BIOSORPTION OF ACTINIDES TOWARDS WIPP MICROORGANISMS

Donald Reed, Julie Swanson, Jean-Francois Lucchini, Katie Nakama, Tom Sontag, and Michael Richmann
Repository Science and Operations Program, Los Alamos National Laboratory, 1400 University Drive, Carlsbad NM USA

LA-UR 13 - 26994

Biosorption of Actinides in the WIPP

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 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 its third recertification (submitted in March 2014) and there are many ongoing discussions about the possibility of expanded missions and additional nuclear repository concepts in a salt geology.

Microbial processes have been shown to influence the long-term migration of actinides in a wide variety of subsurface environments [1]. These studies however tend to focus on the near-surface contaminant problems in low ionic-strength groundwater that is present at many DOE sites. The ongoing recertification of the WIPP TRU repository and the broader consideration of salt repository concepts for the permanent disposal of HLW/SF waste has focused attention on the effects of the halophilic microorganisms that are indigenous to salt and high ionic-strength brine systems.

A key and important actinide microbial interaction is the bioassociation of actinide species with microorganisms to form biocolloids. This interaction can potentially contribute to the "mobile" actinide source when physical transport due to intrusion scenarios is the predominant release pathway. If transport pathways are present, bioassociation can lead to reduced mobilization (e.g., if the microbe itself is not mobile) or enhanced mobilization (if the microbe or the degradation "fragments" are mobile). In the self-sealing geology of a salt repository with no interconnected groundwater, only biocolloidal contributions to the source term are considered in PA..

Herein, we report progress in investigating the bioassociation of actinides toward halophilic microorganisms to extend what has been observed in soil bacteria [2-3] to the microorganisms that are typically found in the high ionic-strength brine systems predicted for the WIPP. A number of isolates have been found and both halophilic archaea and bacteria have been identified [4]. The biosorption of actinides towards these microorganisms is being investigated using redox-invariant analogs (e.g., thorium and neodymium) or actinides that can be stabilized in specific oxidation states (e.g., Am^{3+} or NpO_2^{+}) since the biosorption observed is specific to the oxidation state of the actinide and the its aqueous speciation. These data are used to define the biocolloid enhancement factors which are used in WIPP PA.

Experimental Approach: Biosorption Experiments

Overall Approach

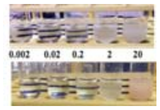
- **Simulated WIPP brine, with simplified brine (sodium perchlorate or chloride) with some variability in ionic strengths**
- **Same-pH mixing of actinide/metal and microorganism (OD_{600} check)**
- **Pre-filtration of actinide/analog to differentiate colloidal contribution (if possible)**
- **~ 1-2 hour experiment duration under constant mixing**
- **ICP-MS analysis of metal after 100K Da (~ 20 nm) filtration (Amicon ultrafilters)**
- **Followup analysis to confirm oxidation state and status of microbes**
- **Reversibility, kinetics and viability/toxicity checks**

WIPP Simulated Brine Composition

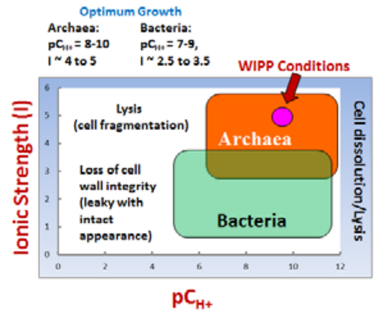
Ion or property[a]	GWB Brine Composition[b]	GWB after reaction with MgO (phase 5), halite, and anhydrite[c]	ERDA-6 Brine Composition[d]	ERDA-6 after reaction with MgO (phase 5), halite, and anhydrite[c]
$B(OH)_x^{3-x}$ (see footnote f)	158 mM	186 mM	63 mM	62.3 mM
Na^{+}	3.53 M	4.77 M	4.87 M	5.30 M
Mg^{2+}	1.02 M	0.330 M	19 mM	136 mM
K^{+}	0.467 M	0.550 M	97 mM	96.0 mM
Ca^{2+}	14 mM	11.1 mM	12 mM	11.6 mM
SO_4^{2-}	177 mM	216 mM	170 mM	182 mM
Cl^{-}	5.86 M	5.36 M	4.8 M	5.24 M
Br^{-}	26.6 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 Propielak et al., 1983
f – Boron species will be present in brine as boric acid, hydroxyl polynuclear forms ($B_3O_3(OH)_4^-$, and/or borate forms (e.g. $B_4O_7^-$)

