ACTINIDE SOLUBILITY AND SPECIATION IN THE WIPP TRANSURANIC REPOSITORY

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Overview

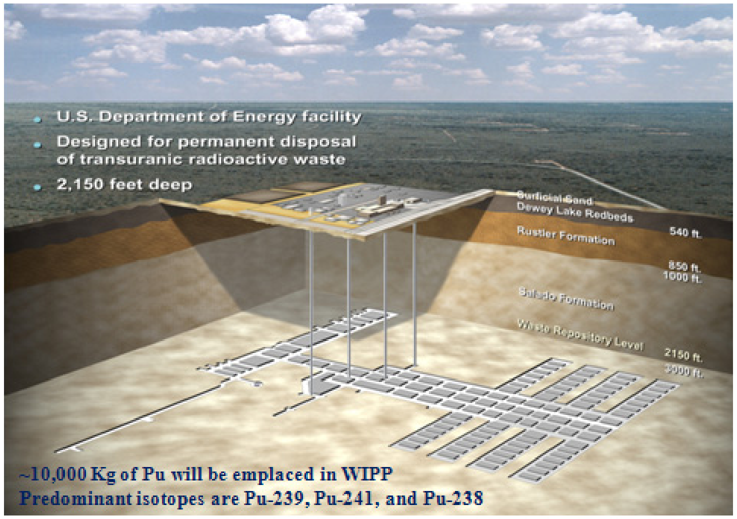
- Repository Science Directions in the US
- WIPP Overview and Status
- Actinide Solubility - Research Status and License Approach
    - Arguments for the reduction of higher-valent actinides
    - Solubility of An(III) – Nd(III) in Brine
    - Solubility of An(IV) - Th(IV) and Pu(IV)
    - Solubility of An(V) –   Inventory limits
    - Solubility of An(VI) – Uranium(VI) in brine
- Summary of Observations

Repository Science: Strategic Elements

Key Concepts for the Geologic Disposal of Nuclear Waste

- Geologic isolation
- Favorable thermodynamics and chemistry
  - Reducing conditions
  - Reactive redox control
  - Mildly alkaline pH
- Cost is an issue
- Transparent process with good societal receptiveness is very critical

WIPP – meets these criteria



Nuclear HLW waste repositories in the US and internationally?

Status of Repository Science in the US

- WIPP continues forward
- Yucca Mountain Project – currently no path forward
- The Blue Ribbon Commission on America's Nuclear Future has recommended a path forward
- Responsibility for managing used fuel and HLW waste lies with DOE Office of Nuclear Energy (NE), they are to study various options for geologic disposal
  - Salt, crystalline (granites) and sedimentary (clay/shale) rocks
  - Repositories and/or deep boreholes
  - International cooperation is a key to progress

Status of Salt-based Repository Concepts

- Second recertification of the WIPP TRU repository received on November 18, 2011. The third recertification application will be submitted in March 2014
- Blue ribbon commission visit to Carlsbad and tour of WIPP in January 2011 – local support continues
- NM State-level support now exists for expanded/additional mission in salt in SE New Mexico
  - NM senate letter to the blue ribbon commission supporting other potential missions (first session 2011)
  - NM house of representatives letter to the blue ribbon commission recommending additional missions including interim storage (first session 2011)
- Alternative options for the salt repository concept are under discussion

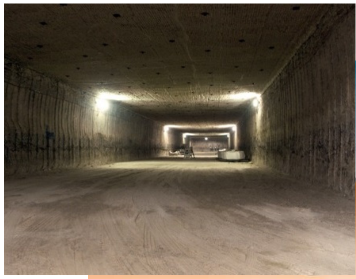
WIPP Background

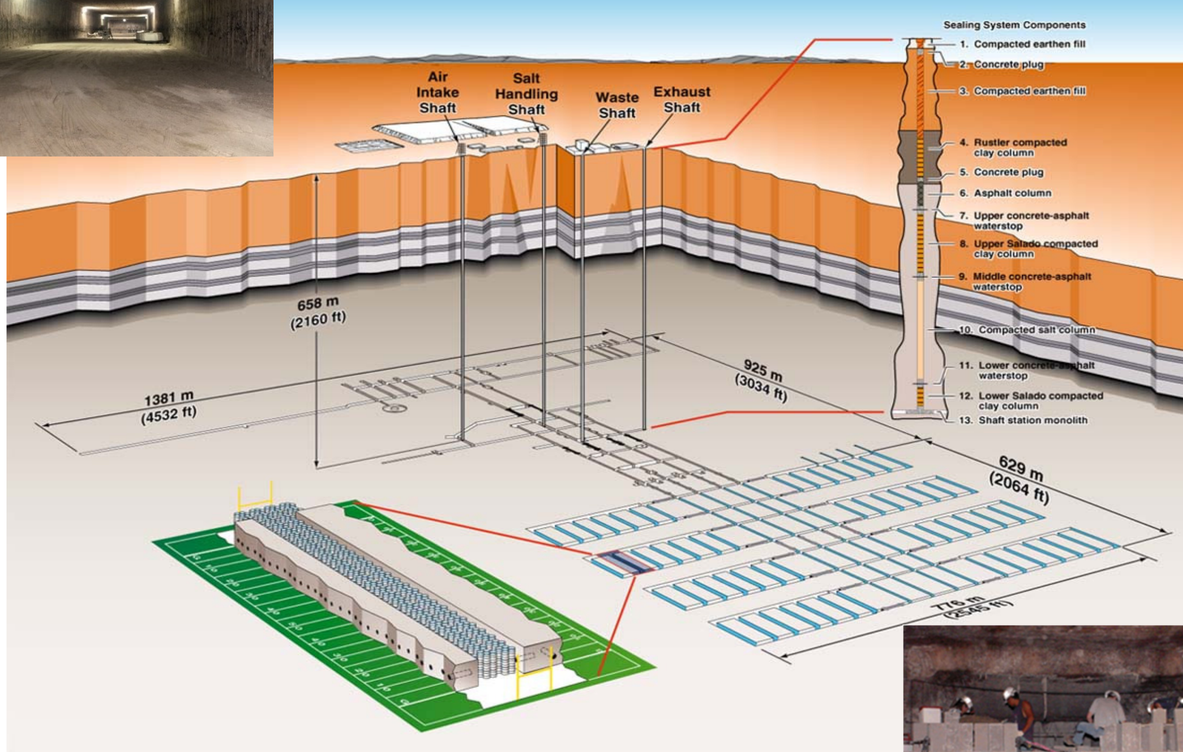
WIPP is a permanent disposal facility for TRU waste

- **Located in southeast New Mexico**
- **First certified in 1998, first shipment in 1999, recertified every 5 years**
- **Operated by U. S. Department of Energy (DOE)**

