Long-term Plutonium Speciation in Fe-Dominated High Ionic-Strength Brines

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Waste Isolation Pilot Plant (WIPP) Transuranic Program

The Waste Isolation Pilot Plant (WIPP) transuranic repository remains a cornerstone of the U.S. Department of Energy's (DOE) nuclear waste management effort. Waste disposal operations began at the WIPP on March 26, 1999 but a requirement of the repository license is that the WIPP needs to be recertified every five years for its disposal operations. The WIPP has just received its second recertification in November 2010. Research by the Los Alamos Actinide Chemistry and Repository Science team [1-4] is centered on the speciation of key actinides under WIPP-specific conditions to improve the robustness of current models and quantify the conservatisms in the current assumptions being made is continuing.

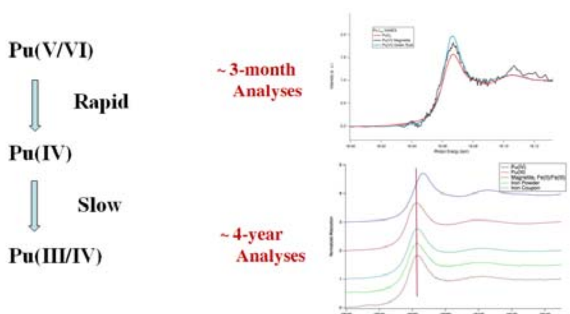
The overall ranking of actinides, from the perspective of potential contribution to release from the WIPP, is: Pu ~ Am > U >> Th and Np. The calculated oxidation-state-specific actinide solubilites over the past recertifications are tabulated in Table 1. Recently, our research emphasis has been on WIPP-specific systems in the following areas: 1) colloidal fraction of +3 and +4 actinides looking at both analog and plutonium systems, 2) redox distribution of plutonium under highly reducing iron-rich brine systems, and 3) the characterization and key interactions of halotolerant microorganisms indigeneous to the WIPP site. These data extend past understanding of WIPP-specific actinide chemistry to brine systems that more closely simulate the expected environment in the WIPP.

Experimental Approach

Plutonium Redox Chemistry in the WIPP

Under the expected conditions in the WIPP, plutonium is predicted to exist predominantly as Pu(III) and Pu(IV) species. In the performance assessment, it is assumed that Pu(IV) exists in all "oxidizing" vectors (50% of the time) and Pu(III) exists in all "reducing" vectors (also 50% of the time) – see table and notations below.

There are two redox pathways that will sustain lower plutonium oxidation states that are likely to occur in the WIPP should brine inundation occur. These are reduction of higher-valent plutonium by reduced iron (Fe(0) or Fe(II)) and indirect or direct effects of microbial activity. In the presence of reduced iron, we have shown that reduction occurs under all anoxic conditions that have been investigated. Measured E_h values between -100 mV and -250 mV are observed. Plutonium (IV) and Pu(III) are observed in both the solids present (XANES) and the aqueous phase (TTA extraction). In most cases, Pu(III) is predominant. The redox trends due to microbial effects should also facilitate the reduction of Pu(V/VI) to Pu(III/IV). This, although implied in work we have completed with U(VI) and Np(V) has not been demonstrated in high ionic strength conditions – although we are expecting to do this in the near future.



Qualitative Redox Indicators for Iron Interactions with Plutonium under Anoxic Conditions				
Experiment	Description	[a] Oxidation State of Pu Solid	[b] $[Fe]_{total}$ in mM (% Fe^{2+} in solution)	[c] E_h Measured (± 3 mV)
PuFe23OX	ERDA-6 brine at pH ~9 with excess magnetite	~87% Pu(III), rest Pu(IV)	0.12 (25%)	-122 mV
PuFeCE8	ERDA-6 brine at pH ~8 with Fe coupon	~100 % Pu(III)	ND	ND
PuFeCE10	ERDA-6 brine at pH ~ 9.6 with Fe coupon	~100% Pu(III)	0.27 (100%)	ND
PuFeP	ERDA-6 brine at pH~9 with excess Fe powder	~100% Pu(III)	0.18 (100%)	-175 mV
PuFeC	ERDA-6 brine at pH ~ 9 with Fe coupon	~90% Pu(III), rest Pu(IV)	0.18 (58%)	-110 mV
PuFeG7	GWB brine at pH ~6.7 with Fe coupon	~ 100% Pu(III)	12.62 (97%)	-210 mV

a. Pu(III) content established by XANES analysis of solids
b. Fe(II) content established by analysis using FerroZene®
c. E_h measurement made using an Orion combination ORP electrode
ND – not determined

TTA extraction confirms Pu(III) as the predominant aqueous species under most WIPP conditions (>90%) when zero valent Fe is present. 20/80 Pu(III/IV) observed for magnetite and 99% Pu(V/VI) for Fe(III) oxide.

