LA-UR- 09-03495

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Title: Overview of Actinide Chemistry in the WIPP

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Intended for: ANS Annual Meeting,
Atlanta, GA
June 16, 2009

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Abstract

LA-UR-09-00133

The year 2009 celebrates 10 years of safe operations at the Waste Isolation Pilot Plant (WIPP), the only nuclear waste repository designated to dispose defense-related transuranic (TRU) waste in the United States. Many elements contributed to the success of this one-of-the-kind facility. One of the most important of these is the chemistry of the actinides under WIPP repository conditions. A reliable understanding of the potential release of actinides from the site to the accessible environment is important to the WIPP performance assessment (PA).

The environmental chemistry of the major actinides disposed at the WIPP continues to be investigated as part of the ongoing recertification efforts of the WIPP project. This presentation provides an overview of the actinide chemistry for the WIPP repository conditions. The WIPP is a salt-based repository; therefore, the inflow of brine into the repository is minimized, due to the natural tendency of excavated salt to re-seal. Reducing anoxic conditions are expected in WIPP because of microbial activity and metal corrosion processes that consume the oxygen initially present. Should brine be introduced through an intrusion scenario, these same processes will re-establish reducing conditions. In the case of an intrusion scenario involving brine, the solubilization of actinides in brine is considered as a potential source of release to the accessible environment.

The following key factors establish the concentrations of dissolved actinides under subsurface conditions:

- Redox chemistry. The solubility of reduced actinides (III and IV oxidation states) is known to be significantly lower than the oxidized forms (V and/or VI oxidation states). In this context, the reducing conditions in the WIPP and the strong coupling of the chemistry for reduced metals and microbiological processes with actinides are important.
- Complexation. For the anoxic, reducing and mildly basic brine systems in the WIPP, the most important inorganic complexants are expected to be carbonate/bicarbonate and hydroxide. There are also organic complexants in TRU waste with the potential to strongly influence actinide solubility.
- Intrinsic and pseudo-actinide colloid formation. Many actinide species in their expected oxidation states tend to form colloids or strongly associate with non actinide colloids present (e.g., microbial, humic and organic).

Abstract cont.

In this context, the relative importance of actinides, based on the TRU waste inventory, with respect to the potential release of actinides from the WIPP, is greater for plutonium and americium, and to less extent for uranium and thorium. The most important oxidation states for WIPP-relevant conditions are III and IV.

We will present an update of the literature on WIPP-specific data, and a summary of the ongoing research related to actinide chemistry in the WIPP performed by the Los Alamos National Laboratory (LANL) Actinide Chemistry and Repository Science (ACRSP) team located in Carlsbad, NM [Reed 2007, Lucchini 2007, and Reed 2006].

References

[Reed 2006]: Reed, D.T., J.-F. Lucchini, S.B. Aase, and A.J. Kropf. 2006. "Reduction of Plutonium (VI) in Brine under SubsurfaceConditions." *Radiochimica Acta, vol. 94: 591–97.*

[Lucchini 2007]: Lucchini, J-F, M. Borkowski, M.K. Richmann, S. Ballard, and D.T. Reed. 2007. "Solubility of Nd3+ and UO22+ in WIPP Brine as Oxidation-State Invariant Analogs for Plutonium." *Journal of Alloys and Compounds, vol. 444/445: 506–11.*

[Reed 2007]: Reed, D.T., S.E. Peper, and B.E. Rittmann. 2007. "Subsurface Bio-Mediated Reduction of Higher-Valent Uranium and Plutonium." *Journal of Alloys and Compounds, vol. 444/445: 376–82.*

Overview of Actinide Chemistry in the WIPP

Earth & Environmental Sciences

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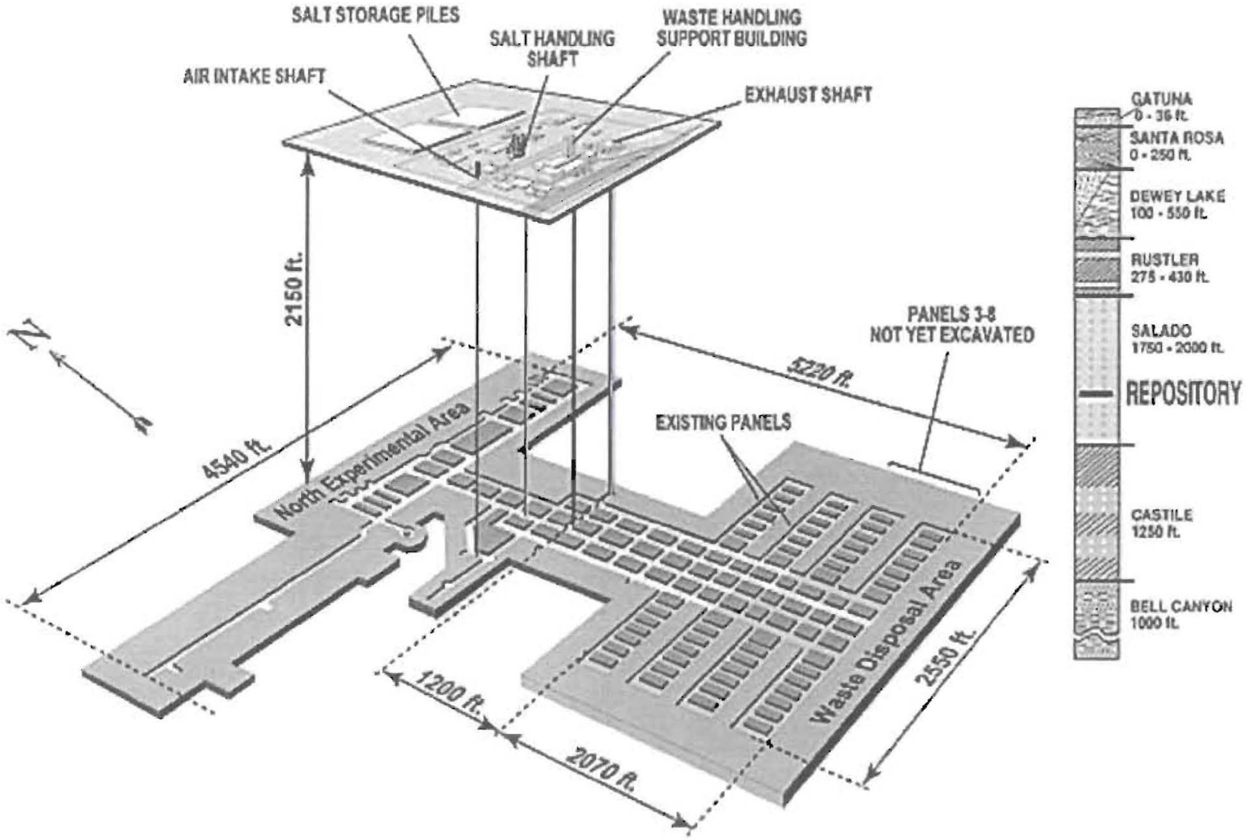
Disposal rooms are excavated in an ancient, stable salt formation 2,150 feet (almost one-half mile) underground. Transuranic waste, which consists of clothing, tools, rags, debris and other disposable items contaminated with radioactive elements, mostly plutonium, are emplaced in 55 gallon steel drums for permanent disposal.