Regulated by U. S. Environmental Protection Agency (EPA) and New Mexico ED

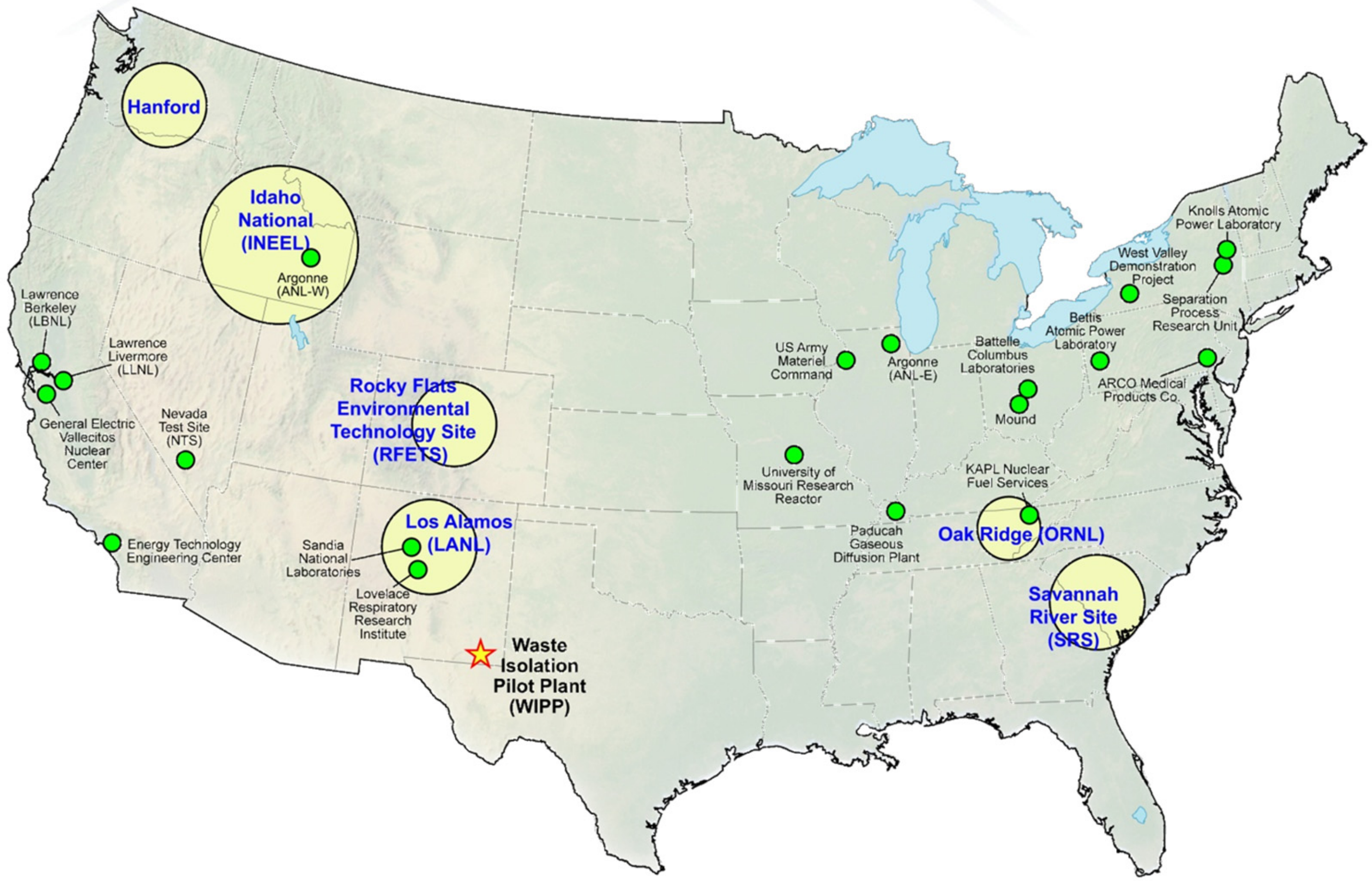
WIPP Design Overview





Repository is at a depth of 655 m in the Salado formation

Location of the Waste Generator Sites



Types of Waste

Contact-handled (CH)

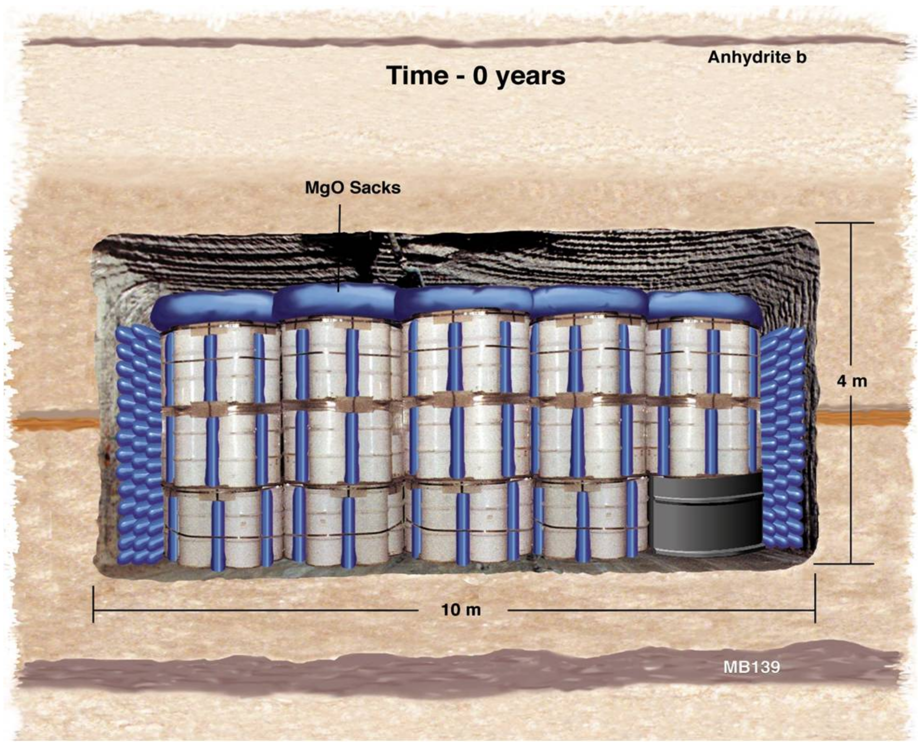
- Large volume
  - ~169,200 m³ capacity
- No shielding required
- Stacked on floor of waste roo

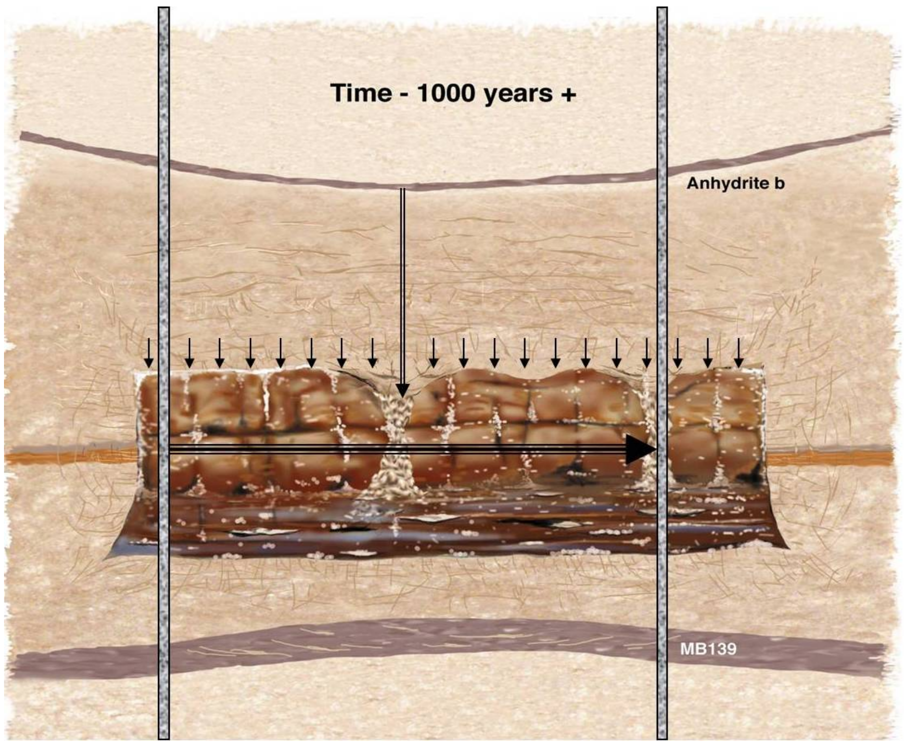
Remote-handled (RH)

- Small volume
  - ~7,000 m³ capacity
- Contains short-lived gamma emitters
- Shielding required
- Emplaced in horizontal boreholes in waste room walls

WIPP Disposal Room: Reliance on Self-Sealing

At Time of Closure … and 1000+ Years Later





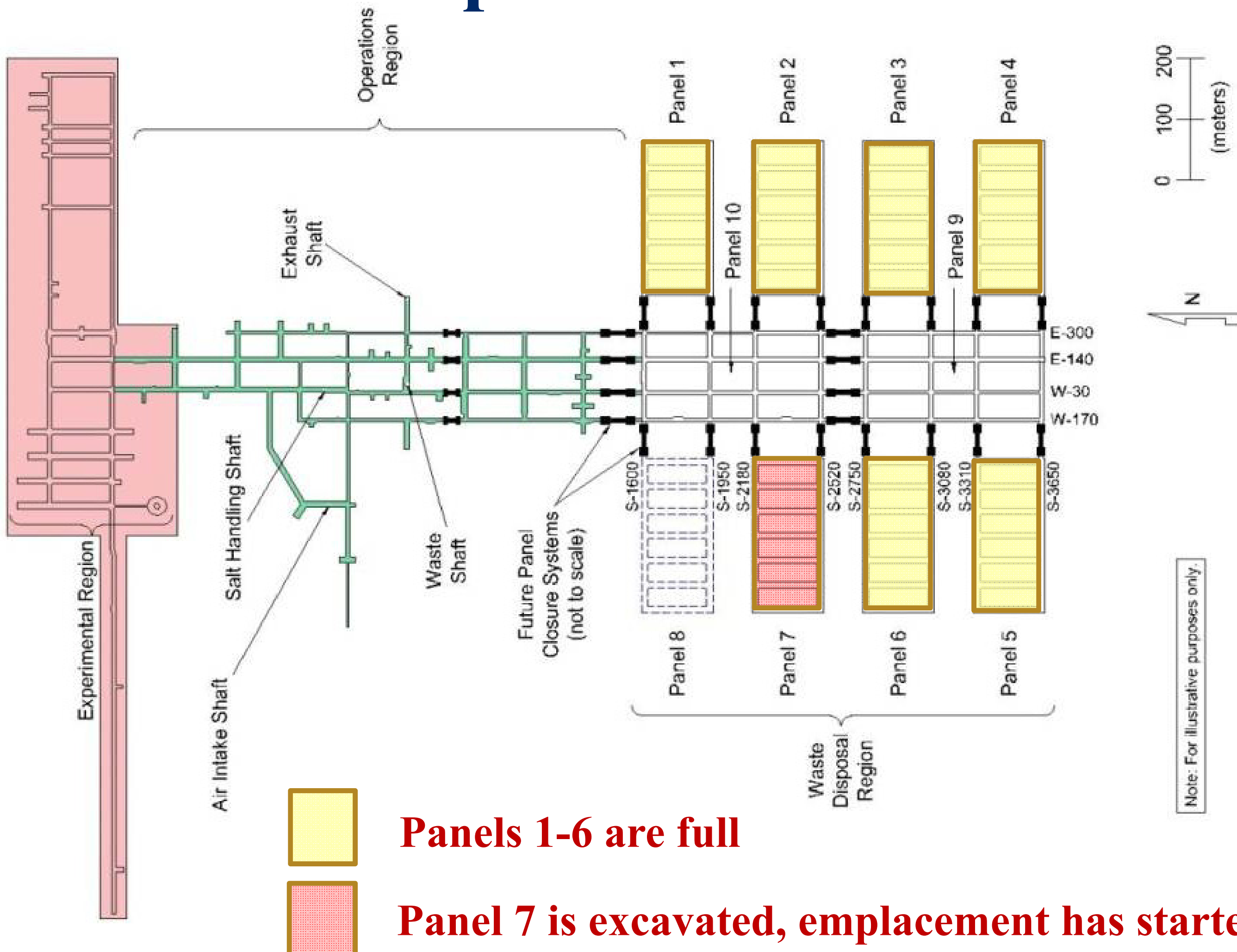
Waste and Actinide Inventory in the WIPP

