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Title: Redox Chemistry of Multivalent Metals and Actinides in the WIPP

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Waste management
Reading Room
RCRA

Redox Chemistry of Multivalent Metals and Actinides in the WIPP

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Overview

- **General Comments**
  - Update on US Repository Programs
  - Redox in Groundwater
  - Actinide Speciation in the Subsurface
- **Redox Approach in the WIPP**
  - Actinides of Importance
  - Oxidation-state Distribution Assumptions
- **Redox Bio-geochemistry of Multivalent Actinides**
  - Fe-Pu Interaction Studies
  - Bio-effects on Redox
- **Summary of Observations**
- **Acknowledgements**

Current DOE Approach

TRU Repository (WIPP)

- Reliance on active controls (MgO and Fe)
- Prevalence of anoxic/reducing environment
- Self-sealing geologic isolation

DOE Site Subsurface Contamination

- Containment <u>not</u> remediation
- Reliance on natural attenuation processes
- Generally, little/no TRU mobility observed

HLW and Spent Fuel ?

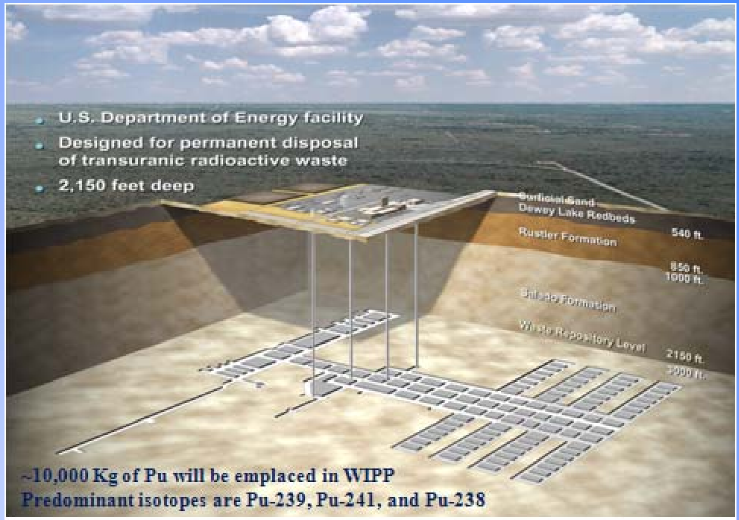
Repository Science: Actinide Chemistry

Key Concepts for the Geologic Disposal of Nuclear Waste

- Geologic isolation
- Favorable thermodynamics
  - Reducing conditions
  - Reactive redox control
- Cost is an issue

Microbial activity can influence both the near-field and far-field in repository performance

WIPP – Existing TRU Repository



HLW?

Status of US Nuclear Repository Programs

- **WIPP TRU repository work continues to move forward**
  - **2nd recertification received in November 2010**
  - **Re-configuration of conceptual model is in progress (for 2014)**
- **Blue Ribbon Panel to establish a path forward on High-level nuclear waste is in progress**
  - **Yucca Mountain Project (YMP) will probably not go forward**
  - **All repository approaches under consideration**
  - **Report/recommendations expected in June 2011**
- **State of New Mexico (where WIPP is located) has sent a letter of encouragement to the Blue Ribbon Panel to consider Southeastern NM for additional and expanded nuclear repository missions in Salt**

Possible Oxidation States for Actinides

Most likely actinide oxidation states as a function of microbial activity and the corresponding biogeochemical zone								
Biogeochemical Zone	**Actinide**							
	89 **Ac**	**90** **Th**	**91** **Pa**	**92** **U**	**93** **Np**	**94** **Pu**	**95** **Am**	**96** **Cm**
Oxidation States Observed under all Conditions	**3**	(3) **4**	(3) 4 **5**	3 4 5 **6**	3 4 **5** 6 7	3 **4** 5 6 (7)	**3** 4 5 6 7?	**3** 4 5? 6?
⇓								
Oxic Conditions in Groundwater	**3**	**4**	**5**	**6**	**5**	**4** **5**	**3** (5)	**3**
⇓								
Microbially Active Suboxic Zone	**3**	**4**	**4**	**4** **6**	**4** *5*	**3** **4**	**3**	**3**
⇓								
Microbially Active Anaerobic Zone	**3**	**4**	**4**	**4**	(3) **4**	**3** **4**	**3**	**3**
( ) = unstable, ? = claimed but unsubstantiated, **bold** = most stable								

Effect of Groundwater Interaction on Actinide Oxidation States

Prevalent Oxidation States in Groundwater				
Redox condition	**U**	**Np**	**Pu**	**Am**
Oxic	6	5	**5, 6?** **4**	3, 5?
Suboxic	6 4	4	**4** **3**	3
Anoxic	4	4	**4** **3**	3

Redox distribution of plutonium is critical and focused on lower oxidation states

- Reduced/Reactive Fe/metals
- Bioreduction
- Organic Interactions (when present)

Prevalent Oxidation States in Groundwater				
Redox condition	U	Np	Pu	Am
Oxic	6	5	5, 6? 4	3, 5?
Suboxic	6 4	4	4 3	3
Anoxic	4	4	4 3	3

Actinide Oxidation-State Distribution in the WIPP

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

Oxidation-specific Actinide Concentrations

Table 3. Oxidation-state-specific solubility of actinides in Salado (high magnesium) and Castile (high sodium chloride) brines				
	Brine	**PAVT 1999**	**PABC 2004**	**PABC 2009**
An(III)	Salado	$1.2x10^{-7}$	$3.9x10^{-7}$	$1.7x10^{-6}$
An(III)	Castile	$1.3x10^{-8}$	$2.9x10^{-7}$	$1.5x10^{-6}$
An(IV)	Salado	$1.3x10^{-8}$	$5.6x10^{-8}$	$5.6x10^{-8}$
An(IV)	Castile	$4.1x10^{-9}$	$6.8x10^{-8}$	$6.8x10^{-8}$

What are the key interactions that define the oxidation state of actinides in the subsurface?

- Reduced/Reactive Fe/metals
- Bioreduction
- Organic Interactions

Can the DOE make the case for natural attenuation as a containment strategy for actinides in the subsurface?

Can the DOE select or impose reducing conditions that will immobilize actinides in a geologic repository?