WIPP Facility and Stratigraphic Sequence



General View of WIPP, Waste and MgO Placement in a WIPP Disposal Room

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**

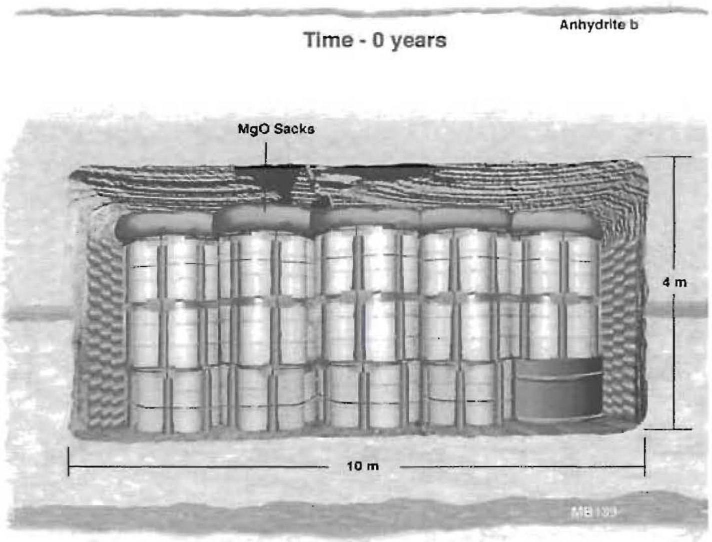
Importance of actinides

From the point of view of radioactivity release:

Pu ≈ Am >> U > Th >> Np, Cm (fission products)

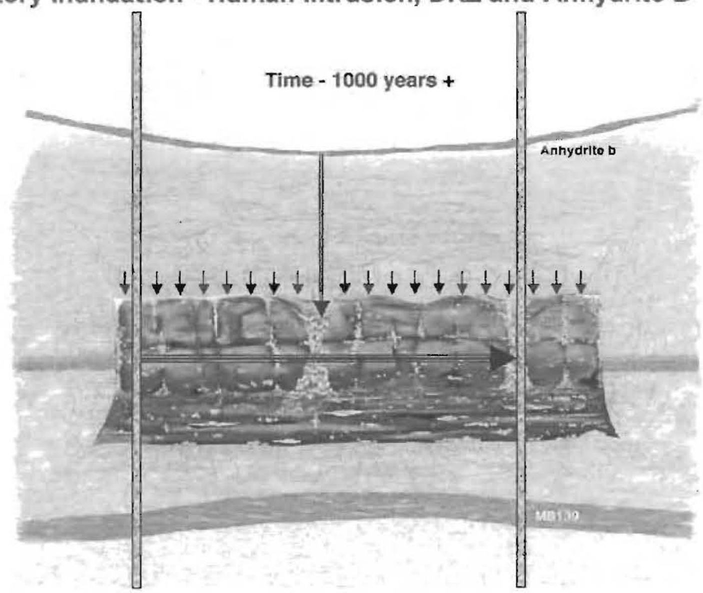
WIPP Disposal Room
in a Time of Closure and 1000+ Years Later