Projected Actinide Inventories in the WIPP		
Element	2033 (0 years) Ci (Kg)	12033 (10,000 years) Ci (Kg)
Th	7.04 (1.35E4)	127 (1.35E4)
U	528 (2.26E5)	769 (2.28E5)
Np	23.2 (32.5)	170 (238)
Pu	2.02E6 (1.20 E4)	5.00E5 (9.12E3)
Am	7.05E5 (203)	21.1 (0.0994)
Cm	9.97E3 (0.122)	0.00 (0.00)
Cs	2.35E5 (2.67)	0.00 (0.00)
Sr	2.09E5 (1.51)	0.00 (0.00)

Projected Inventory of Waste Materials	
Material	Total (kg)
Iron-based metals/alloys	4.91E7
Aluminum-based metals/alloys	4.57E5
Lead	8.28E3
Cellulosics	4.65E6
Plastics	9.51E6
Rubber	1.25E6
CPR Total	1.54E7
Cement	1.08E7
MgO	Anticipated to be > 4 x 10^6
Organic Ligands (all from Waste)	Acetate: 2.41E4
	Oxalate: 1.85E4
	Citrate: 7.78E3
	EDTA: 3.76E2

WIPP Panels: Status of Waste Emplacement

Experimental area



Panels 1-6 are full

Panel 7 is excavated, emplacement has started

WIPP Record of Operation

Almost 15 years of operation

- >11,000 shipments received
- ~380,000 loaded drum equivalent containers disposed
- >86,000 cubic meters of TRU waste disposed (~ 165,000 containers)
- >12,000,000 loaded miles
- ~7 waste panels mined. Six panels are full, waste emplacement in panel 7 initiated
- 21 storage sites cleaned of legacy TRU waste
- Emplaced waste contains about 10,000 Kg of Pu

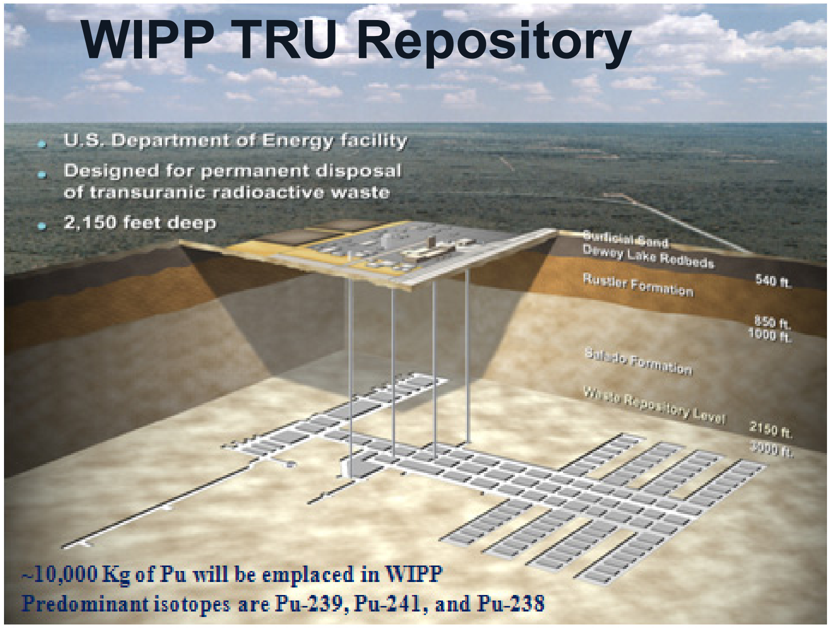
Impact on the near environment and personnel

- 0 contaminated WIPP personnel
- Negligible impact on the near-field environment
- Over 24 years as NM "Mine Operator of the Year"

Motivation and Application of the Research

WIPP-specific goals

- Support ongoing recertification (next is CRA-2014)
- Support model changes and updates under consideration (2-year program plan)
- Measure needed/planned parameter updates



Rationale for the work beyond WIPP

1) Groundwork for all WIPP repository options
2) Possible expansion of Salt-based repositories into HLW

Approach to Actinide Concentrations in the WIPP

1. Assess and track actinide inventory
   a) Pu, Am, Cm, U, and Th are potentially important
   b) Cm and Np is eliminated as a consideration
   c) Available chelating/complexing ligands
2. Assign oxidation state distribution by expert opinion
   a) Built-in conservatism
   b) Fe/microbially-induced redox environment that is reducing
   c) Support with WIPP-specific data
3. Establish effective solution concentration
   Model/measure actinide solubilities using redox-invariant analogs
   a) Account for colloidal contribution by process-specific enhancement factors: intrinsic, bio, inorganic, HA
   b) Assign an uncertainty distribution based on literature data review

Importance of Actinides and Oxidation States in the WIPP

Overall Release: Pu ~ Am >> U > Th >> Np, Cm and fission products

Oxidation State: III > IV >> VI > V

- Overall we are concerned with the release Am(III) and Pu(III/IV)
- Base safety case is that the repository stays dry due to self-sealing
- Brine inundation is a low-probability event that drives the potential for dissolved brine release (DBR) from the WIPP

Assumptions on the Actinide Oxidation-State Distribution in the WIPP

Oxidizing:
U(VI), Pu(IV), Np(V)

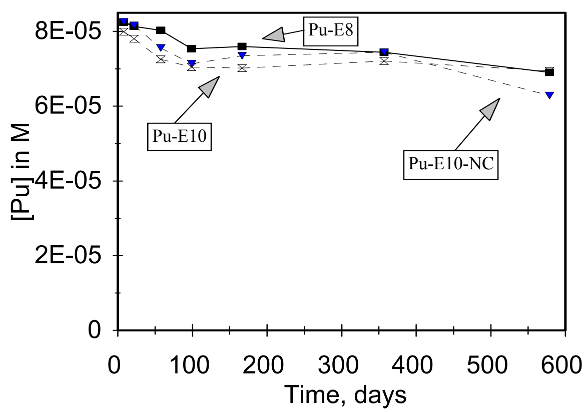
Reducing:
U(IV), Pu(III), Np(IV)

E_h independent
Th(IV), Am(III), Cm(III)

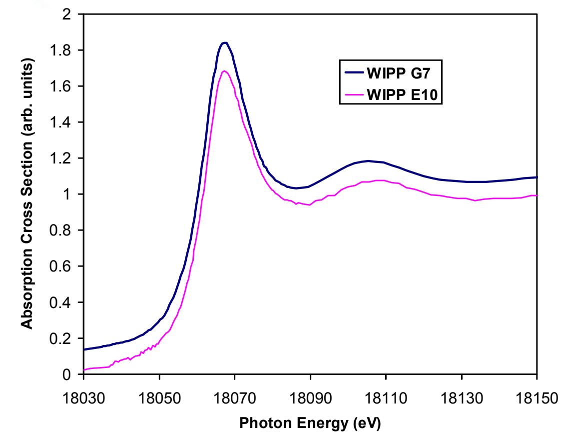
Table 2. Actinide Oxidation State Distribution Assumed in the WIPP Performance Assessment Model