Bacteria
***Chromohalobacter* sp.**
isolated from area ground-water, borehole seep, WIPP and Gorleben halites; strain used tolerates pC_{H+} 5-9, 0.9-4.3 M NaCl; 0.3-0.5 x 1.5-2 µm size

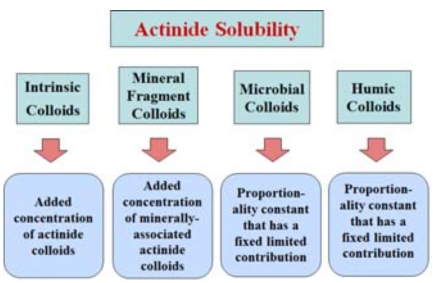


Archaea
Halobacterium noricense
isolated from incubations of halite in generic media and in WIPP brines; detected in other subterranean salts worldwide (including Germany); requires 2.5-5 M NaCl, tolerates pC_{H+} 6-10; 0.3-1.5 x 0.3-1.5 µm size



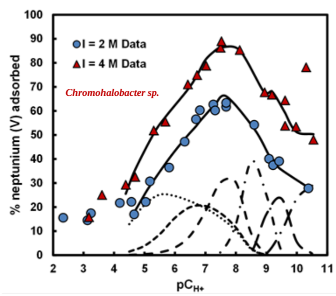
Actinide Biocolloids in Brine

The biocolloidal contribution to dissolved actinide concentrations was re-evaluated using WIPP-indigenous microorganisms as a function of pC_{H+} and brine composition. In almost all cases investigated biosorption was observed although these were often coupled with precipitation at high pH. Estimated biosorption effects were used to develop enhancement factors to determine the biocolloidal contribution to the mobile actinide concentration source term.

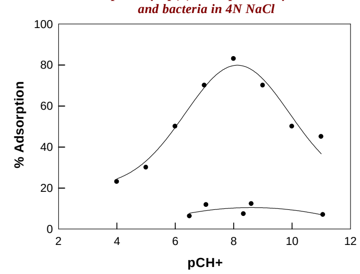


Model/Developmental Study: Biosorption of Np(V)

Np(V) was used as a model/developmental system since it does not readily hydrolyze and micro-molar concentrations are stable towards precipitation across the pH range of interest.



Biosorption of Np(V): Comparison of archaea and bacteria in 4N NaCl

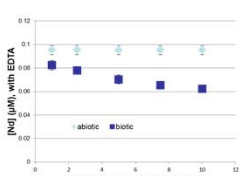


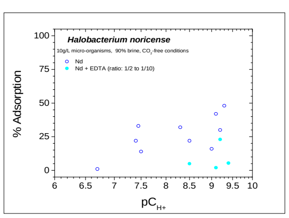
- **For *Chromohalobacter sp.*, titration data at 2 and 4 M have the same shape and are similar what is seen with other organisms at low ionic strength - best-fit model invokes 4 surface complexation sites (as with soil bacteria)**
  - **Differences observed in sorption at 2 and 4M over pC_{H+} range**
  - **Model invoking carbonate complexation reactions fits best at higher pC_{H+}**
- **For *Halobacterium noricense*, much lower sorption was noted for the same biomass that likely reflects a different functional group distribution than observed for the bacteria**

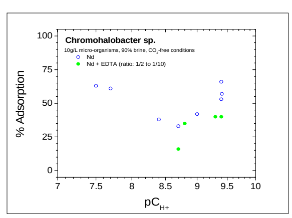
Biosorption of Nd^{3+} and Th^{4+}

Thorium and neodymium were used as the redox-invariant analogs for the An(IV) and An(III) oxidation state to avoid surface moderated redox changes in the biosorption experiments.