Plutonium Solubility and Speciation in the WIPP

The solubility of plutonium is modeled using a combination of Am(III)/Nd(III) data and Th(IV) data as analogs. Current WIPP-specific calculations are shown below. The speciation of Pu(III) will be dominated by EDTA/Citrate complexation and the assumed concentration of these organic complexants defines the current predicted solubilities. This is confirmed experimentally in our Nd^{3+} studies. The solubility of thorium(IV) is not significantly affected by pH and the range of carbonate and organic complexants expected in the WIPP. Plutonium concentrations expected are however 100 to 1000 times lower in Fe dominated systems. Strong association with very fine Fe phases is there appears to be a greater tendency towards colloid formation with Pu (vs. Th). Plutonium studies are underway to further evaluate the colloidal contribution and overall solubility as a function of brine and ionic strength.

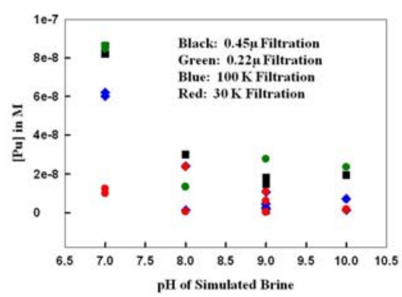
Calculated Oxidation-state-specific solubility (M) of actinides in Salado (high magnesium) and Castile (high sodium chloride) brines (Reed et. al, 2011)				
Actinide Oxidation State	Brine	[a]PAVT 1999	[b]PABC 2004	[c]PABC 2009
An(III)	Salado	$1.2x10^{-7}$	$3.9x10^{-7}$	$1.7x10^{-6}$
An(III)	Castile	$1.3x10^{-8}$	$2.9x10^{-7}$	$1.5x10^{-6}$
An(IV)	Salado	$1.3x10^{-8}$	$5.6x10^{-8}$	$5.6x10^{-8}$
An(IV)	Castile	$4.1x10^{-9}$	$6.8x10^{-8}$	$6.8x10^{-8}$

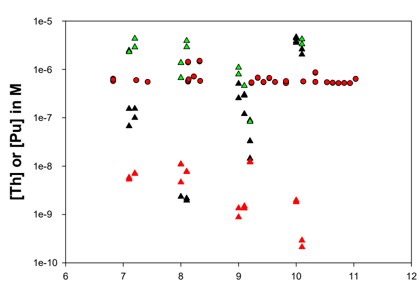
[a] Performance Assessment Verification Test - initial WIPP license application
[b] Performance Assessment Baseline Calculation - 1st recertification in 2004
[c] Performance Assessment Baseline Calculation - 2cnd recertification in 2009

PA Assumptions on Colloid Concentrations in Brine				
Actinide and Oxidation State	Concentration of Mineral Colloids	Concentration of Intrinsic Colloids	Microbial Colloids: Proportionality (moles colloid/moles dissolved actinide)	Microbial Colloids: Maximum added concentration
Pu(III)	$2.6 x 10^{-8}$ M	$1 x 10^{-9}$ M	0.3	$6.8 x 10^{-5}$ M
Am(III)	$2.6 x 10^{-8}$ M	0	3.6	1.0 M
Th(IV)	$2.6 x 10^{-8}$ M	0	3.1	0.0019 M
U(IV)	$2.6 x 10^{-8}$ M	0	0.0021	0.0021 M
Np(IV)	$2.6 x 10^{-8}$ M	0	12	0.0027 M
Pu(IV)	$2.6 x 10^{-8}$ M	$1 x 10^{-9}$ M	0.3	$6.8 x 10^{-5}$ M
Np(V)	$2.6 x 10^{-8}$ M	0	12	0.0027 M
U(VI)	$2.6 x 10^{-8}$ M	0	0.0021	0.0021 M

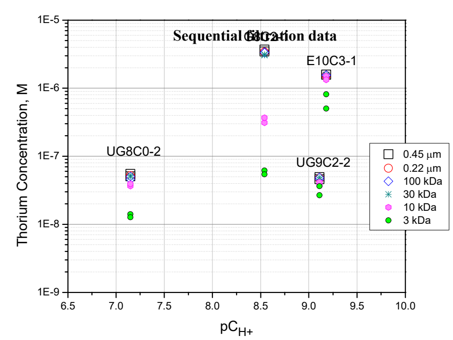
Distribution of Plutonium in long-term solubility studies

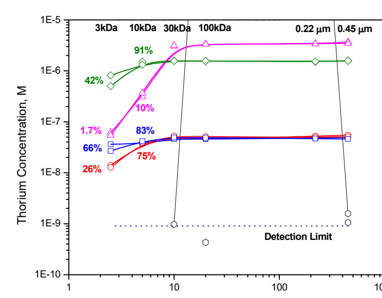
Comparison of Th (red circles) and Pu (triangles - green unfiltered, black 0.2 micron filtered, and red





Distribution of Thorium in long-term solubility studies





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