View of the WIPP Disposal Room

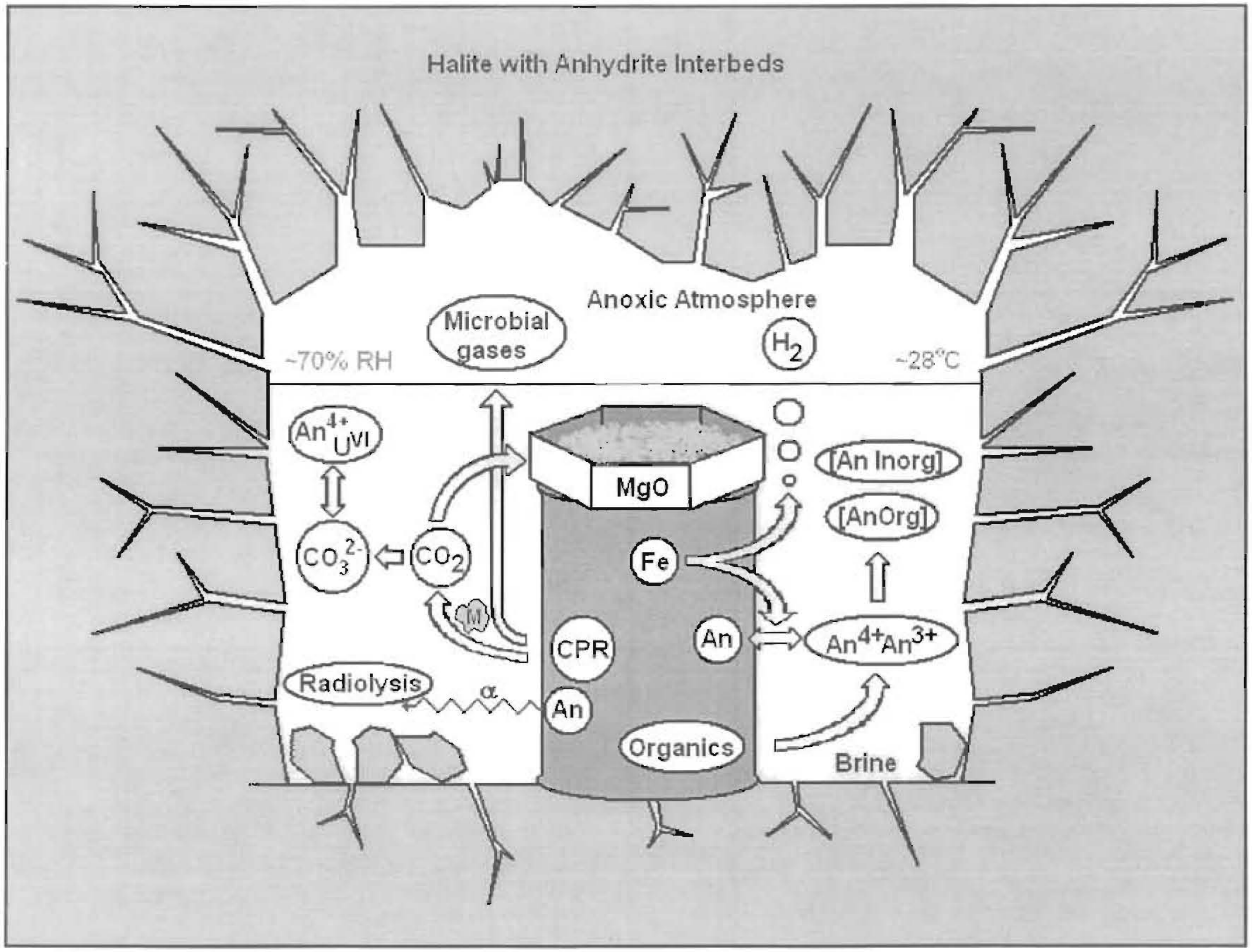


Courtesy of Frank Hansen, SNL

Repository Inundation - Human Intrusion, DRZ and Anhydrite B



Possible chemical reactions in the WIPP



Summary of Current WIPP Chemistry Model

Geochemistry	Predominantly pure halite Salado formation salt with anhydrite interbeds
Temperature	Ambient is 28°C, an increase of up to 3°C is possible due to the emplacement of TRU waste
Water Content	Unsaturated for short period of time with a humidity ~70% RH at the repository temperature. Brine inclusions, in the salt range from 0.1 to 0.2 %, by mass, brine inclusions are present in pre-excavated salt. Brine saturation will occur through human intrusion scenarios over a wide range of repository time.
Pressure	~15 MPa (147 atm) lithostatic, up to ~ 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 microbially generated gases at pressures up to lithostatic.
Minimum brine volume for DBR	The calculated minimum volume of brine, from any source, needed for DBR release is 17,000 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, in the repository.

Overall goals of the chemistry repository science program:

1. **Solubility of transuranium elements in WIPP brine (effect of pC_{H+}, carbonate, organic ligands, etc.)**
2. **Effect of**

   microbial activity,

   repository components, and

   radiolytic products of brine,

   on redox speciation of plutonium, americium and uranium.

Brine Composition Used in Actinide Solubility Studies

	ERDA-6		GWB		$MgCl_2$ simplified		NaCl simplified	
Component	g/L	M	g/L	M	g/L	M	g/L	M
NaCl	248.6	4.254	167.8	2.874			292.2	5.0
$MgCl_2.6H_2O$	3.667	0.018	193.4	0.953	751.9	3.704		
Na_2SO_4	22.52	0.159	23.61	0.166				
NaBr	1.074	0.010	2.565	0.025				
$Na_2B_4O_7.10H_2O$	5.7	0.015	14.03	0.037				
KCl	6.869	0.092	32.57	0.437				
LiCl	-	-	0.174	0.004				
$CaCl_2.2H_2O$	1.672	0.011	1.896	0.013				
Ionic strength	4.965 M		6.839 M		11.1 M		5.0 M	
Density g/mL	1.183		1.216		1.252		1.185	