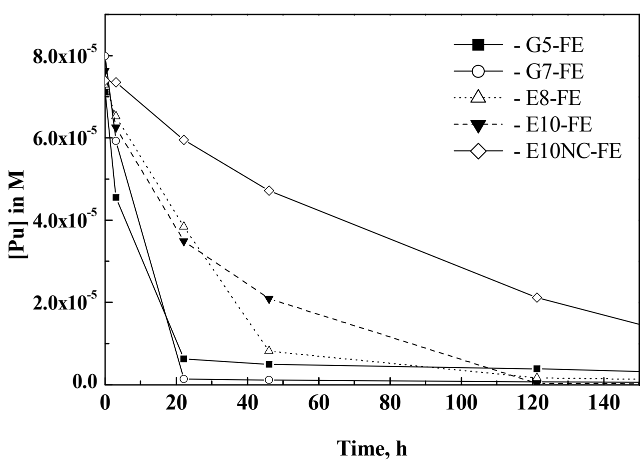
Actinide	Oxidation State				Speciation Data used in Model Predictions
	III	IV	V	VI	
Thorium		100%			Thorium
Uranium		50%		50%	Thorium for U(IV), 1 mM fixed value for U(VI)
Neptunium		50%	50%		Thorium for Np(IV), neptunium for Np(V)
Plutonium	50%	50%			Americium/neodymium for Pu(III) and thorium for Pu(IV)
Americium	100%				Americium/neodymium
Curium	100%				Americium/neodymium

Plutonium Oxidation State in Brine 1990s Experiments

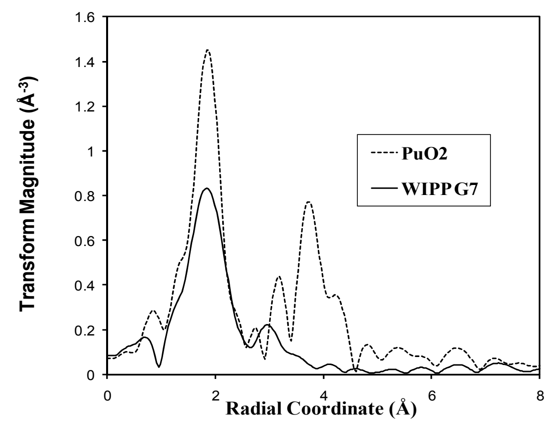


No reductant

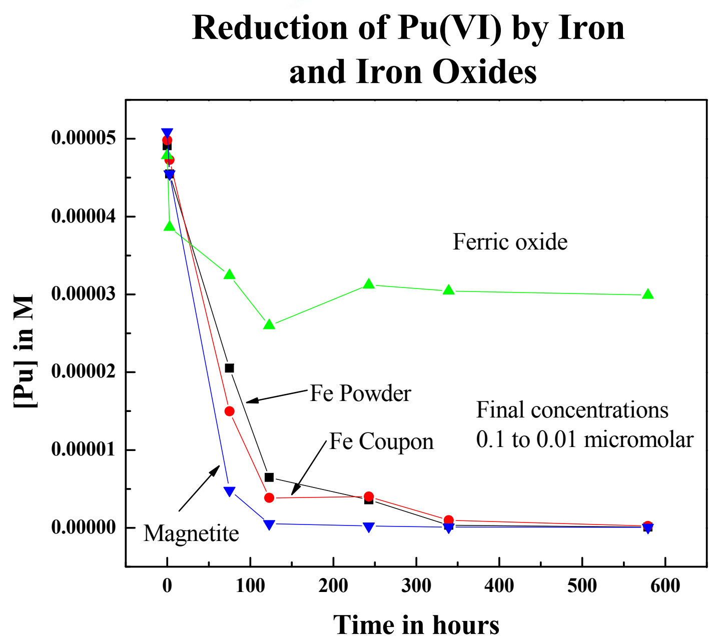


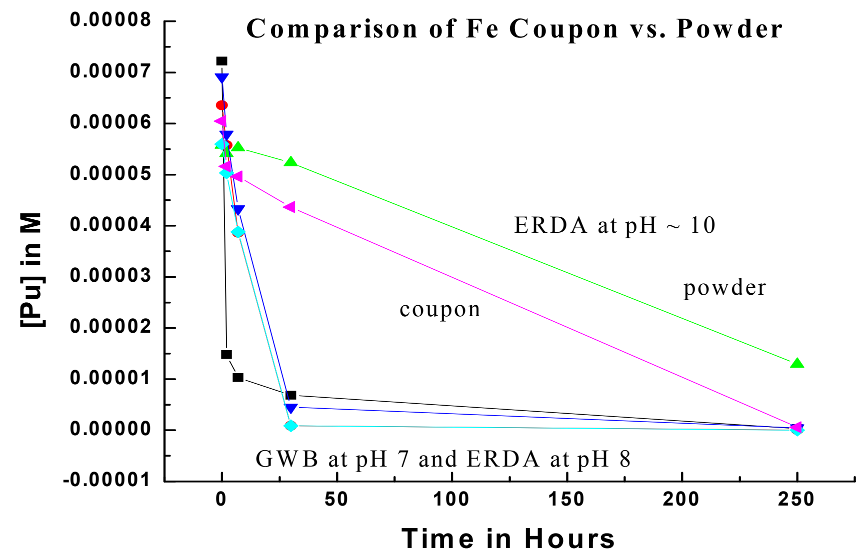


Fe Added



Plutonium Oxidation State Distribution in Brine LANL Experiments



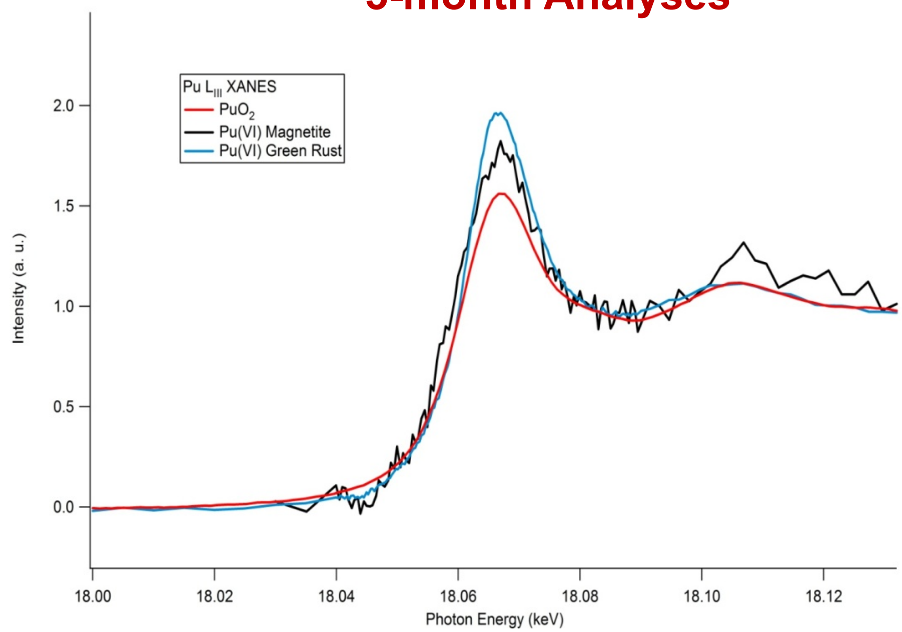


Pu(V/VI) reduction was always observed when reduced Fe, Fe(0/II), was present

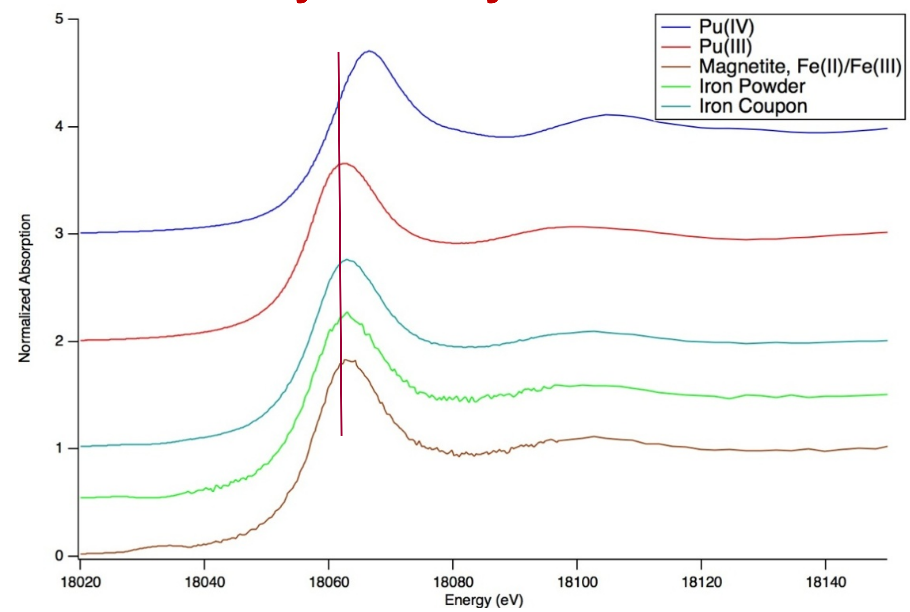
Pu(V/VI) Reduction by Lower-Valent Fe in Brine

