ACTINIDE SOLUBILITY AND SPECIATION IN THE WASTE ISOLATION PILOT PLANT (WIPP) REPOSITORY

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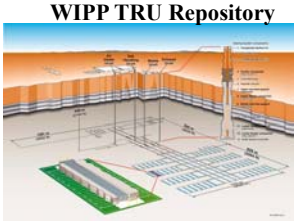
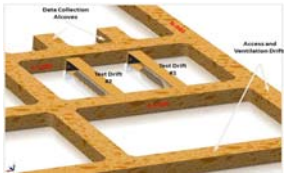
WIPP Project and Actinide Solubility

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 is now pursuing it third recertification (to be submitted in March 2014) and there are many ongoing discussion about possible expanded missions and additional nuclear repository concepts in a Salt geology.

The overall ranking of actinides, from the perspective of potential contribution to release from the WIPP, is: Pu ~ Am > U >> Th and Np and remains unchanged from past recertification. The oxidation state distribution of key multivalent actinides also remains unchanged: U – 50% U(IV) and 50% U(VI); Pu – 50% Pu(III) and 50% Pu(IV); with Am/Cm as the III oxidation state and thorium as the IV oxidation state. In this recertification cycle, thorium solubility studies in brine were completed and the PA approach to define the continuation of colloids to the actinide source term was re-examined and will be updated. These data continue to extend our understanding of high ionic-strength actinide chemistry.

WIPP TRU Repository





SDDI
Salt Defense Disposal Investigations

WIPP Status and Future Directions for Salt-based Nuclear Repositories

Status of the WIPP Project

- 12+ years of safe operation
- 21 waste storage sites in the US cleaned up
- Over 10,500 CH and ~ 600 RH shipments received
- Over 86,000m^3 of waste emplaced (~165,000 containers)
- Five panels are full, panel 6 is being filled, and panel 7 is being excavated.
- Emplaced waste will contain approximately 10,000 kg Pu and 51,000 metric tons of iron
- Second Recertification granted by the EPA in November 2010; third recertification is in progress and scheduled for 2014

Future Directions for Salt-Based Nuclear Repositories

- Blue Ribbon Commission (BRC) report was issued and supports future options for Salt-based repositories
- State of New Mexico has expressed strong support for an expanded WIPP role and additional salt-based repositories in New Mexico
- Planning is underway to establish and experimental station for thermal testing to support other repository options in salt (SDDI)

CRA-2014 Actinide Solubility

In low-probability brine inundation scenarios, brine will enter the repository and react with the waste and barrier material to solubilize the TRU in the waste. This leads to high magnesium brines (GWB is the simulation of this) at an expected pC_{H+} of 9.5 ± 1. Actinide solubility is calculated at this pC_{H+} using the Pitzer approach with EQ3/6. The current calculational results and oxidations state assumptions are shown on the right. Actinide solubility has increased somewhat over time due to better accounting for the effects of organic complexation (primarily EDTA) in WIPP waste.

WIPP Simulated Brine Composition

Ion or property*	GWB Brine Composition*	GWB after reaction with MgO (phase S), halite, and anhydrite*	ERDA-6 Brine Composition*	ERDA-6 after reaction with MgO (phase S), halite, and anhydrite*
Br^-	150 mM	186 mM	63 mM	62.3 mM
Ionic fraction (I)				
Na^+	3.53 M	4.77 M	4.87 M	5.30 M
Mg^{2+}	1.02 M	0.339 M	19 mM	136 mM
K^+	0.467 M	0.550 M	97 mM	96.0 mM
Ca^{2+}	10 mM	11.1 mM	12 mM	11.6 mM
SO_4^{2-}	177 mM	236 mM	170 mM	182 mM
Cl^-	5.86 M	5.36 M	4.8 M	5.24 M
Br	26.0 mM	31.3 mM	11 mM	10.9 mM
Total Inorganic C (as HCO_3^-)	Not reported	0.379 mM	16 mM	0.455 mM
pH	Not reported	8.82	6.17	8.99
Ionic Strength (M)	7.44	6.44	5.32	5.99

a – ions listed represent the total of all species with this ion.
b – From Snider 2003a
c – From Brush and Domski 2013a
d – From Popielak et al., 1983
e – Boron species will be present in brine as boric acid, hydroxyl polynuclear forms ($B_3(OH)_4^-$), and/or borate forms (e.g. $B(OH)_4^-$)

Actinide Solubility in Brine-Inundation Scenarios

Calculated Oxidation-Specific Solubility of Actinides in Equilibrated WIPP Brine (GWB – high Mg brine, ERDA-6 – NaCl brine) [Brush and Domski, 2013]

Actinide Oxidation State, and Brine	Actinide/ Analog Used	CRA-2004 PABC (M)	CRA-2009 PABC (M)	CRA-2014 PA (M)
III, GWB	Am/Nd	3.87×10^{-7}	1.66×10^{-6}	2.59×10^{-6}
III, ERDA-6	Am/Nd	2.88×10^{-7}	1.51×10^{-6}	1.48×10^{-6}
IV, GWB	Th	5.64×10^{-8}	5.63×10^{-8}	6.05×10^{-8}
IV, ERDA-6	Th	6.79×10^{-8}	6.98×10^{-8}	7.02×10^{-8}
V, GWB	Np	3.55×10^{-7}	3.90×10^{-7}	2.77×10^{-7}
V, ERDA-6	Np	8.24×10^{-7}	8.75×10^{-7}	8.76×10^{-7}