Subsurface Redox Distribution of Plutonium

Pu(V) stable under most oxic conditions

Pu(V/VI)

?

Reduced Fe
Microbial
Organics
Radiolysis
Role of colloids

Pu (III/IV)

Pu(IV)

?

Pu(III)

Long-term stability of phases? Redox cycling is key to generating high-mobility species?

Apparent disconnect between modeling and experiment

Pu Oxidation-State Distribution Experiments in Brine

General Conditions

- Variable pH (5-10), brine composition and activity
- Presence and absence of carbonate
- Anoxic with H_2 overpressure or N_2 atmosphere
- Long-term 2-5 year experiments (some ongoing
- Fe, Fe^{2+}, Fe(II) oxides
- Measurable corrosion

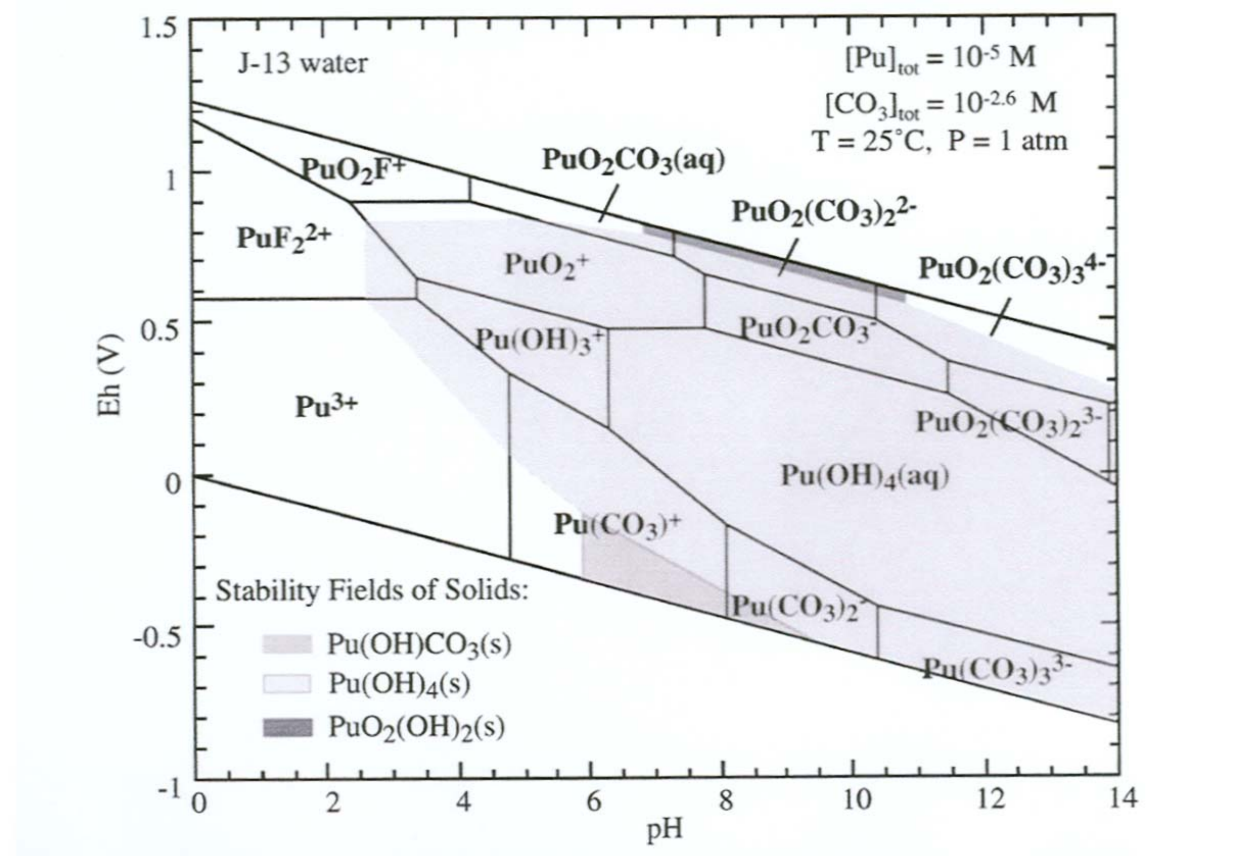
Differences:

ANL: Pu-239, once through N_2. Fe, Fe^{2+}

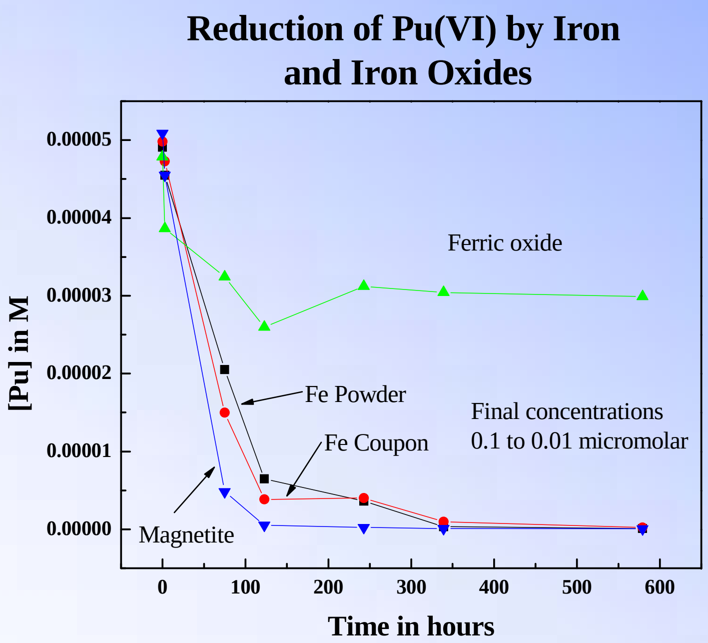
LANL: Pu-242, re-circulating 0.1 ppm O_2, Fe, powder, oxides, Fe^{2+}