Final Pu oxidation state is mostly Pu(III) and Pu(IV) colloid based on TTA extraction, ~ no extractable Pu(IV)

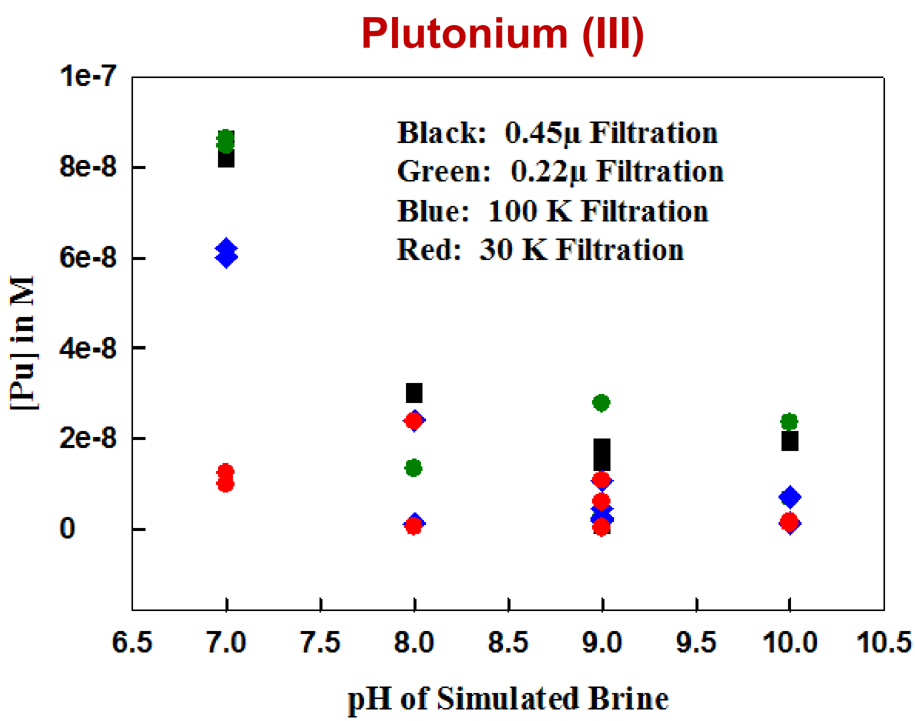
~ 3-month Analyses

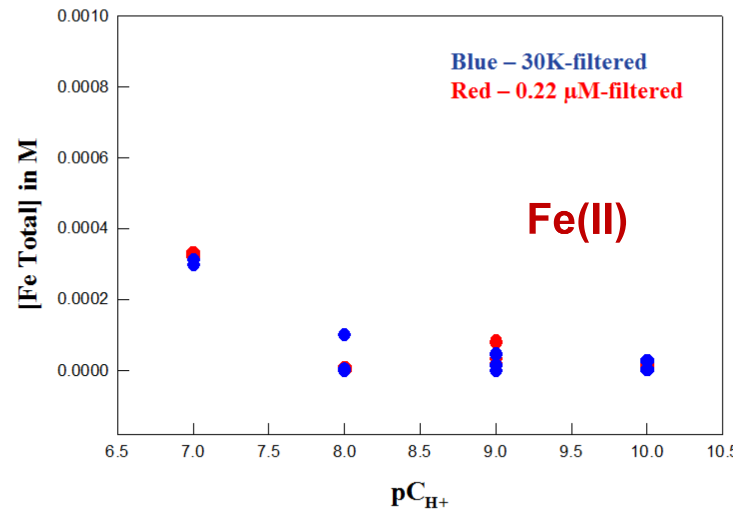


~ 6-year Analyses



Plutonium (III) Association with Iron Colloids

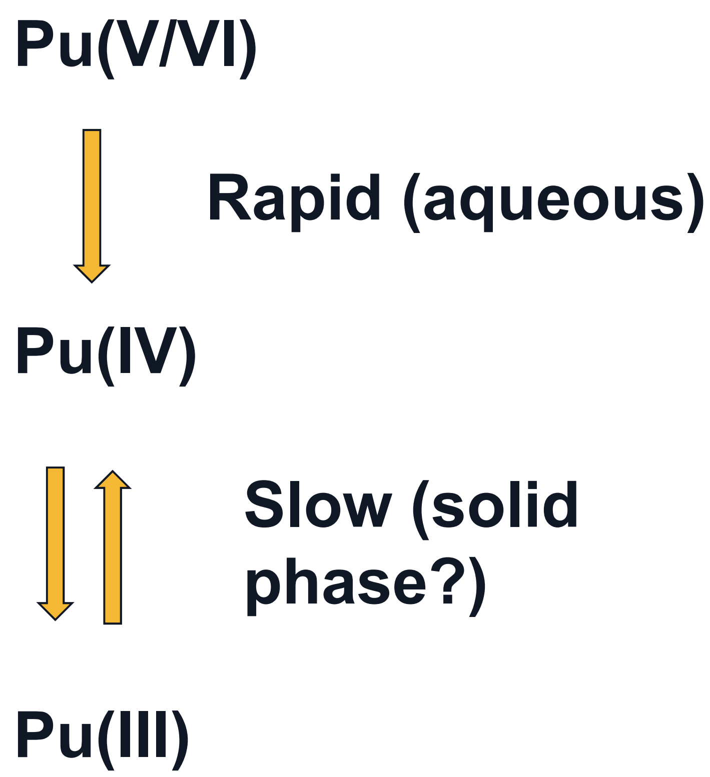




Long-term Pu studies with iron show colloidal enhancement well above the >10 nm operational definition of intrinsic plutonium colloids and correlates with the [Fe] present in solution. states

Summary: Pu Redox in the WIPP

- Reducing conditions are generated due to anoxic corrosion that leads to Fe^{2+} production
- Pu(III) predominates in solid and aqueous phase for Pu-242 and the presence of reduced iron – the long-term role of Pu(III) is not understood
- Radiolysis and the presence of organics may shift this redox to Pu(IV) even under Fe-dominated anoxic conditions (still under investigation)



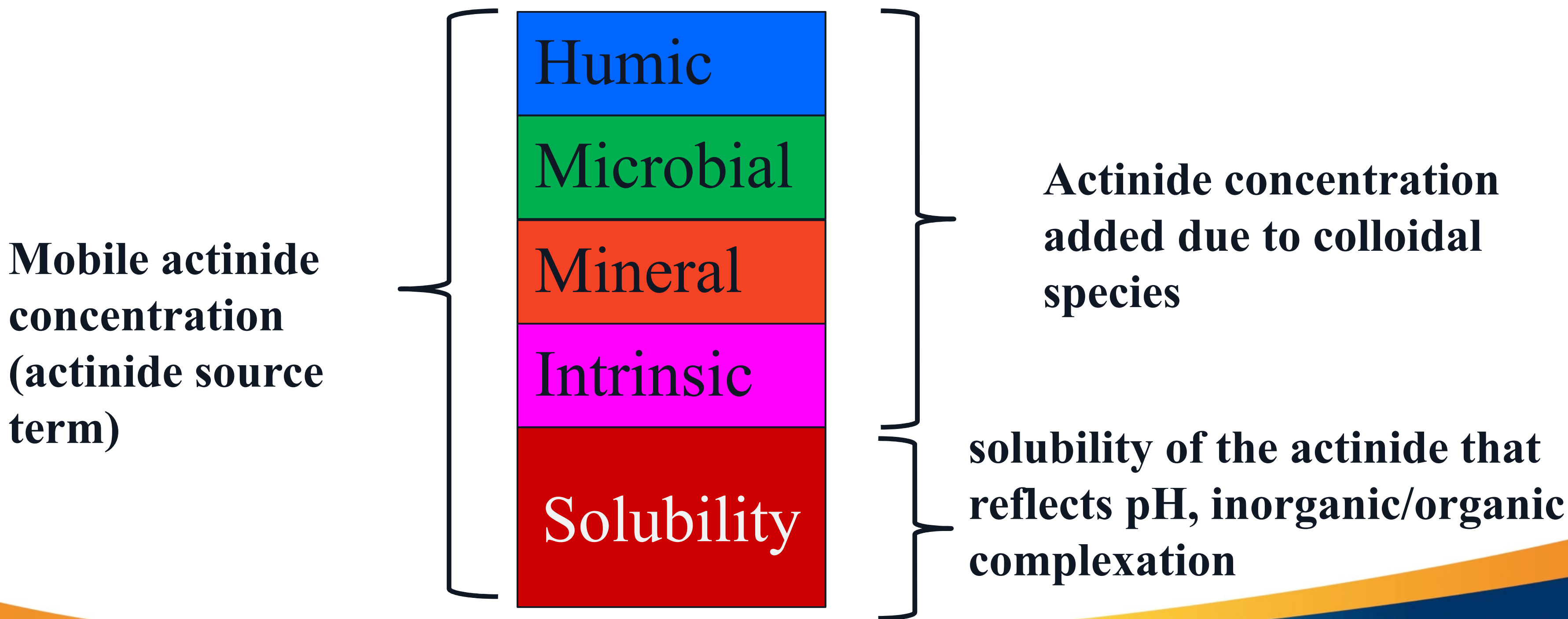
Actinide Solubility: General Approach

- Pitzer parameter approach (all brines at I> 5M)
- Use of simplified thermodynamic speciation models that can be defined as conservative
- Use of oxidation-state invariant analogs is critical to experimentally assure that the oxidation state distribution is known – this also introduces conservatisms
- Simulated brine approach to calculations and experiments (GWB and ERDA-6)
  - pH ~ 8.7 to 8.9 (corresponds to pC_{H+} = 9.2-9.4)
  - Organic complexants based on inventory – only EDTA and Citrate can affect actinide solubilities
  - Carbonate is fixed by MgO buffering, expected is ~ 10 mM maximum
- Reliance on modeling first, confirmation by experiment

