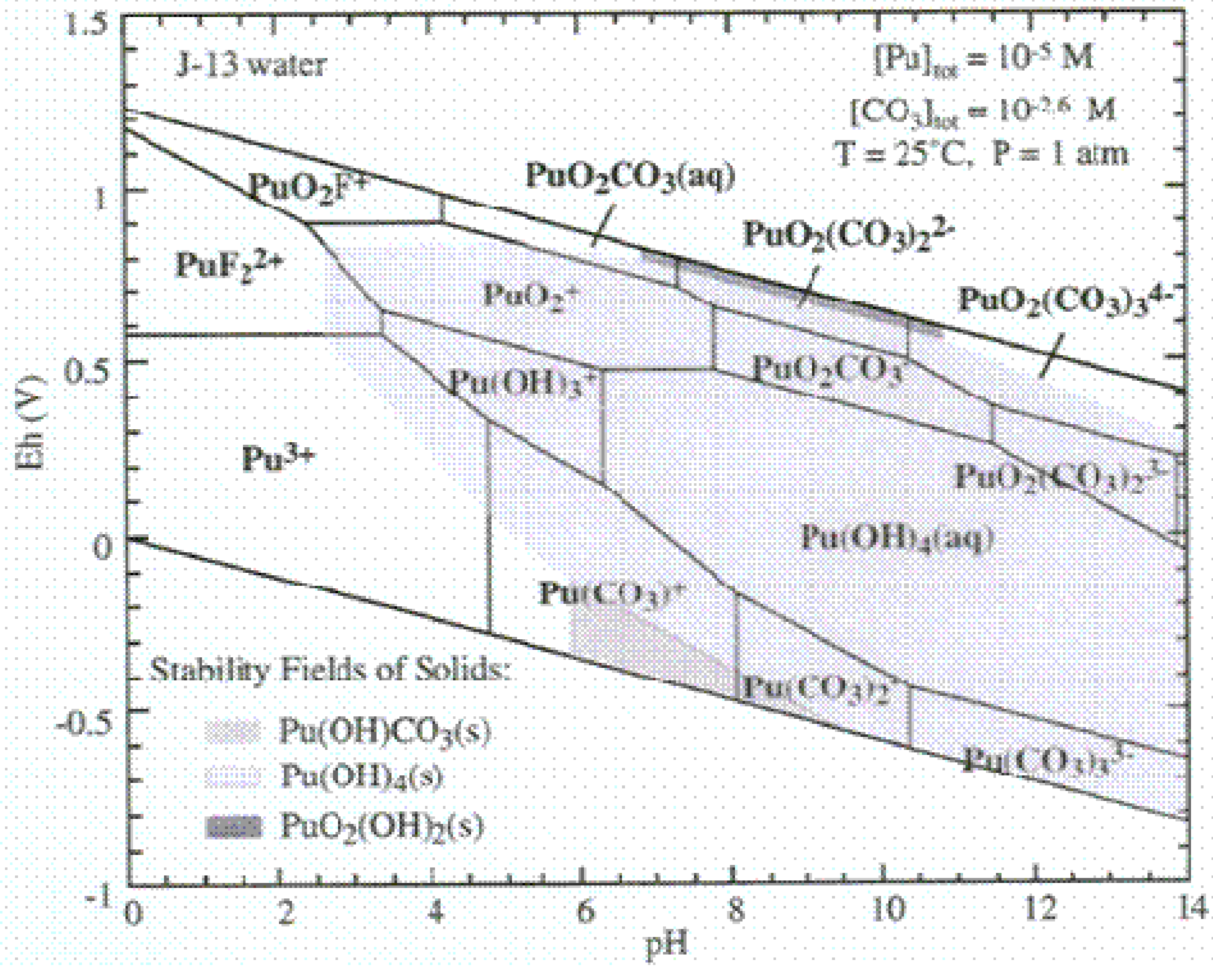
Predominant Species of An(IV) in WIPP Brine Calculated for Th(IV)