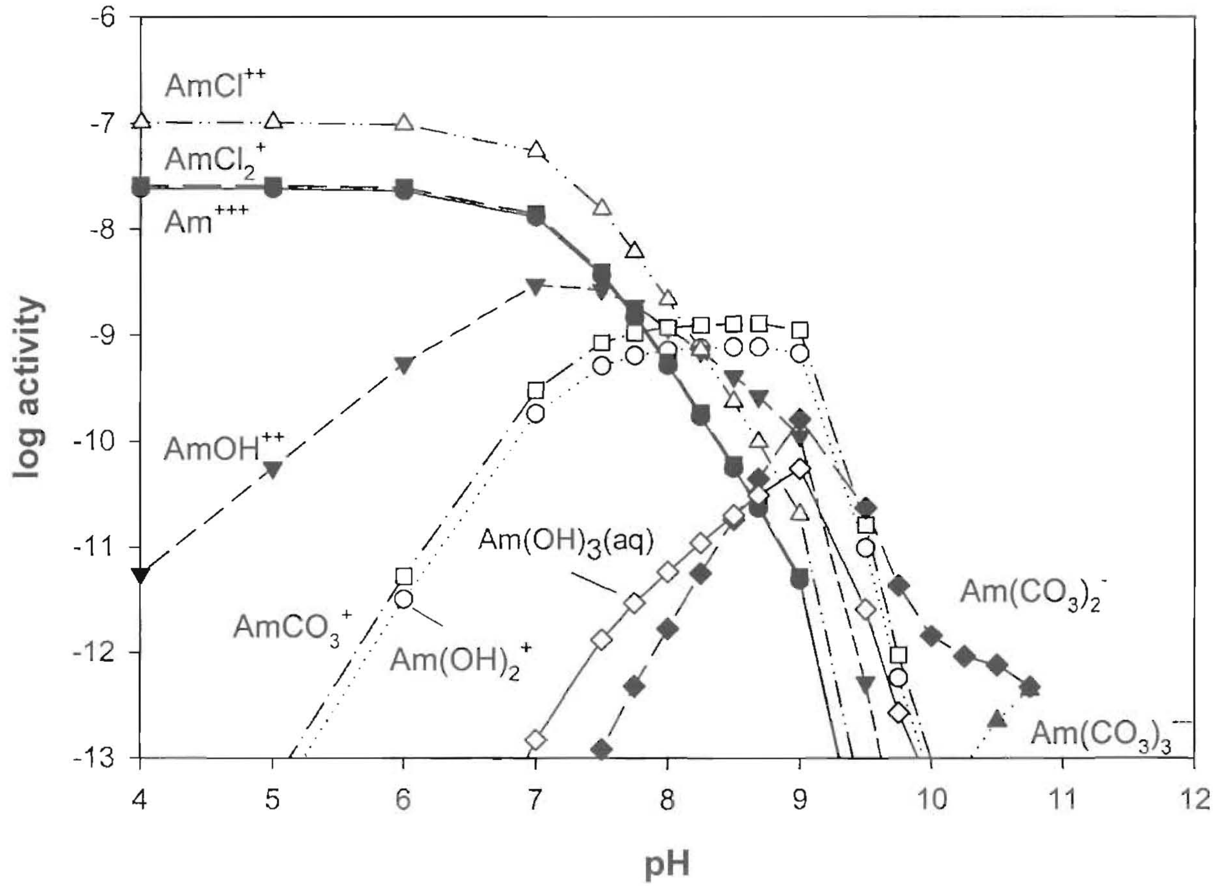
GWB - Generic Weep Brine

ERDA-6 - Energy Research and Development Administration Well 6 – Castile formation brine.

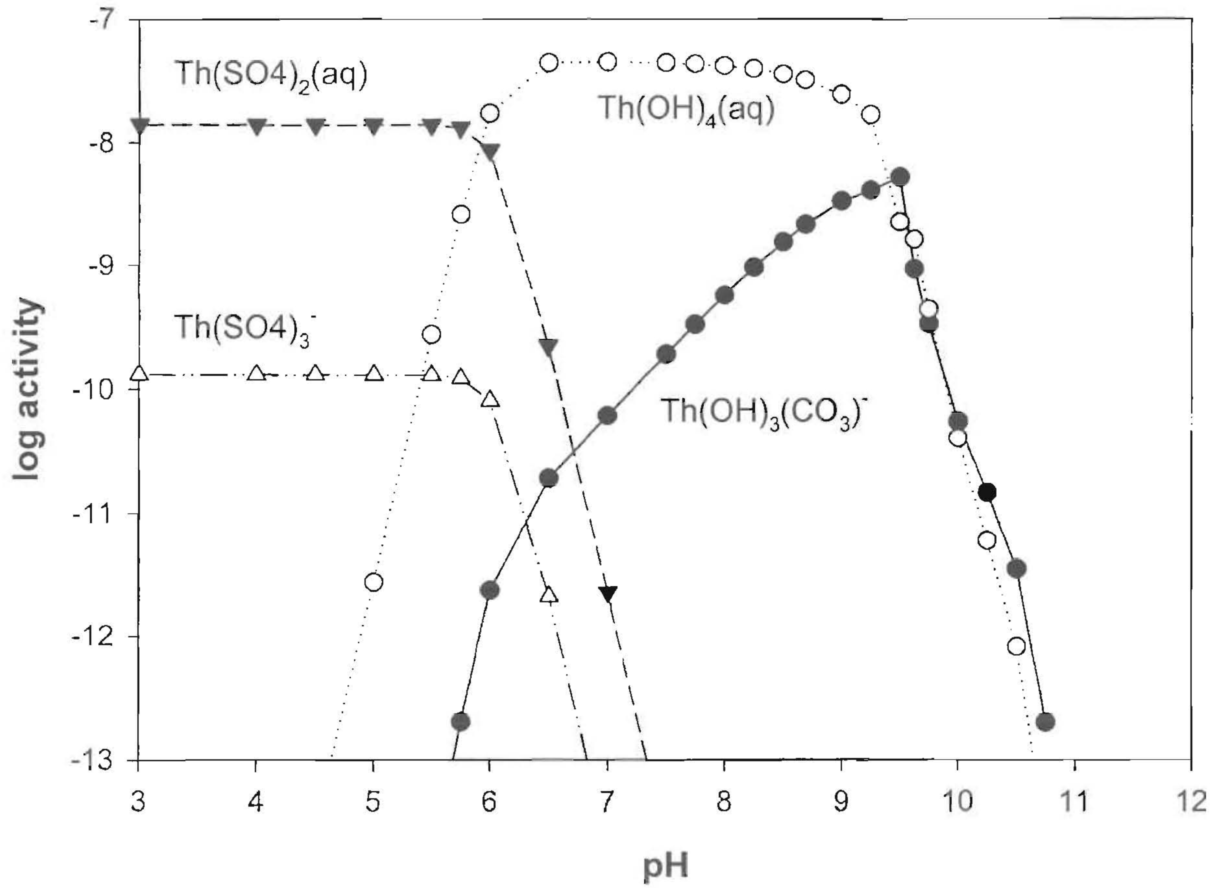
Actinide Solubility and Speciation in WIPP