WIPP Model (~1995) for the Mobile Actinide Concentration

In the WIPP concept, colloidal species contribute to the source term in dissolved brine release (DBR) release scenarios

- **Colloidal transport is not a significant issue**
- **Structure and physical properties are not important**



Completed/Ongoing LANL Actinide Solubility/Speciation Studies

An(III) Solubility Studies: Nd(III) and Am(III); Pu(III) stability

An(IV) Solubility Studies: Th(IV) and Np(IV)

An(VI) Solubility Studies: U(VI)

Colloid Studies: intrinsic colloids, mineral colloids

Microbial interactions studies: Bioreduction and Biosorption

Selected Example

Thorium Solubility Studies: Experimental Approach

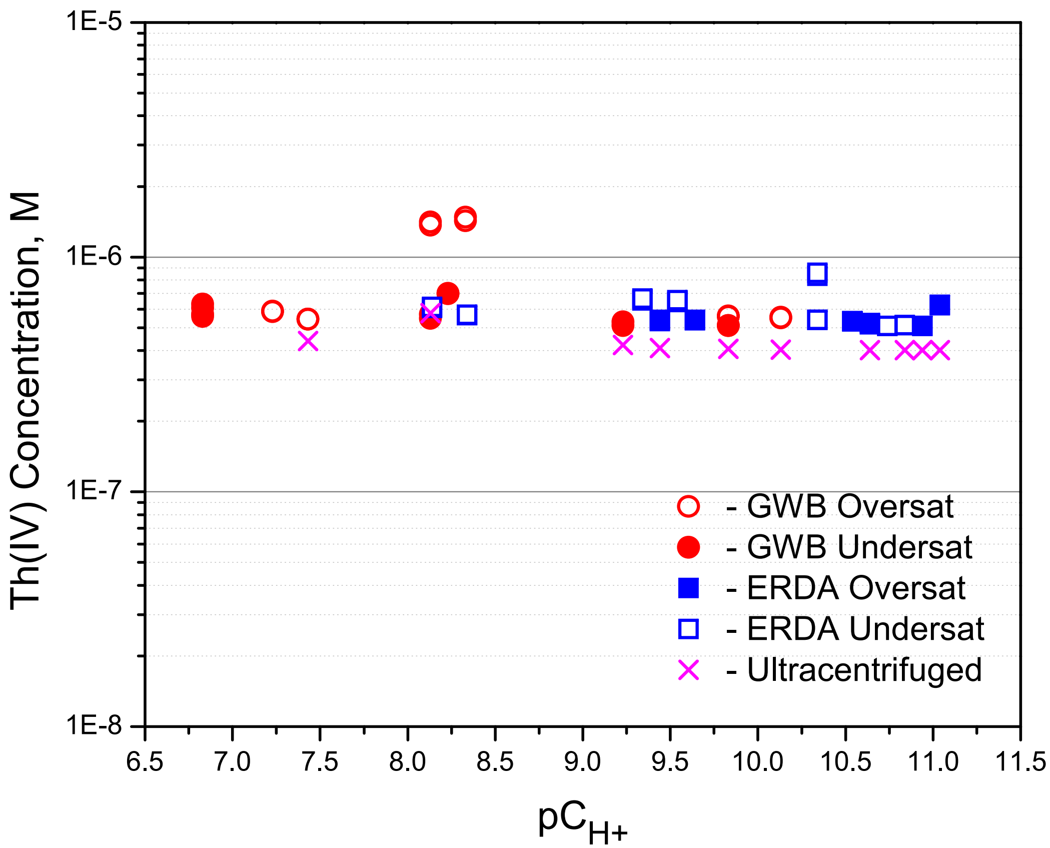
Brine Systems:

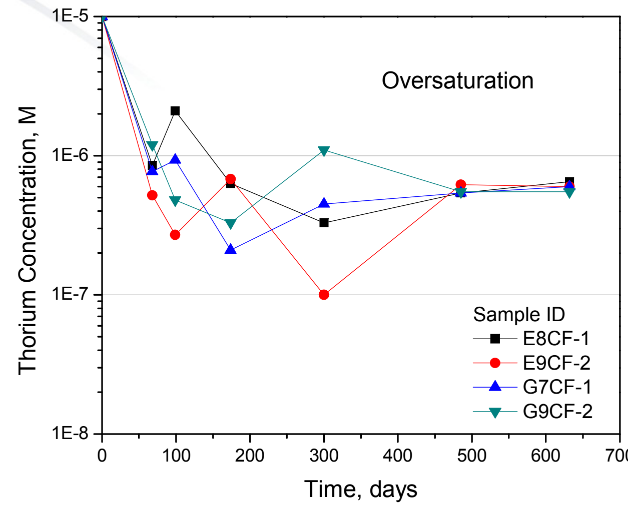
- GWB and ERDA-6 Brine – Bracketing approach
- Anoxic conditions in Glovebox
- pH range of 7-12

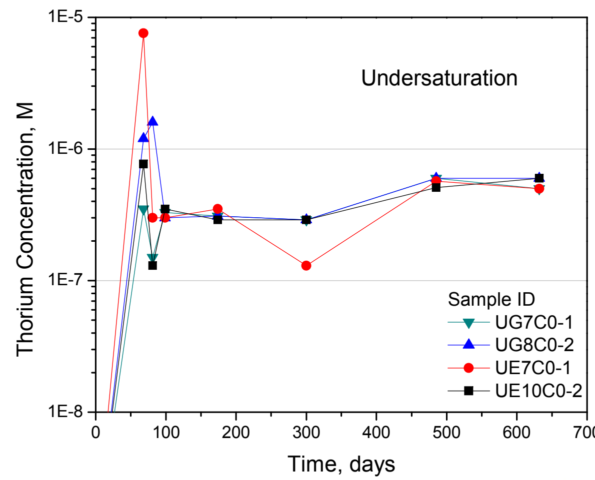
General Approach:

- Long-term (approaching 3 years) data
- Routinely filtered to 100K MWCO (~20 nm)
- ICP-MS analysis to measure concentration
- Effects of organics and carbonate evaluated