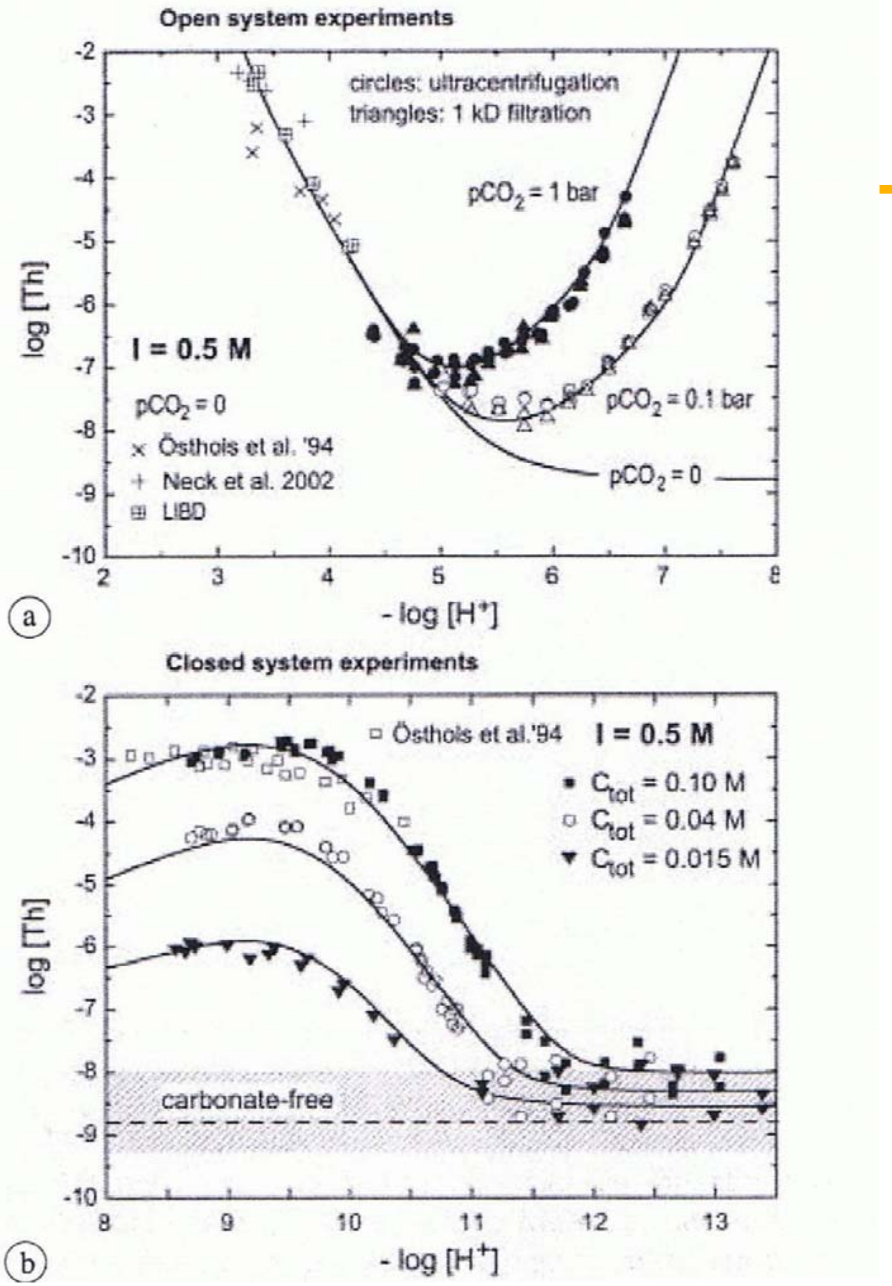
Plutonium Phase Diagram

Runde et. al.

YMP work



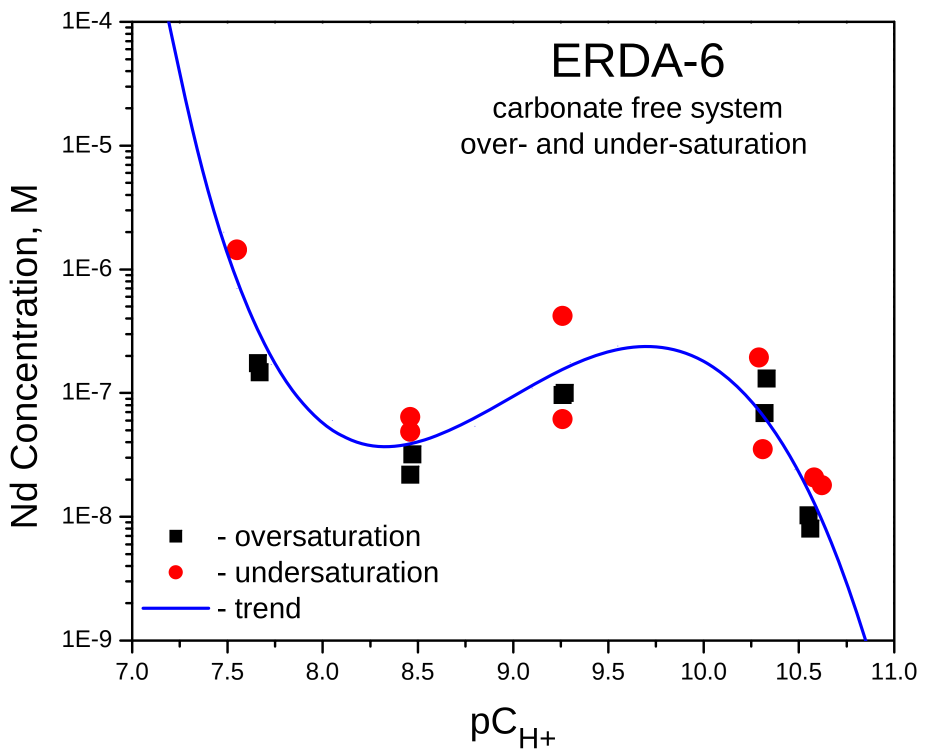
Pu(IV) Solubility Measured by Analogy Using Th(IV)