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

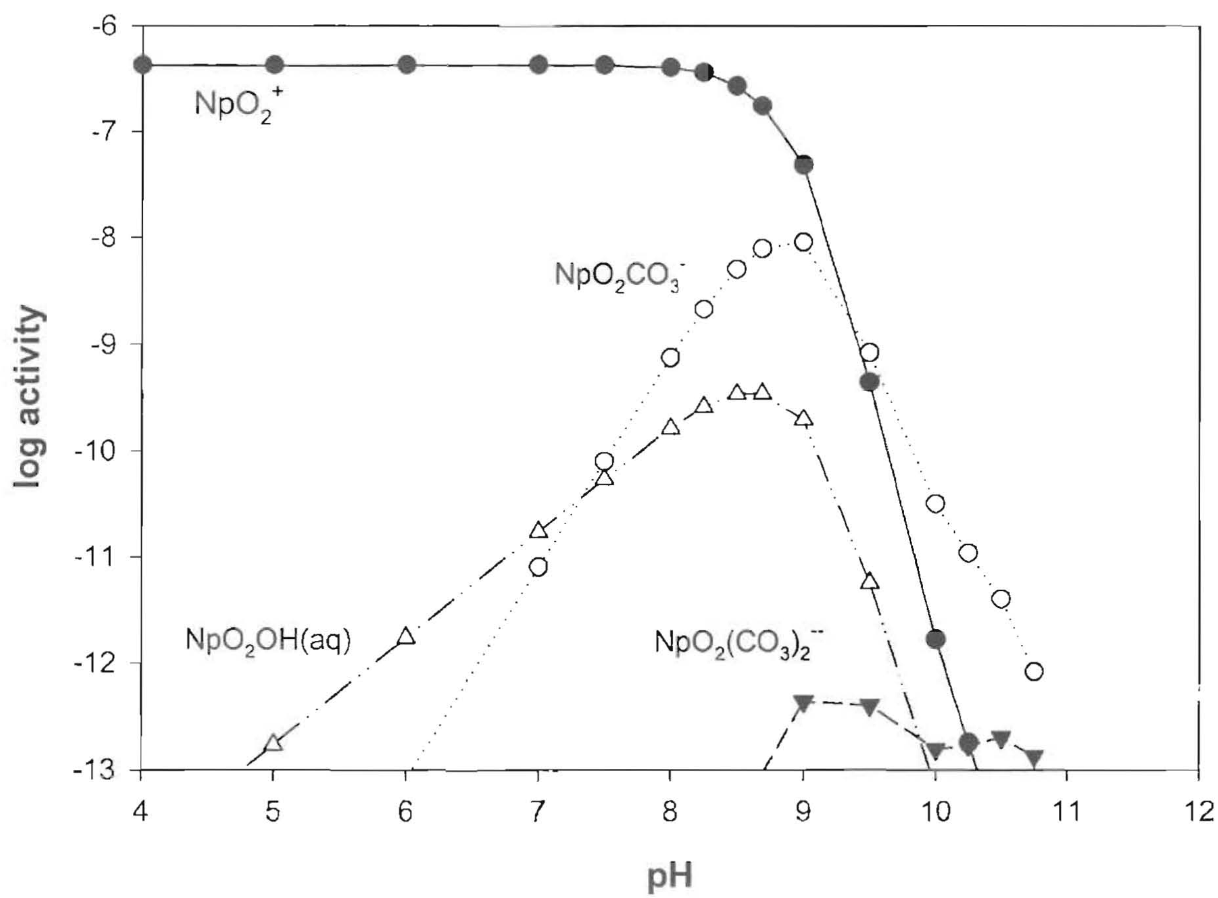
Calculated Am(III) speciation as a function of pH



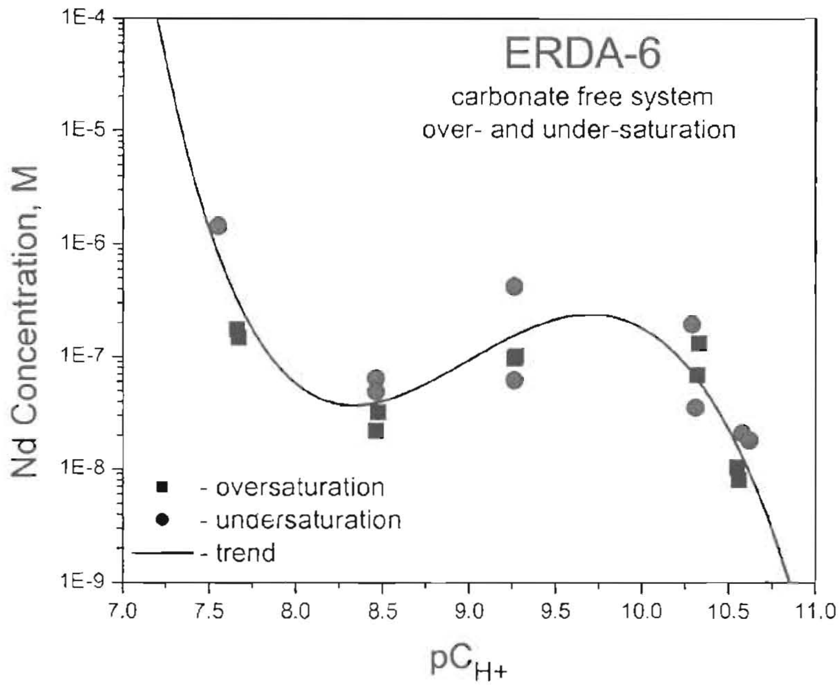
Calculated Th(IV) speciation as a function of pH



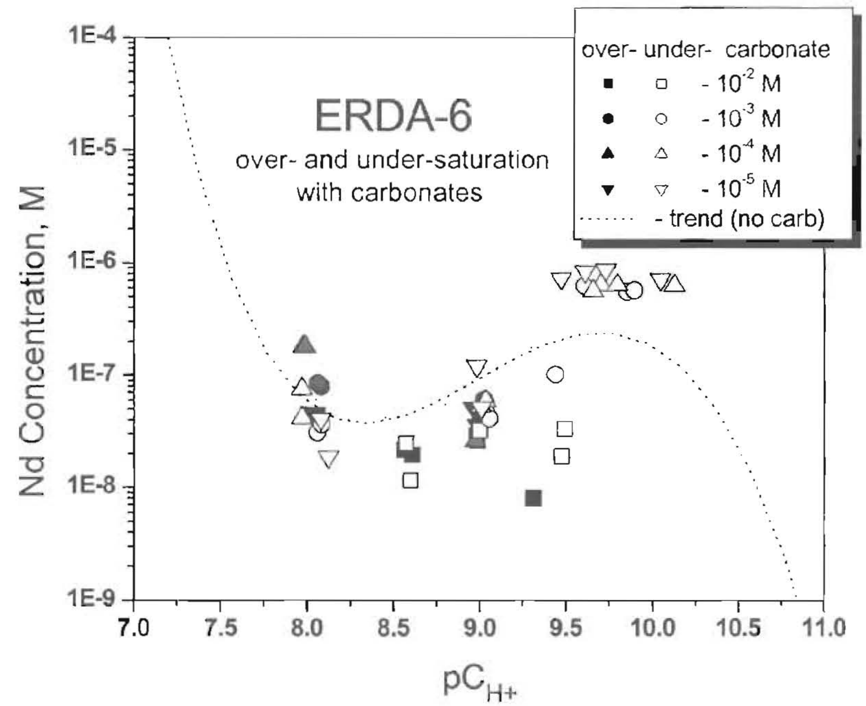
Calculated Np(V) speciation as a function of pH