An(IV): Solubility of Thorium in WIPP

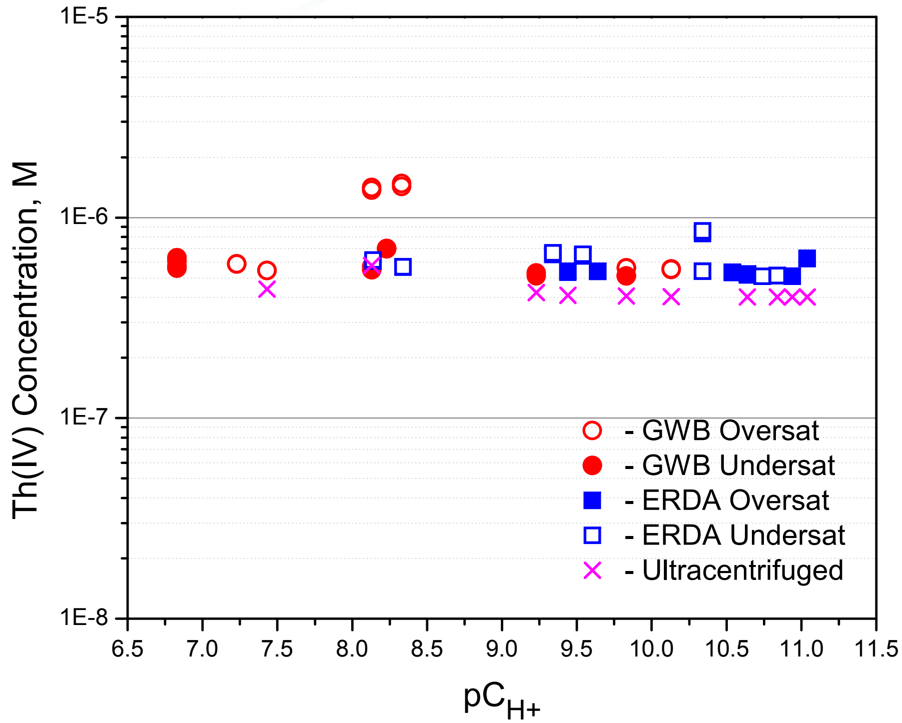




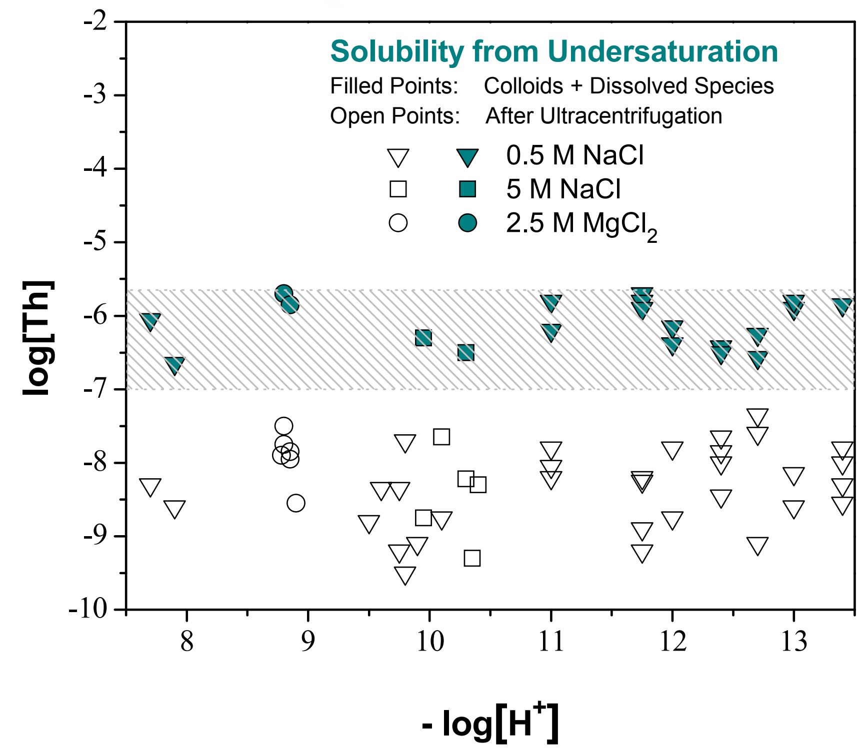


Intrinsic Colloids: Thorium Data

LANL/WIPP



INE/Germany

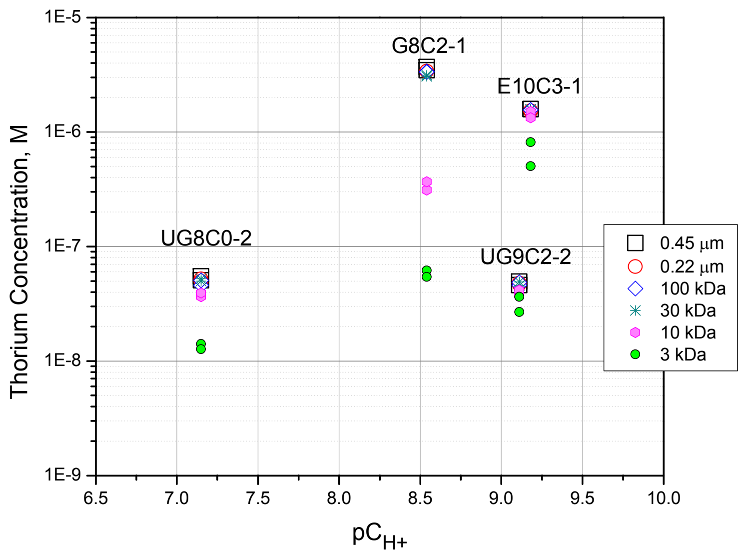


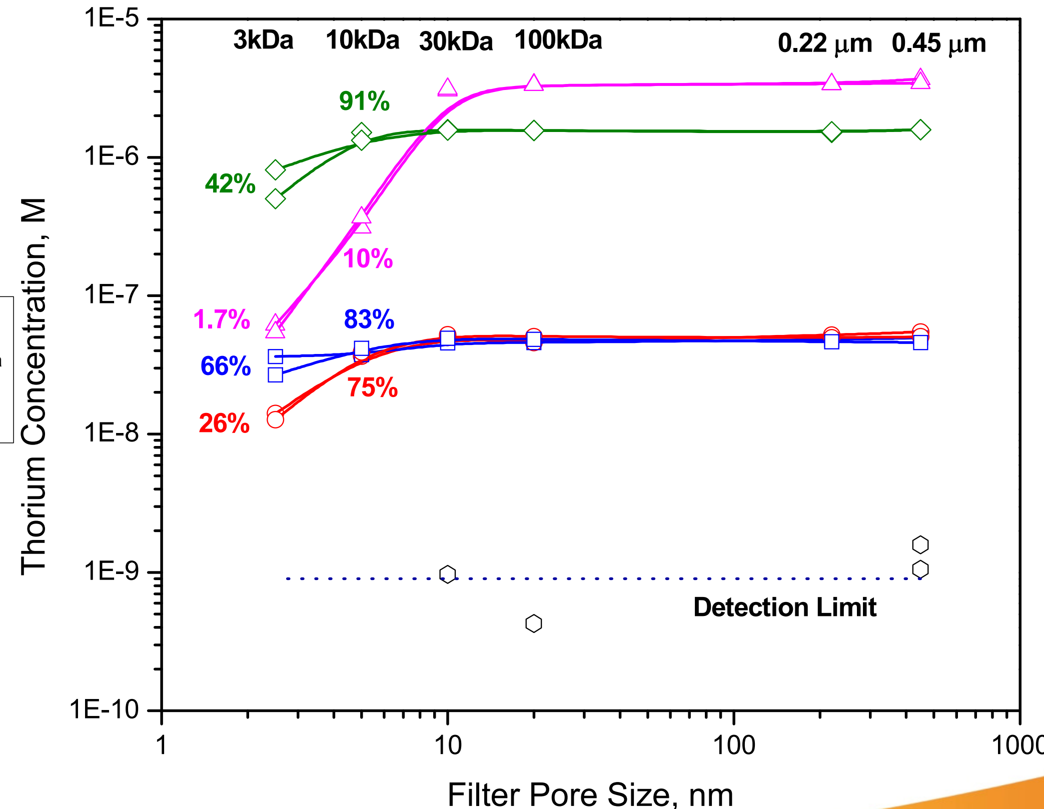
Why are these different?

1) **Brine Composition and degree of saturation – Mg colloidal content**
2) **Time – colloidal fraction decreases with time**

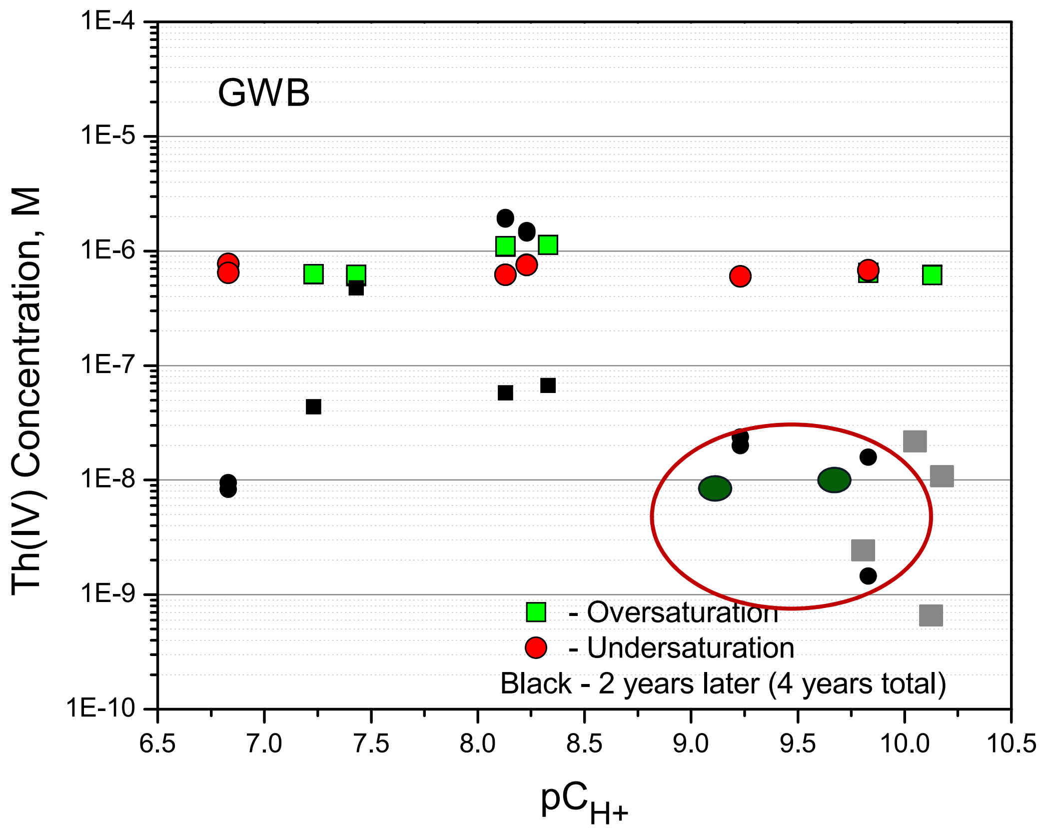
Effect of Filtration on Thorium Concentrations