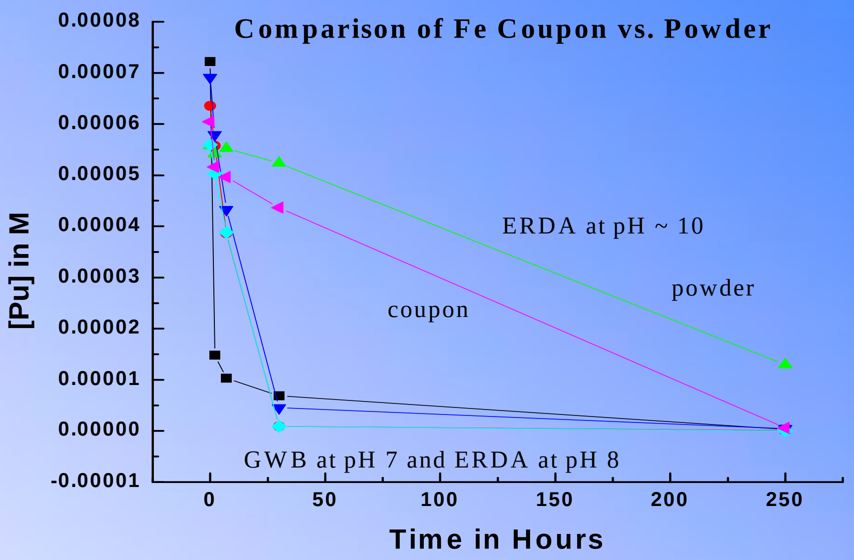
Eh-pH Diagram

Runde et. al., Low ionic strength groundwater case



Plutonium Oxidation State in Brine: ACRSP Experiments (Current/ongoing)





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

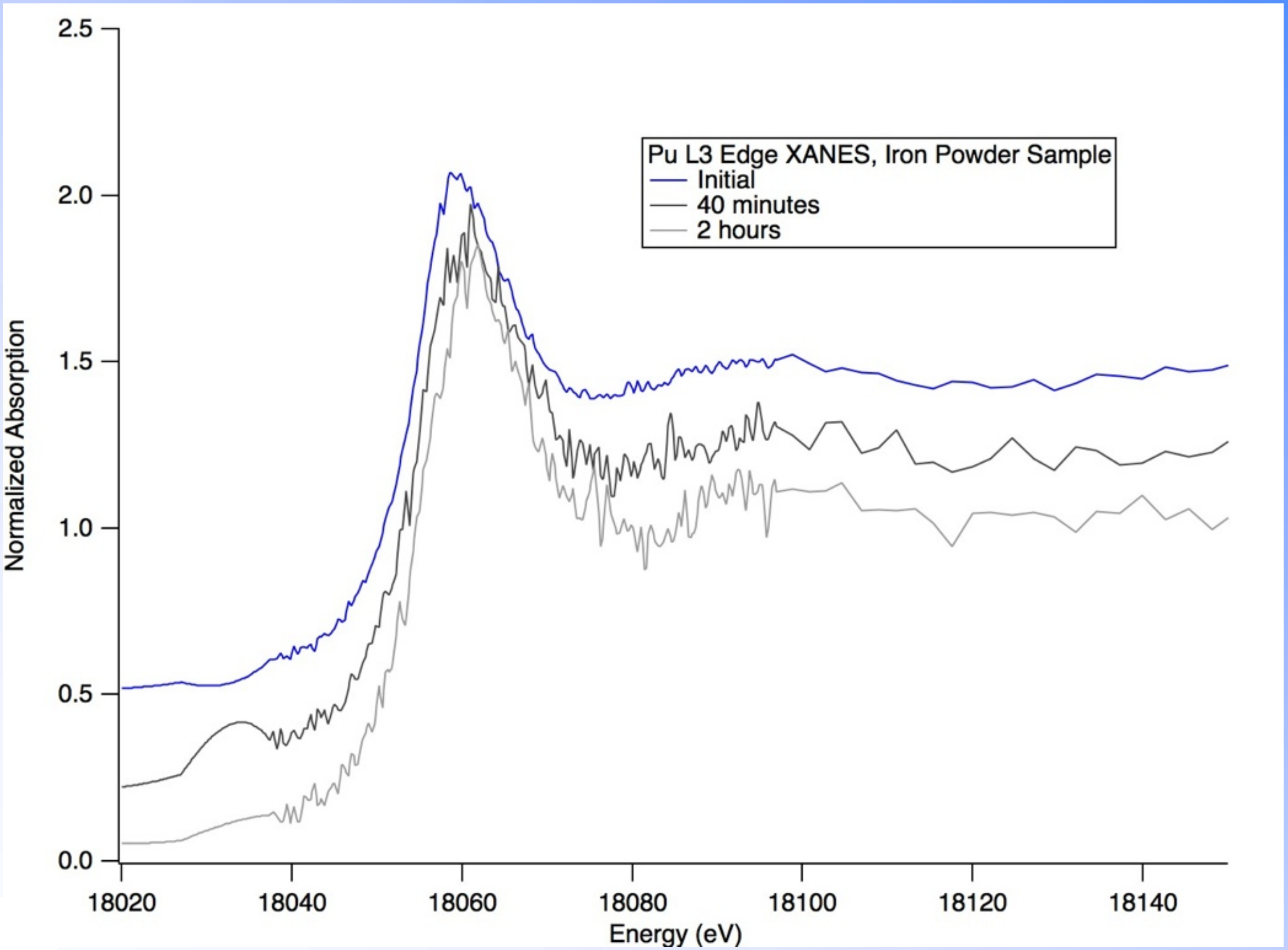
E_h, Fe (II/III) and Pu (III/IV) in Pu-Fe Studies

Table 1. Qualitative Redox Indicators for Iron Interactions with Plutonium under Anoxic Conditions

Experiment	Description	Oxidation State of Solid	$\%Fe^{2+}$ in dissolved iron	E_h Measured
PuFe23OX	ERDA-6 brine at pH ~9 with excess magnetite	~87% Pu(III), rest Pu(IV)	25	-122 mV
PuFeCE8	ERDA-6 brine at pH ~8 with Fe coupon	~100 % Pu(III)	ND	ND
PuFeCE10	ERDA-6 brine at pH ~ 10 with Fe coupon	~100% Pu(III)	100	ND
PuFeP	ERDA-6 brine at pH~9 with excess Fe powder	~100% Pu(III)	100	-175 mV
PuFeC	ERDA-6 brine at pH ~ 9 with Fe coupon	~90% Pu(III)	58	-110 mV
PuFeG7	GWB brine at pH ~7 with Fe coupon	~ 100% Pu(III)	97	-210 mV