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



carbonate-free

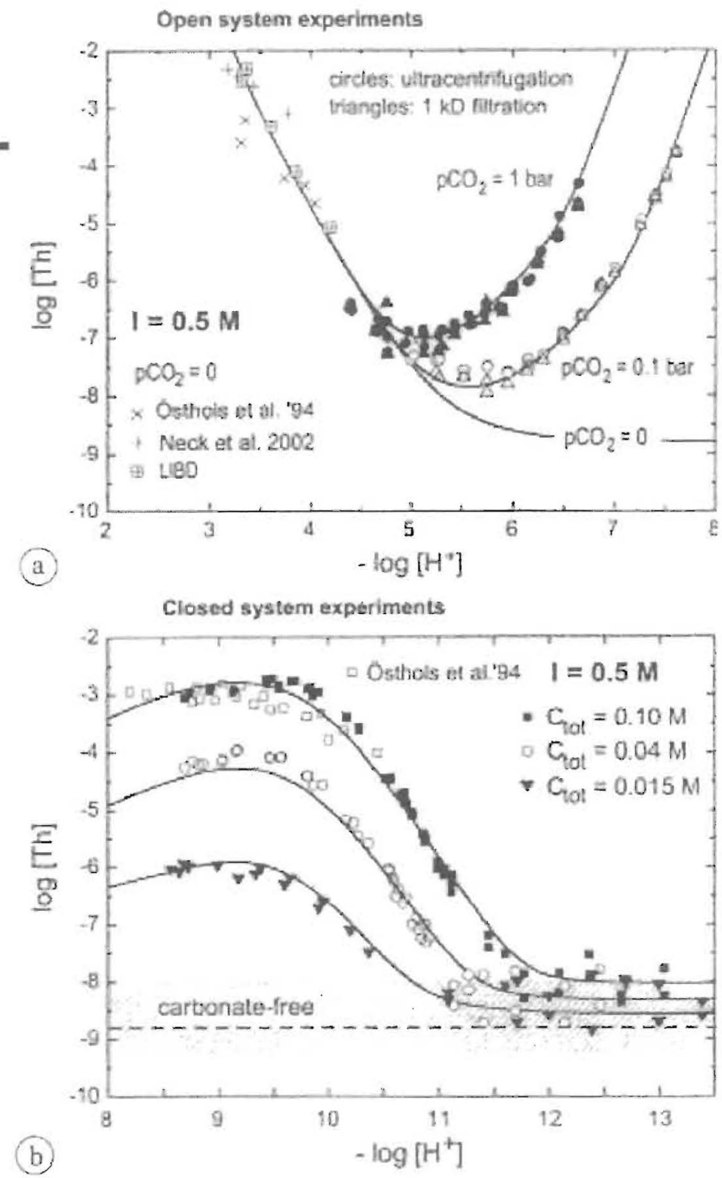


with carbonate

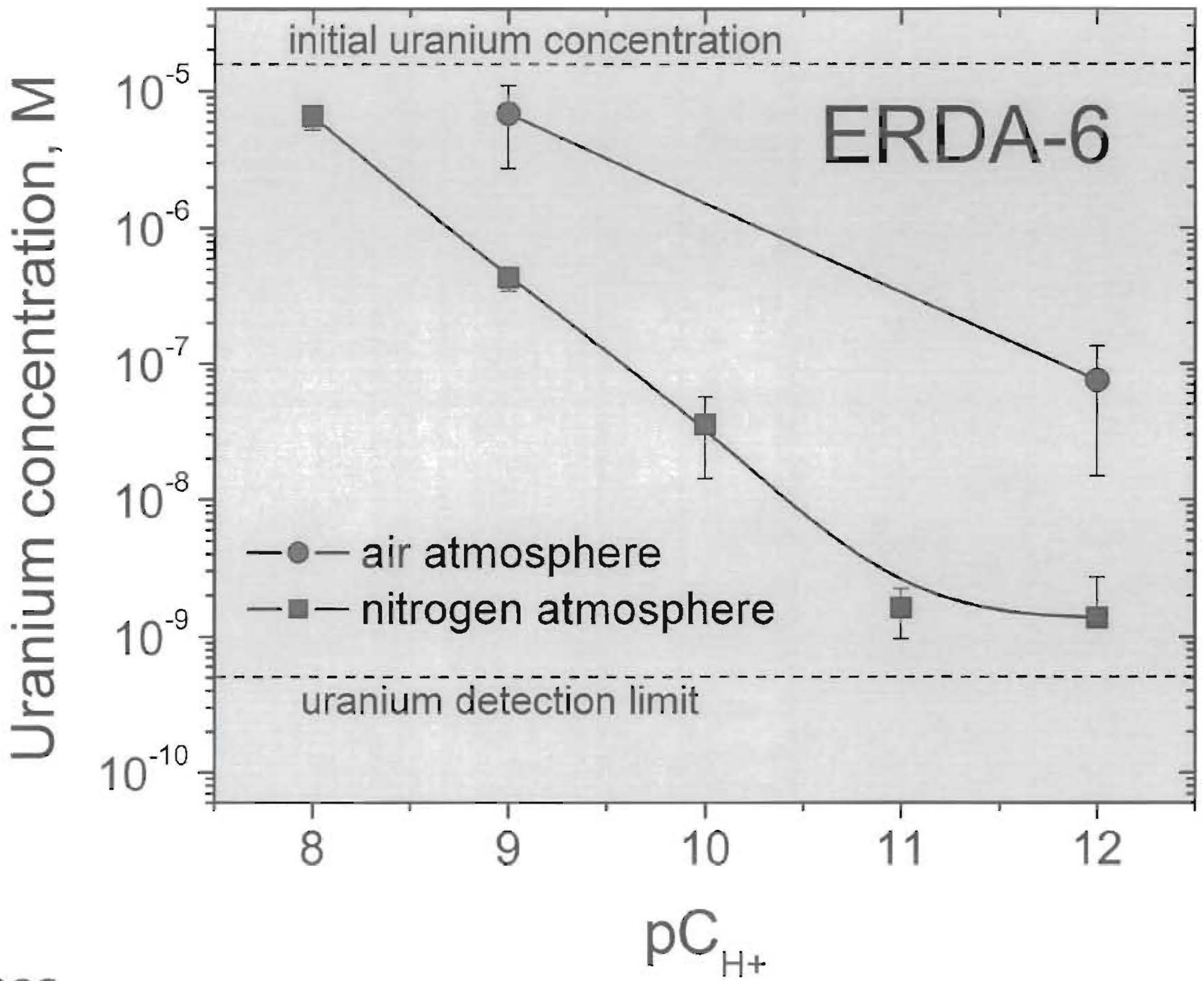
An(IV) Solubility Measured by Analogy Using Th(IV)

