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Intrinsic, Mineral and Microbial Colloid Enhancement Parameters for the WIPP Actinide Source Term

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EXECUTIVE SUMMARY

The mineral, intrinsic and microbial contribution to the WIPP mobile colloidal actinide source term model was re-examined in light of recent literature results and new WIPP-specific data. The potential for colloidal species to have a role in defining the solution concentration and mobility of actinides in the WIPP was recognized early in the WIPP licensing process. This led to the development of a colloid model that accounts for these colloidal species. This model was based on an extensive literature review, some WIPP-specific experimental data, and some conservative simplifications that were extensively peer reviewed prior to the first license application (CCA). In this model, four types of colloids that could contribute to the actinide source term are identified: intrinsic, mineral, microbial and humic. The EPA found this model and approach to be satisfactory in the WIPP certification and subsequently in the CRA-2004 and CRA-2009 recertification. There has been essentially no change in this model since its initial certification by the EPA.

In this report, we performed an updated literature review, compiled lists of the assumptions/simplifications built into the current model as well as the review comments that have been made during and since the CCA, summarize new WIPP-specific data on intrinsic, mineral and microbial colloids, and recommend some updates to the colloid enhancement parameters. There is no plan to change the WIPP colloid model itself in the upcoming recertification effort.

A significant amount of literature results have been published since the CCA. These are focused on low ionic-strength groundwaters and continue to show that the importance and role of colloidal transport in the subsurface remains poorly understood. A number of contaminated sites report the existence of actinide colloids in their groundwater and there are new data that point toward specific nano-structures for some of these colloidal species. Additionally, there has been significant progress made in the understanding of the interactions of microorganisms and actinide species to form biocolloids.

There are relatively few new data on actinide mineral colloids. The literature results and the WIPP-specific experiments conducted, however, re-affirm two aspects of the current model: First, the most important mineral colloids are likely to be the metal oxide minerals since these are predominant in nature as well as in the iron-containing experiments performed. This is consistent with the pre-CCA data that is the basis of the current WIPP model. Second, there was no evidence for the formation of significant amounts of Mg-derived mineral colloid species. This result eliminates a potential regulator concern since the possibility that these mineral colloids would form was overlooked in the initial CCA. Based on these results and observations, there are no changes recommended to the mineral colloid enhancement parameters.

The literature survey and WIPP-specific experiments indicate that nano-sized intrinsic colloids (typically < 10 nm) are almost always present in brine, even after multiyear equilibration times. This is not consistent with the conclusions summarized as part of the CCA process where it was concluded that only plutonium colloids were significant. For these reasons, it is recommended that the intrinsic colloid enhancement parameters be updated to be more consistent with the literature and WIPP-specific laboratory results.

Lastly, an extensive amount of work under WIPP-specific conditions was completed to re-assess the microbial colloid enhancement parameters. There are some discrepancies in the current model in this area due to the lack of extensive WIPP-specific data at the time of the

CCA. These experiments build on the more extensive understanding that we now have about the microbial ecology in the WIPP. Microbial colloid enhancement parameters based on these new data are recommended and these are, in general, more realistic and lead to a lower overall contribution of microorganisms on the actinide source term.

As a whole, the WIPP-specific data summarized in this report address the oft-stated concern by the regulator that there was a significant lack of WIPP-specific data on colloids at the time of the CCA. These data, although not complete, provide significant improvement in our understanding of the potential contribution of colloidal species to the actinide source term. Additionally, some inconsistencies between the known solution chemistry and literature observation are addressed. A summary of the updated parameters recommend are given in the following three Tables and are discussed more extensively within this report.

Table 1 Summary of CRA-2009 and recommended/updated enhancement parameters for mineral and intrinsic colloids					
Actinide Oxidation State	Mineral Colloid Enhancement Parameter		Intrinsic Colloid Enhancement Parameter		
	CRA-2009	Proposed	¹ CRA-2009	Proposed Oxidation-State Specific	² Proposed Element-Specific
Th(IV)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	2 x 10 ⁻⁸ M	2 x 10 ⁻⁸ M
U(IV)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	2 x 10 ⁻⁸ M	3 x 10 ⁻⁸ M
U(VI)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	3 x 10 ⁻⁸ M	
Np(IV)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	2 x 10 ⁻⁸ M	2 x 10 ⁻⁸ M
Np(V)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	ND	
Pu(III)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	1 x 10 ⁻⁹ M	4 x 10 ⁻⁹ M	2 x 10 ⁻⁸ M
Pu(IV)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	1 x 10 ⁻⁹ M	2 x 10 ⁻⁸ M	
Am(III)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	4 x 10 ⁻⁹ M	4 x 10 ⁻⁹ M
1 - for CRA-2009, only plutonium intrinsic colloids are considered 2 – for the element-specific case, the highest value is proposed ND – not determined					