Pu(III) content established by XANES analysis of solids
Fe(II) content established by analysis using Ferrozine [xx]
Eh measurement made using an orion xxx electrode

In-beam Oxidation of Pu(III) at the APS

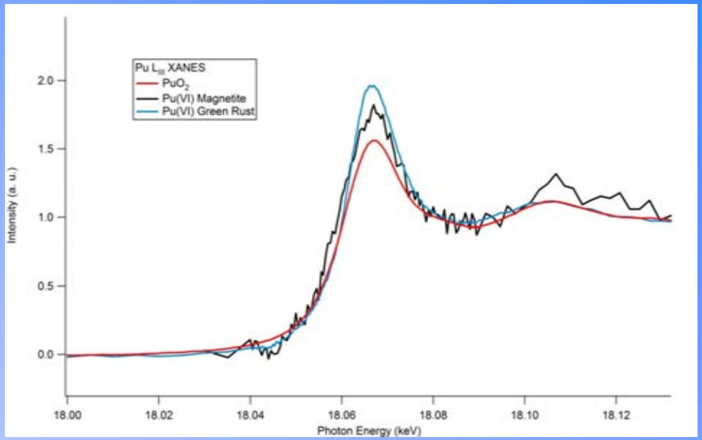


Pu(V/VI) Reduction by Lower-Valent Fe in Brine

Pu(V/VI)

Rapid (aqueous)

~ 3-month Analyses

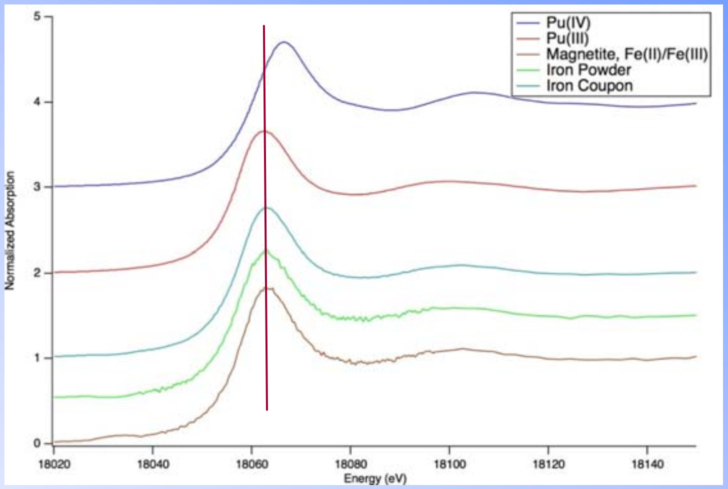


Pu(IV)

Slow (solid phase?)

Pu(III)

~ 4-year Analyses



Microbial Interactions lead to Multiple Effects on Actinide Speciation that Affect Mobility

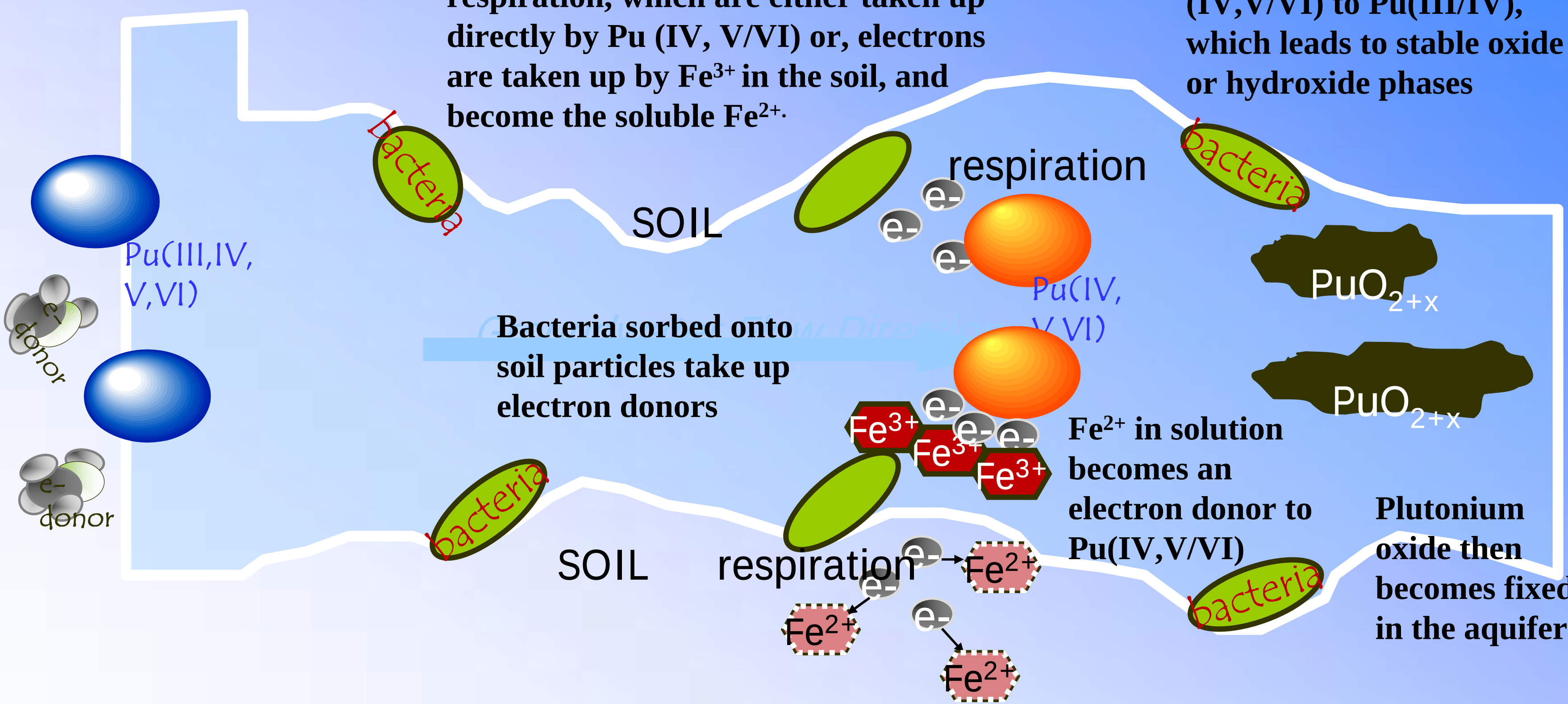
Bacteria release electrons during respiration, which are either taken up directly by Pu (IV, V/VI) or, electrons are taken up by Fe^{3+} in the soil, and become the soluble Fe^{2+}.