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)*



U(VI) Solubility



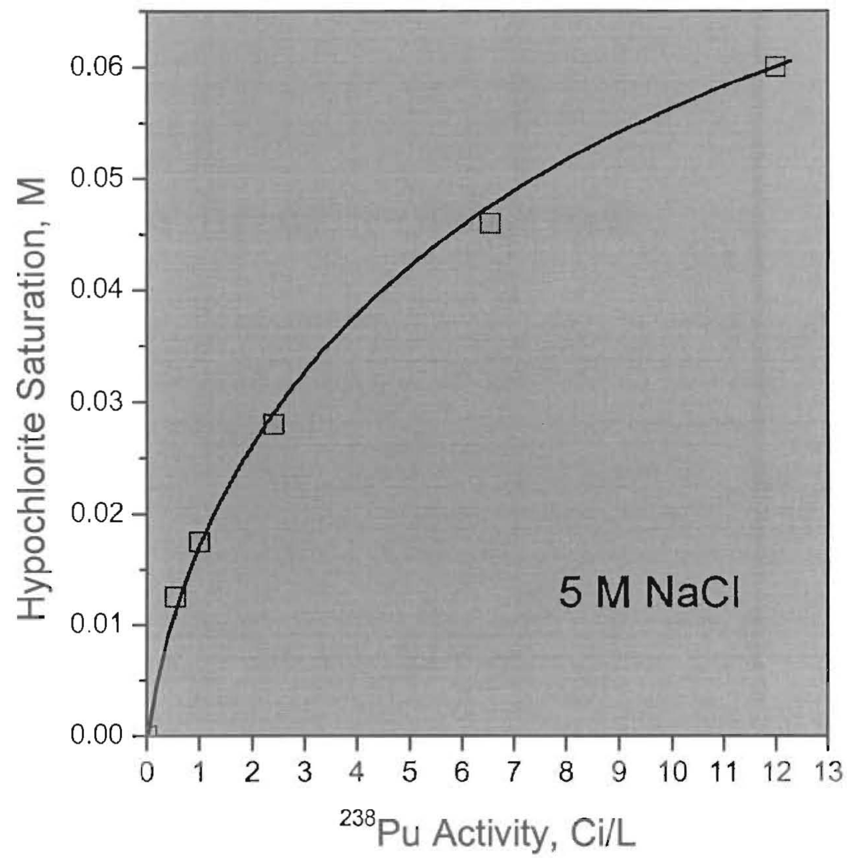
Solubility of An(III), An(IV) and An(V) Calculated Using Pitzer Formalism

Solubilities of the Oxidation State Analogs, in moles/liter, with MgO Backfill calculated for PABC-2004				
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

Primary G-values calculated for different chloride concentrations

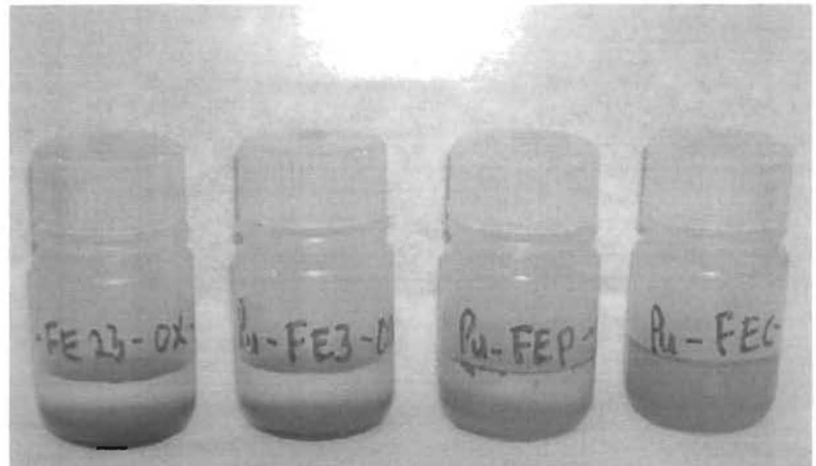
Cl^- concentration, [M]	G_{H2O2}	$G_{ClOH\cdot}$
5	0.23	0.55
4	0.27	0.50
3	0.32	0.44
2	0.40	0.38



*Kelm M., I. Pashalidis, I.J. Kim Applied Radiation and Isotopes, **51,** (1999) 637-642.*