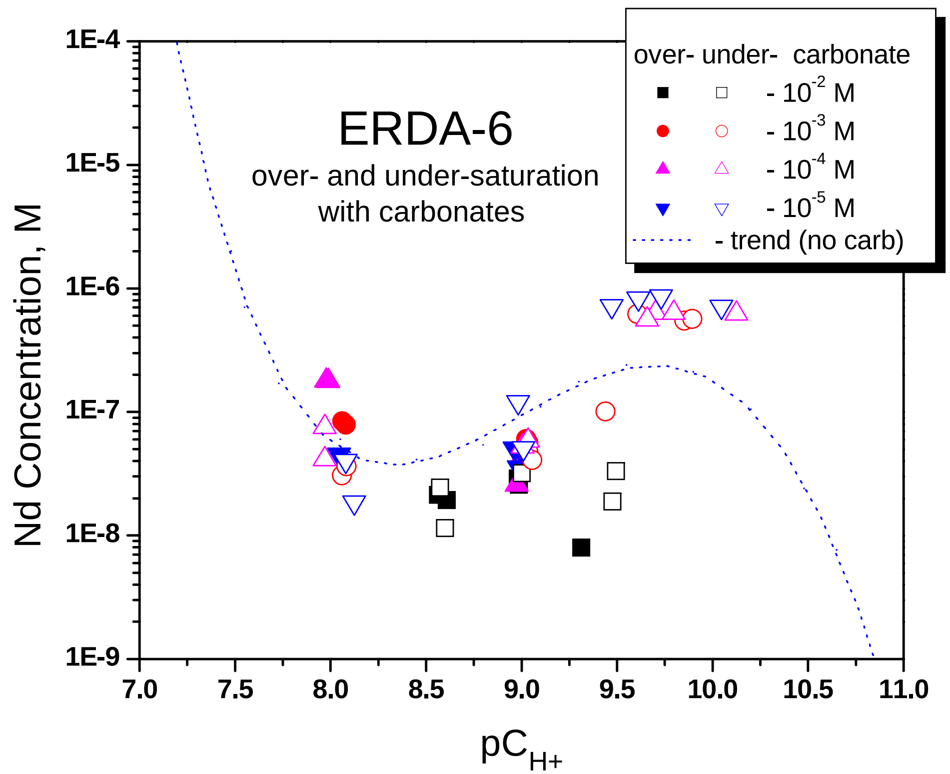
Solubility of amorphous Th(IV) oxyhydroxide in the presence and absence of carbonate in 5 M sodium chloride as a function of pH. The solid lines are the calculated solubilities.

*Altmaier et al. Radiochimica Acta, **93**, 83-92 (2005)*

Pu(III) Solubility Measured by Analogy Using Nd(III)



carbonate-free



with carbonate

Solubility of An(III), An(IV) and An(V) Calculated Using Pitzer Formalism

Solubilities of the Oxidation State Analogs, in moles/liter, with MgO Backfill calculated for PABC-2005				
Brine	FMT Name	Actinide Oxidation		
		(III)	(IV)	(V)
GWB	hmag. w organics	3.87×10^{-7}	5.64×10^{-8}	3.55×10^{-7}
ERDA-6	hmag. w organics	2.88×10^{-7}	6.79×10^{-8}	8.24×10^{-7}

hmag. – hydromagnesite

Conclusions

- Salt-based repository, due to the self sealing mechanism, will become geologically insulated and saturated with brine in relatively short time.
- Corrosion of metallic containers (mostly iron) will consume oxygen and will maintain strongly reducing environment.
- Combination of anaerobic microbial activity and reaction with reduced forms of metals ($Fe^{II,0}$) will lead to reduction of higher oxidation states of plutonium. Pu(VI) and Pu(V) will be reduced to Pu(IV) and Pu(III).
- Carbon dioxide generated by microbes and pH~9 maintained by MgO, engineered barrier, will affect chemical speciation of Pu(III) and Pu(IV).
- Organic ligands (e.g. EDTA, citrate) may affect speciation and solubility of plutonium but this depends on the amounts of organics in the waste.