Both processes reduce Pu (IV,V/VI) to Pu(III/IV), which leads to stable oxide or hydroxide phases

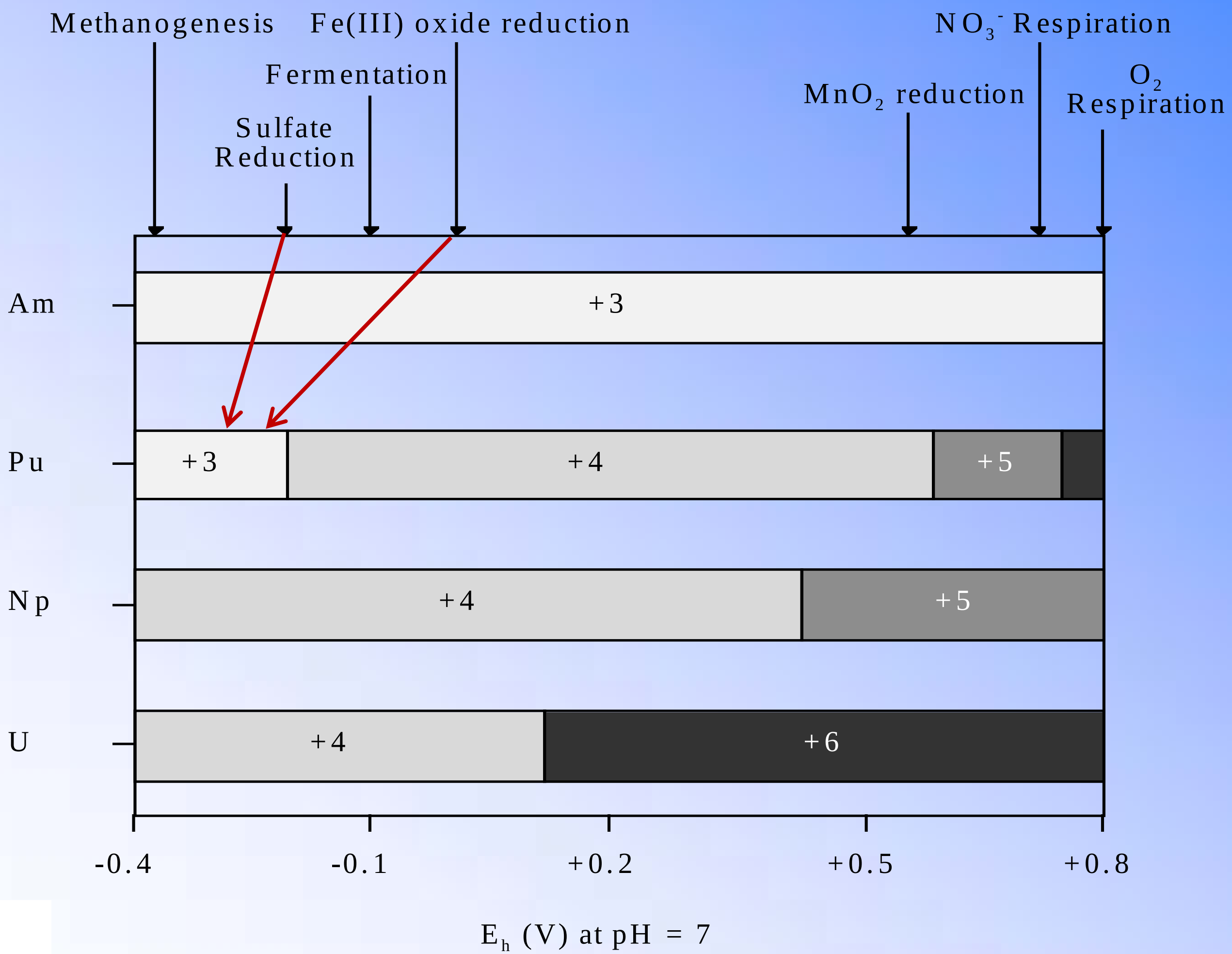
Bacteria sorbed onto soil particles take up electron donors

Fe^{2+} in solution becomes an electron donor to Pu(IV,V/VI)

Plutonium oxide then becomes fixed in the aquifer

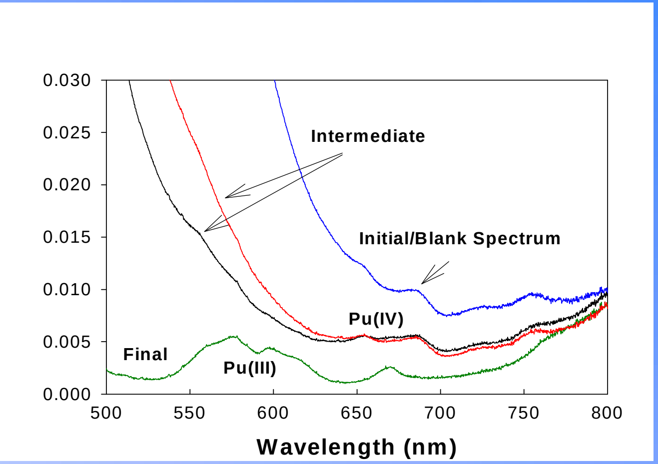


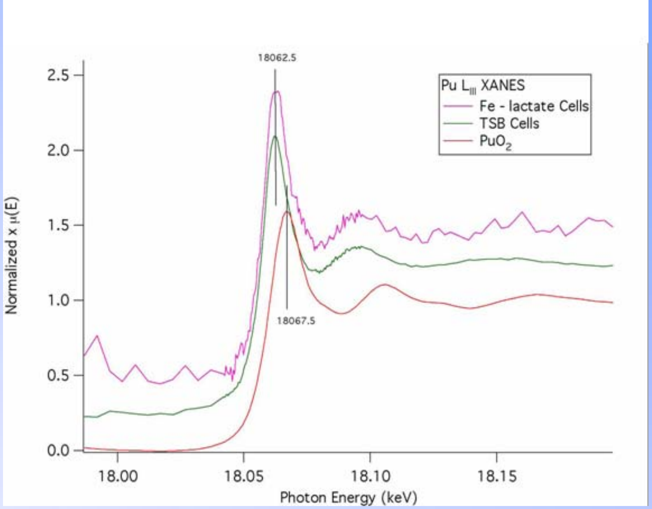
Linkage between Microbial Processes and Actinide Reduction