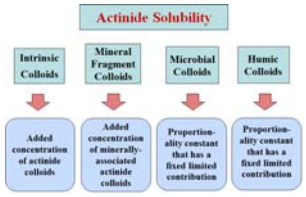
Actinide Oxidation-State Distribution

Oxidation State Distribution of Key Actinides in WIPP Performance Assessment

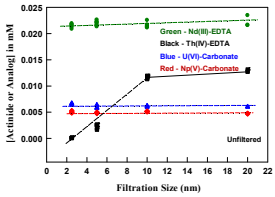
Actinide	Oxidation State				Speciation Data used in Model Predictions
	III	IV	V	VI	
Uranium		50%		50%	Thorium for U(IV), 1 mM fixed value for U(VI)
Plutonium	50%	50%			Am/Nd for Pu(III) and thorium for Pu(IV)
Americium	100%				Americium/neodymium

Intrinsic Actinide Colloids in Brine

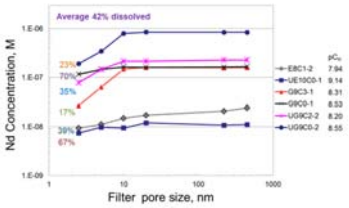
The intrinsic colloidal contribution to dissolved actinide concentrations was re-evaluated using sequential filtration of the dissolved actinides in long-term multi-year actinide solubility experiments as a function of pC_{H+} and brine composition. In almost all cases investigated, filterable species that were < 10 nm in size were observed (see Figures on the right for Nd, Pu, Th and U). These were used to develop enhancement factors that were used to estimate dissolved actinide concentrations.



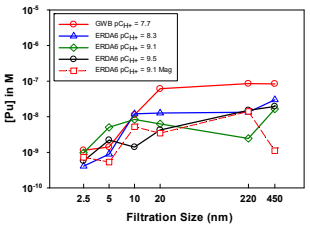
Technique demonstration: of sequential filtration



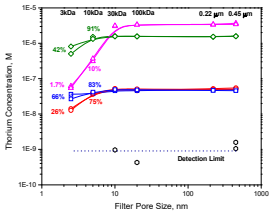
Nd (III) sequential filtration data



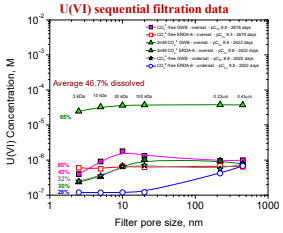
Pu(III) sequential filtration data



Th(IV) sequential filtration data

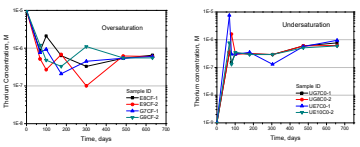


U(VI) sequential filtration data

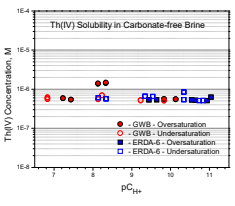


Solubility of Th(IV) in Brine

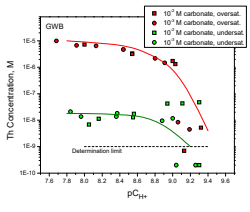
Thorium is the analog for the An(IV) oxidation state and thorium data are conservatively used to predict dissolved An(IV) concentrations. Long-term solubility studies were completed to investigate the effects of pC_{H+}, brine composition, and the presence/absence of organic chelating agents and carbonate. Key results are shown to the right. Initially, metastable and relatively high concentrations that were independent of pH were observed. In time equilibration led to a thorium solubility of ~ 10-7 M that was in good agreement with the model-predicted values. Thorium is a particularly complex system that can persist in very high concentrations as a metastable species that always has a significant colloidal contribution. Equilibration appears to be between the colloidal (nano-cluster), dissolved and solid thorium species. The prevalence of the colloidal species may be technique/approach-specific and data interpretation needs to be done carefully.

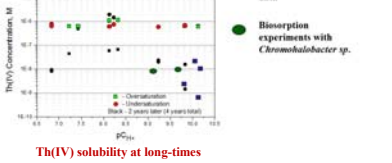


Th(IV) solubility in carbonate-free brine after ~ 2 years equilibration



Th(IV) solubility in the presence of carbonate after ~ 2 years equilibration



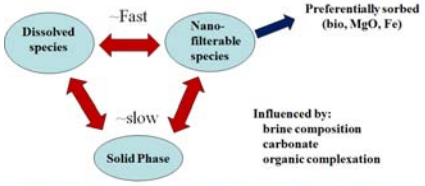


Altmaier et al., 2004 – 5 M NaCl ultracentrifugation data

Biosorption experiments with *Chromohalobacter sp.*

Th(IV) solubility at long-times

Overall Observation on the Interactions between Colloidal, Dissolved and Solid Phases in Brine Systems



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

Acknowledgements

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