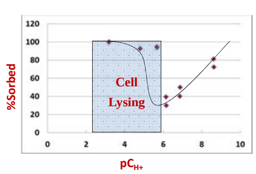
Nd^{3+}

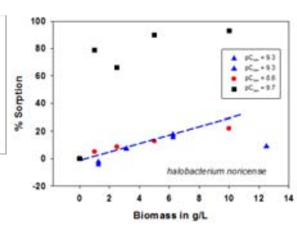


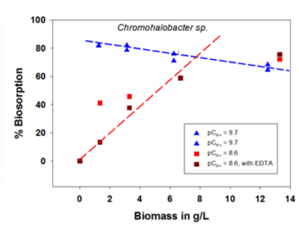




Th^{4+}







Summary of Observations: Nd and Th Results

- Np(V) – at 5 g/L
  - *Archaea*: ~ 10% sorption
  - *Bacteria*: 70-85% sorption
- Nd(III) – at 10 g/L
  - *Archaea*: ~ 25% sorption
  - *Bacteria*: 50-65% sorption
  - EDTA reduced sorption in both cases by ~ 40%
- Th(IV) – at 10 g/L
  - *Archaea*: ~ 10-20% (no EDTA) and ~0% (EDTA) sorption
  - *Bacteria*: ~ 80% (no EDTA) and 57% (EDTA) sorption
  - At $pC_{H+} > 9$, cannot differentiate between sorption and precipitation, due to colloids and "induced" precipitation

References:

[1] D.T. Reed, R. Deo, and B.E. Rittmann. (2010). "Subsurface Interactions of Actinide Species and Microorganisms," Chapter 33 in The Chemistry of the Actinide and Transactinide Elements, 3rd edition, L.R. Morss, N.M. Edelstein and J. Fuger eds., Springer Press, Netherlands.
[2] R.P. Deo, W. Songkasiri, B.E. Rittmann, and D.T. Reed (2010). "Surface Complexation of Neptunium (V) onto Whole Cells and Cell Components of *Shewanella alga*: Modeling and Experimental Study," *Env. Sci. and Tech.*, vol. 44: 4930-4935.
[3] W. Songkasiri, D.T. Reed and B.E. Rittmann (2002). "Bio-sorption of Neptunium (V) by *Pseudomonas fluorescens*," *Radiochimica Acta*, vol. 90: 785-789.
[4] J. S. Swanson, D. T. Reed, D. A. Ams, D. Norden, and K. A. Simmons (2012). "Status Report on the Microbial Characterization of Halite and Groundwater Samples from the WIPP," Los Alamos National Laboratory Report, LA-UR-12-22824.
[5] D. A. Ams, J. S. Swanson, J.E. S. Szymanowski, J. B. Fein, M. Richmann, and D. T. Reed (2013). "The Effect of High Ionic Strength on Neptunium (V) Adsorption to a Halophilic Bacterium," *Geochimica et Comoschimica Acta*, vol. 110: 45-57.
[6] V. Neck, Th. Fanghänel, G. Rudolph and J.I. Kim (1995). "Thermodynamics of Neptunium(V) in Concentrated Salt Solutions: Chloride Complexation and Ion Interaction (Pitzer) Parameters for the NpO_2^+ Ion," *Radiochimica Acta*, vol. 69: 39-47.
[7] Th. Fanghänel, V. Neck, and J.I. Kim (1995). "Thermodynamics of Neptunium(V) in Concentrated Salt Solutions: II. Ion Interaction (Pitzer) Parameters for Np(V) Hydrolysis Species and Carbonate Complexes," *Radiochimica Acta*, vol. 69: 169-176.

Acknowledgements

This research was performed by the Actinide Chemistry and Repository Science Team (Los Alamos, Repository Science and Operations Program) at the Carlsbad Environmental Monitoring and Research Center (operated by New Mexico State University). Research was funded by the Waste Isolation Pilot Plant, Department of Energy, Carlsbad Field Office (Russ Patterson program manager).