Bioreduction of Higher-Valent Plutonium

- Toxicity is low
- Metal reducing bacteria, under anaerobic conditions, generate Pu(III) when a solubilization mechanism exists
- Essentially no work in this area with halo-tolerant bacteria and *Archaea*





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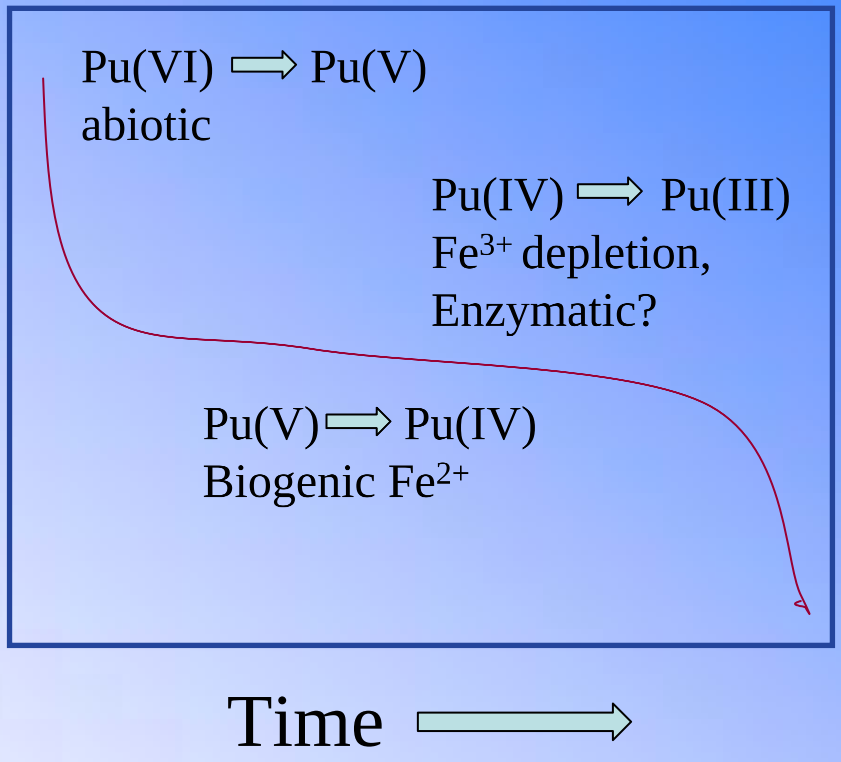
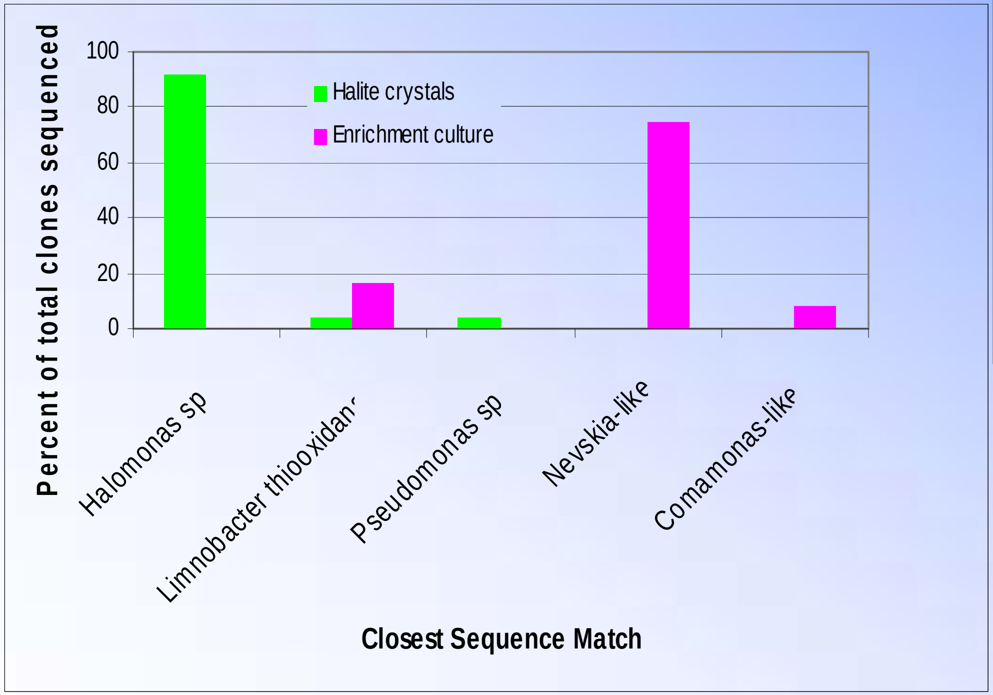
Fate of Solubilized Pu(V/VI) in Microbially-Active Anaerobic Systems