~ no effect to 10 nm, 6 nm data matches ultracentrifugation results





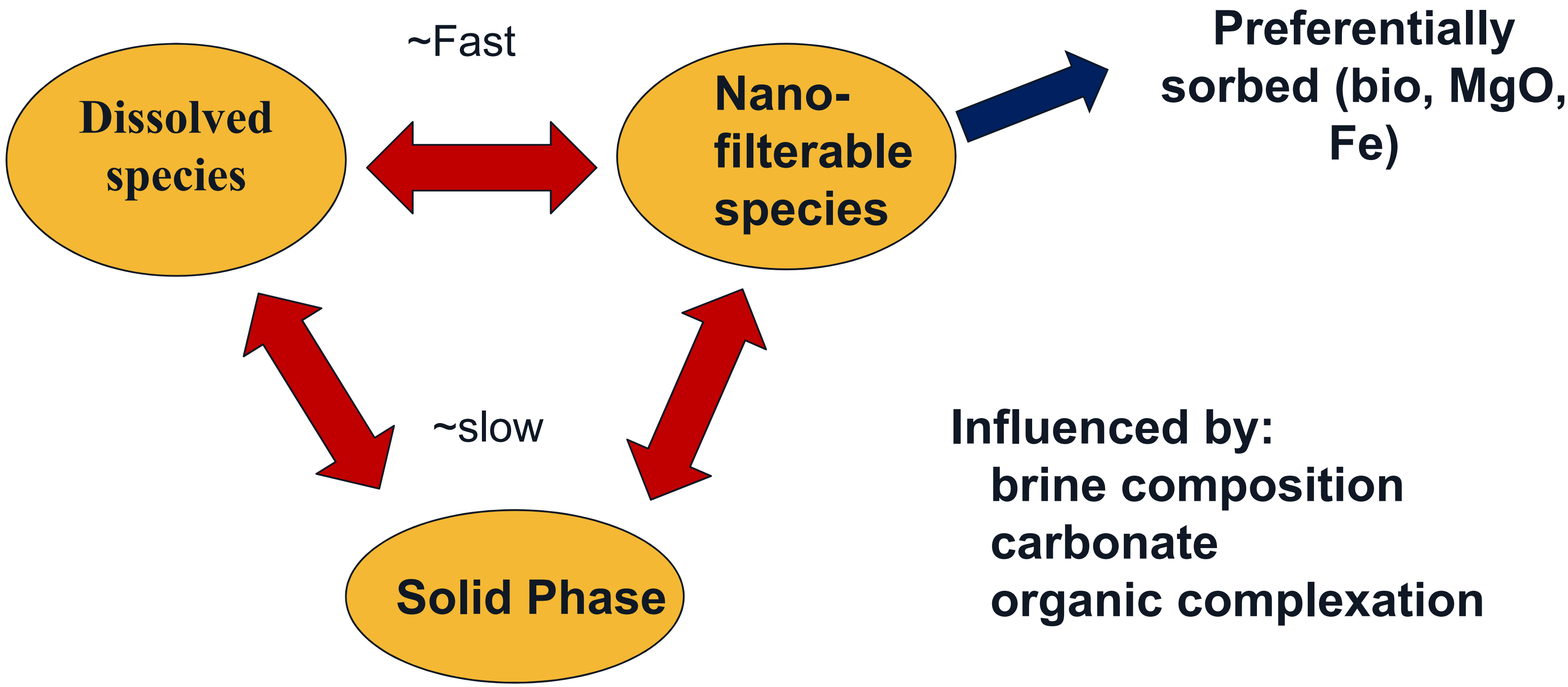
Results of Th(IV) solubility measured after 4 years of equilibration



Altmaier et al., 2004 – 5 M NaCl ultracentrifugation data

Biosorption experiments with *Chromohalobacter sp.*

Summary of Observations: Thorium Brine System



Influenced by:
- **brine composition**
- **carbonate**
- **organic complexation**

Also proposed in Altmaier, Neck, Fanghanel. Radiochimica Acta 92(9-11), 537-543 (2004).

Oxidation-State-Specific Actinide Concentrations

Calculated Actinide Solubility: Historical Trends			
Actinide Oxidation State, and Brine	CRA-2004 PABC (M)	CRA-2009 PABC (M)	CRA-2014 PA (M)
III, GWB	3.87×10^{-7}	1.66×10^{-6}	2.59×10^{-6}
III, ERDA-6	2.88×10^{-7}	1.51×10^{-6}	1.48×10^{-6}
IV, GWB	5.64×10^{-8}	5.63×10^{-8}	6.05×10^{-8}
IV, ERDA-6	6.79×10^{-8}	6.98×10^{-8}	7.02×10^{-8}
V, GWB	3.55×10^{-7}	3.90×10^{-7}	2.77×10^{-7}
V, ERDA-6	8.24×10^{-7}	8.75×10^{-7}	8.76×10^{-7}

Summary of Observations

- **WIPP, overall, continues to have success, alternative options in salt are under consideration**
- **Establishing a favorable redox environment in the near-field is critical to a successful remediation or long-term repository strategy for actinides:**
  - **Under reducing anoxic conditions higher-valent actinides are not expected to contribute to long-term subsurface migration**
  - **Lower solubility and immobility predominate**
- **WIPP addresses actinide redox through expert judgment that defined conservative oxidation-state distributions**
  - **WIPP-specific Pu-Fe interaction studies show reduced Pu oxidation states are established**
  - **Good success in showing that indigenous microorganisms impact redox in similar ways as soil bacteria – but we are not there yet**

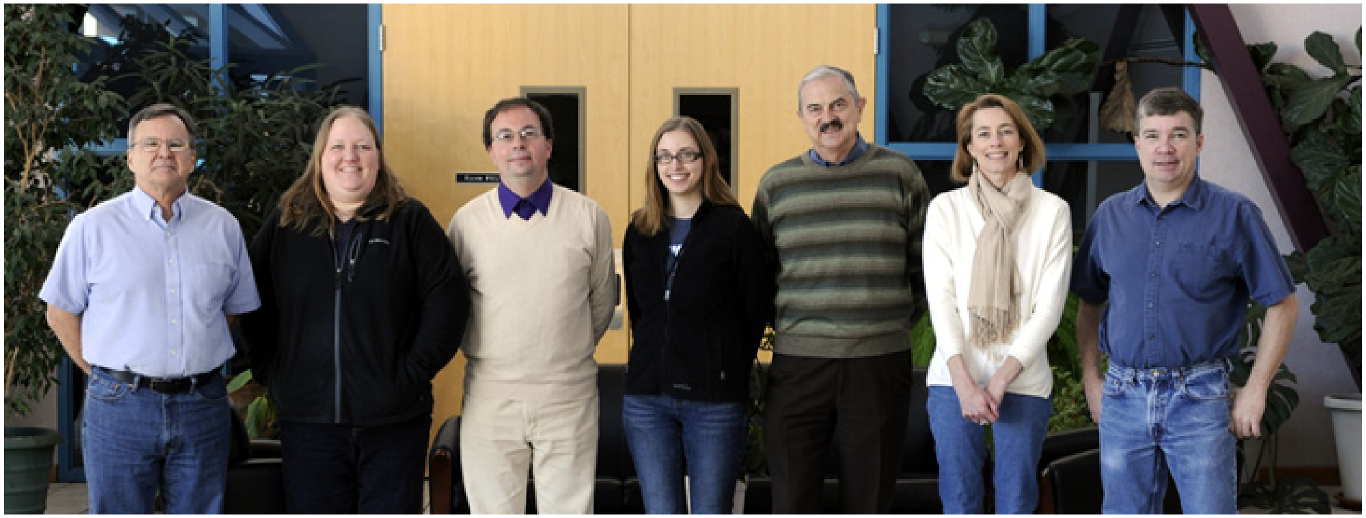
Summary of Observations – cont.

- **Correlation was observed between the Eh measurements, Fe(II/III) ratios and Pu(III/IV) ratios**
  - E_h in iron dominated system is likely meaningful
  - Need Pitzer data to properly model the system
  - Role of Pu(III) is not fully understood and is the focus of continued research
- **Measured WIPP-specific solubilities are consistent with, but slightly higher than model predictions**
  - Nd(III) solubility slightly impacted by borate, significant impact by organics
  - Th(IV) shows little colloid formation and is largely unaffected by organics, borate, carbonate and pH under WIPP conditions

Thanks for your attention

Acknowledgements

LANL
ACRSP
Team



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- Research is supported by the Waste Isolation Pilot Plant, Department of Energy, Carlsbad Field Office