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

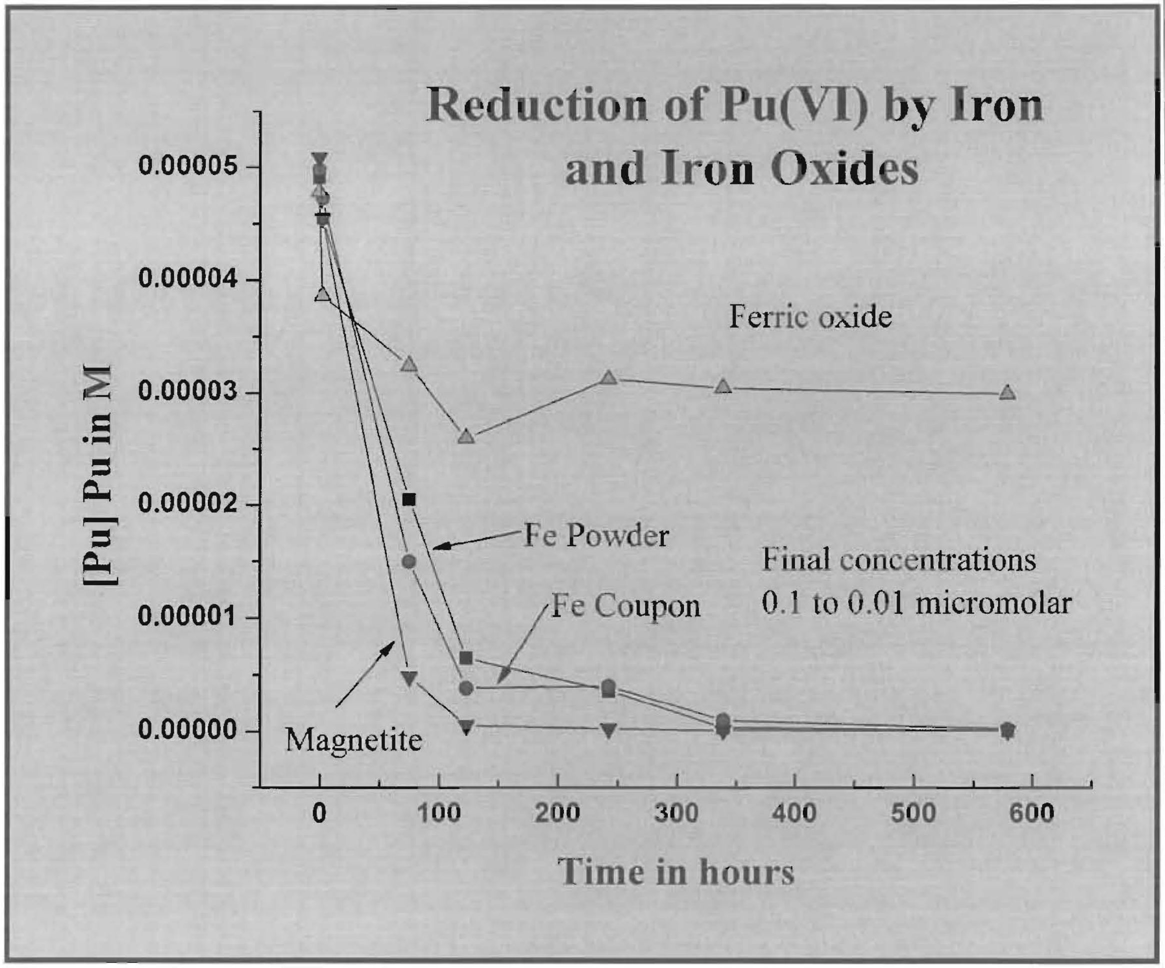
- Very different appearances in iron reaction products were noted depending on pH, brine and initial iron phase
- Plutonium was associated with the Fe phases
- Green rust was often noted at the higher pH
- XANES established the green rust to be an Fe2/3 phase with a bromide center
- This green rust phase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



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

Reduction of Pu(VI) by Iron Oxides

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



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 and cowerkers; also Pu polymer solubilization and reduction was noted

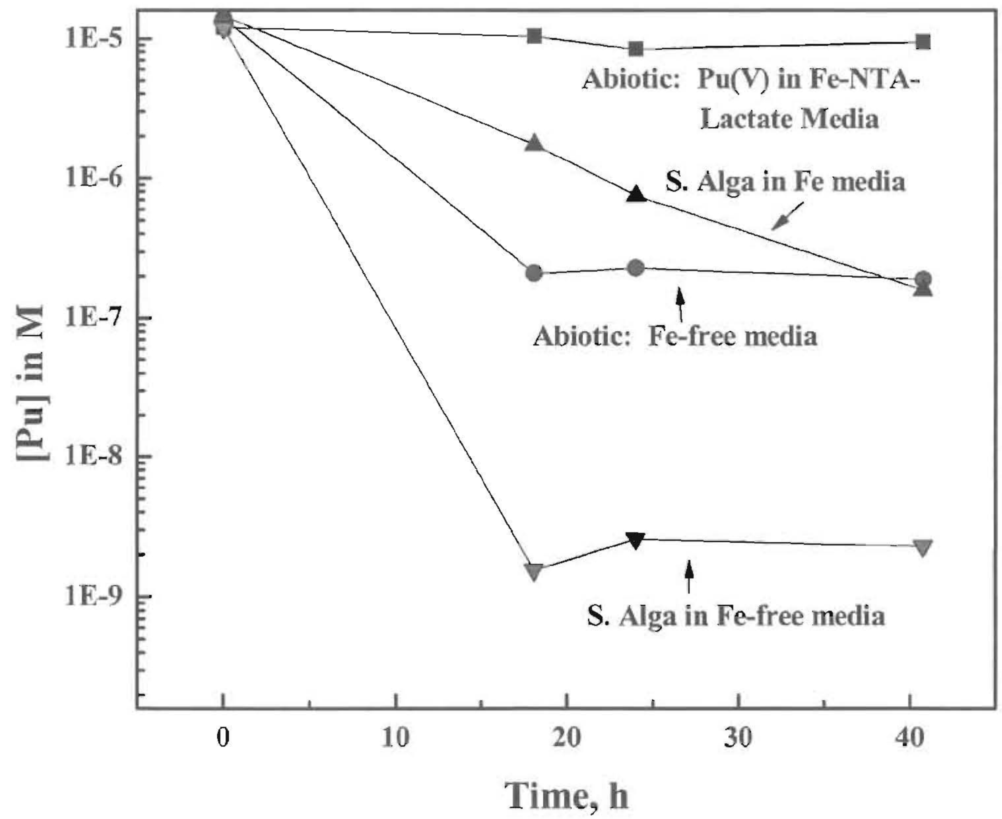


Figure 8. Bioreduction of higher-valent plutonium by *Shewanella alga BrY* under anaerobic conditions in the presence and absence of iron. Uncertainty in the plutonium concentration data is ± 10%.

Conclusions

- Salt-based repository, because of the self sealing mechanism, will become geologically isolated.
- Corrosion of metallic containers (mostly iron) will consume oxygen and will maintain strongly reducing environment throughout repository time.
- 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, americium and possibly uranium. Pu(VI) and Pu(V) will be reduced to Pu(IV) and Pu(III), stabilized Am(III) and U(VI) may be reduced to U(IV).
- Carbon dioxide generated by microbes and pH~8.7 maintained by the MgO, engineered barrier, will affect the chemical speciation of Pu(IV) and U(VI) – equilibrium between hydroxo- and cabonato- complexes.
- The WIPP is a robust and excellent geologic repository for the permanent storage of Transuranic Nuclear Waste.