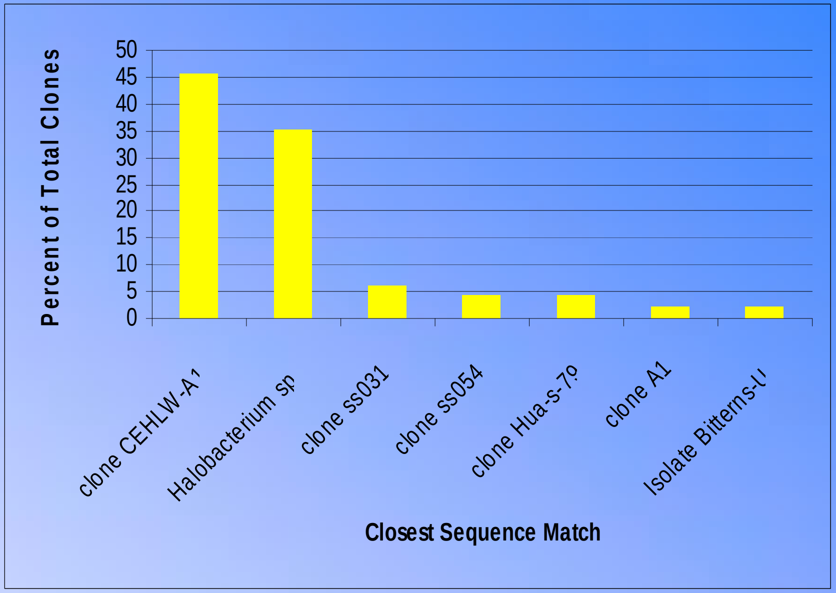
- **Pu (III) formation is observed**
  - **confirmed in solution by spectroscopy**
  - **confirmed in bio-associated material by XANES**
- ***Shewanella* can grow on Pu(IV) in the absence of Fe?**
- **Pu(III) is oxidized by most chelating agents**
- **Long-term stability of Pu(III) is unknown but it is not expected**



Indigenous Microbes in Salt/Brine Repository

Halo-tolerant bacteria

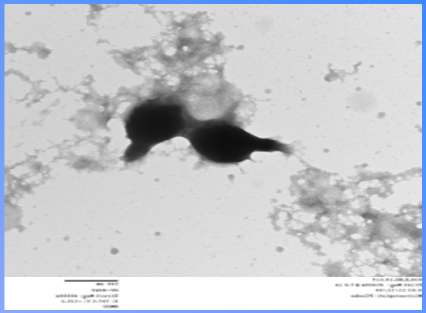




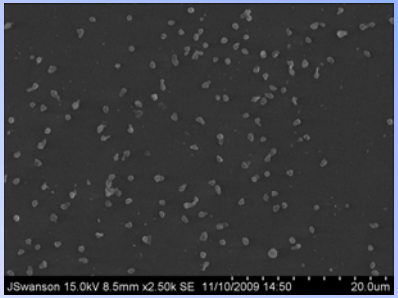
Archaea

Selection of Metal-Reducing Halo-tolerant Microbes

- Sampling of salt, groundwater and surface high-ionic strength ponds
- Long-term incubations (~6 months) to up-select microorganisms with specific functional characteristics
  - Facultative growth properties
  - Metal reduction – Fe(III) reduction
  - Biodegradation of organics
  - Sulfate reduction
  - Methanogenesis
- Identify/isolate microorganisms
- Perform biodegradation or bioreduction experiments



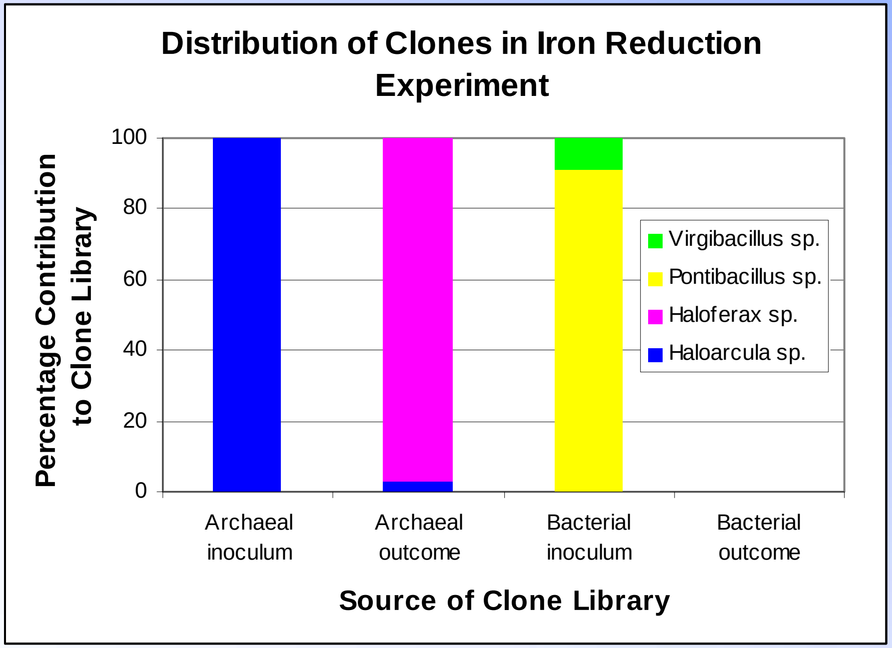
TEM image of *Halobacterium* isolate

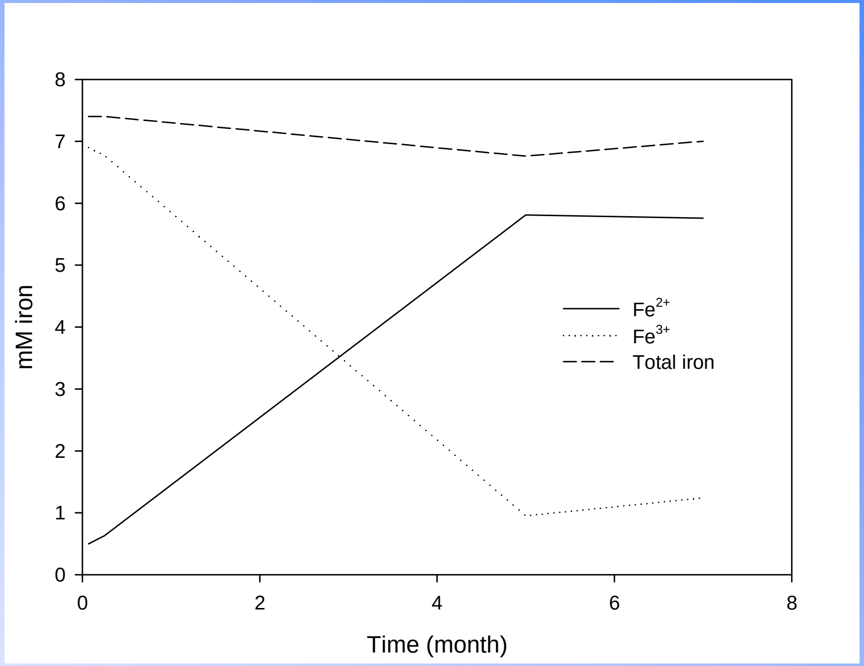


SEM image of mixed enrichment culture

Fe^{3+} Reduction by *Halophiles* and *Archaea*

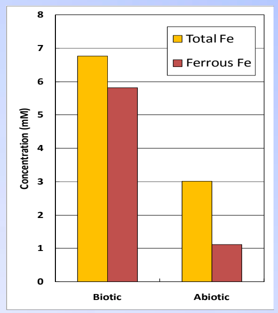
Fe^{3+} Reduction with time

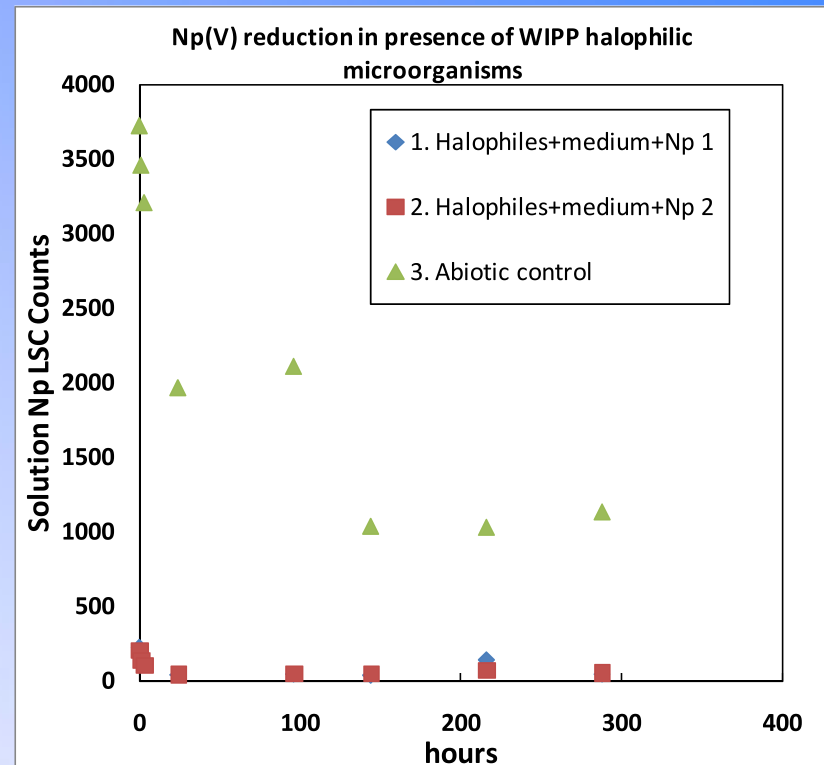




Reduction of Np(V) by halo-tolerant micro-organisms

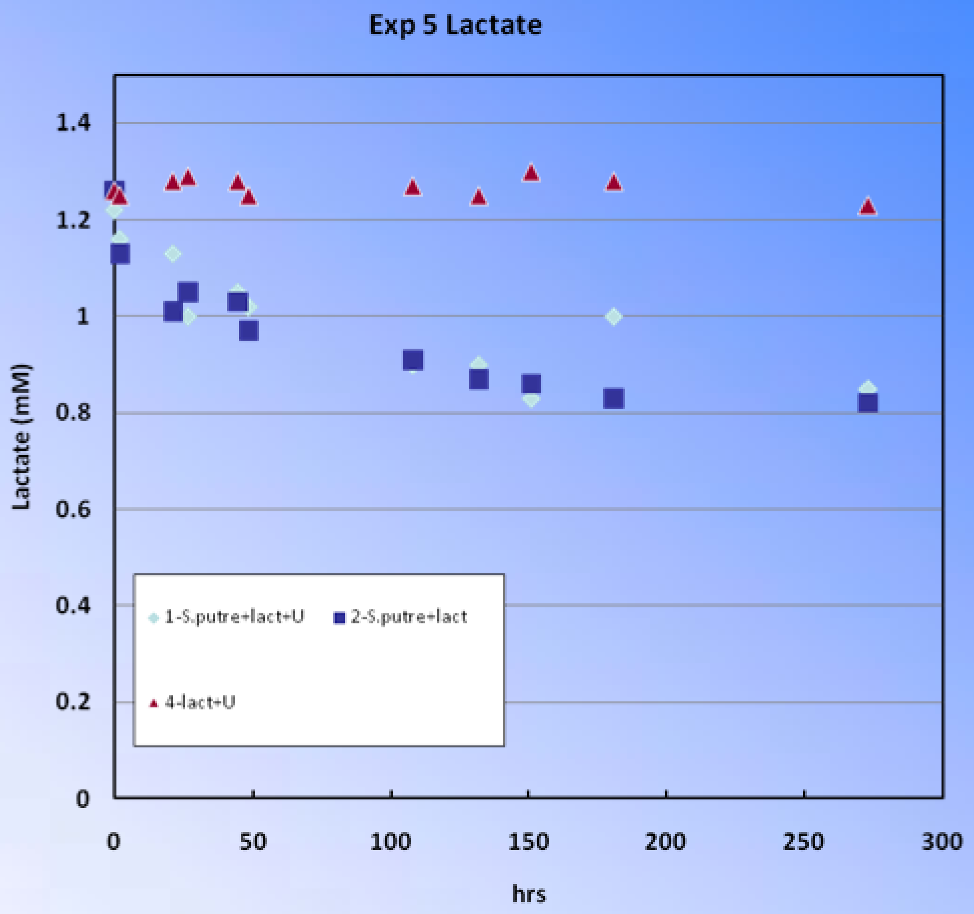
- Organisms up-selected from brine (GW) using and Fe^{3+} growth media
- 3 organisms selected, all *Archaea?*
- Iron and Np reduction observed





Bio-enhanced Reduction of U(VI) by Halophiles

- Analogous to the Np Experiments
- Slow process
- U(IV) not yet confirmed, but is expected/likely product



Summary of Observations

- **US repository program is moving forward (Fukushima?)**
- **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**

Acknowledgements

LANL ACRSP Team

- **Russ Patterson: DOE program manager for this research**
- **Carlsbad Environmental Monitoring and Research Center and operated by New Mexico State University**
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Plutonium Speciation (Altmaier/Neck – INE)