Table 2 Summary of CRA-2009 and recommended/updated oxidation-state specific enhancement parameters for microbial colloids						
Actinide Oxidation State	PROPMIC			CAPMIC (M)		
	CRA-2009 (M)	Proposed (M)		CRA-2009	Proposed	
		Archaea	Bacteria		Archaea	Bacteria
Th(IV)	3.1	0.21	1.76	0.0019	3.8 E-8	2.3 E-6
U(IV)	0.0021	0.21	1.76	0.0021	3.8 E-8	2.3 E-6
U(VI)	0.0021	ND	ND	0.0021	ND	ND
Np(IV)	12	0.21	1.76	0.0027	3.8 E-8	2.3 E-6
Np(V)	12	ND	1.4	0.0027	ND	4 E-6
Pu(III)	0.3	0.05	0.32	6.8E-5	3.9 E-10	3.1 E-8
Pu(IV)	0.3	0.21	1.76	6.8E-5	3.8 E-8	2.3 E-6
Am(III)	3.6	0.05	0.32	1.0	3.9 E-10	3.1 E-8
ND – not determined, no new recommendation						

Table 3 Summary of CRA-2009 and recommended/updated element-specific enhancement parameters for microbial colloids						
Actinide Oxidation State	¹PROPMIC			¹CAPMIC (M)		
	CRA-2009 (M)	Proposed (M)		CRA-2009	Proposed (M)	
		Archaea	Bacteria		Archaea	Bacteria
Th(IV)	3.1	0.21	1.76	0.0019	3.8 E-8	2.3 E-6
U(IV)	0.0021	0.21	1.76	0.0021	3.8 E-8	2.3 E-6
U(VI)	0.0021			0.0021		
Np(IV)	12	0.21	1.76	0.0027	3.8 E-8	2.3 E-6
Np(V)	12			0.0027		
Pu(III)	0.3	0.21	1.76	6.8E-5	3.8 E-8	2.3 E-6
Pu(IV)	0.3			6.8E-5		
Am(III)	3.6	0.05	0.32	1.0	3.9 E-10	3.1 E-8
ND – not determined, no new recommendation						
1 – highest value for a particular element is recommended for the element, this is extended to all oxidation states even if they are “ND”						

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LIST OF COMMONLY-USED ACRONYMS

ACRSP	Actinide Chemistry and Repository Science Program (LANL-CO)
An	Generic actinide
BAB	Microbial culture enriched in WIPP Brine A (Francis et al., studies)
CBFO	Carlsbad Field Office (DOE)
CCA	Compliance certification application (for WIPP)
Chromo	Chromohalobacter, sp. – halophilic bacteria (isolate) used in biosorption experiments
CRA	Compliance recertification application (for WIPP)
DBR	Dissolved brine release – release scenario from the WIPP
DOE	Department of Energy
EPA	Environment Protection Agency
Hbt	<i>Halobacterium</i> – archaea (isolate) used in Los Alamos biosorption experiments
Hmn	<i>Halomonas</i> (halophilic microorganism)
kDa	Kilo Dalton (unit of size)
LANL-CO	Los Alamos National Laboratory-Carlsbad Operations
Nd	Neodymium
NMED	New Mexico Environment Department
Np	Neptunium
PA	Performance Assessment
PABC	Performance Assessment Baseline Calculation
PAVT	Performance Assessment Verification Test
Pu	Plutonium
QAP	Quality Assurance Program
SNL	Sandia National Laboratories
SOTERM	Actinide Source Term (Appendix/Attachment for the WIPP application)
SOTERM	Actinide Source Term description (appendix or attachment to certification)
Th	Thorium
U	Uranium
WIPP	Waste Isolation Pilot Plant – Transuranic waste repository

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INTRINSIC, MINERAL AND MICROBIAL COLLOID ENHANCEMENT PARAMETERS FOR THE WIPP ACTINIDE SOURCE TERM

1.0 INTRODUCTION AND GOALS

The Waste Isolation Pilot Plant (WIPP) is the only working nuclear permanent geologic repository in the United States. This defense transuranic waste repository is located in the northern portion of the Delaware Basin in southeastern New Mexico east of Carlsbad at a 665m (2150 ft) depth in the Salado salt Formation. It was certified by the Environment Protection Agency (EPA) in May 1998 as a TRU waste repository and it is currently operated by the Department of Energy, Carlsbad Field Office (DOE CBFO). The regulatory guidelines for the WIPP are given in 40CFR191/194 [DOE-CCA]. Based on these regulations, the WIPP is required to undergo re-certification by the EPA every five years and by the New Mexico Environment Department (NMED) every 10 years.

The potential presence of colloids in high ionic-strength brines is accounted for in the WIPP performance assessment (PA) model. These colloidal contributions are defined by colloid enhancement parameters that are used to calculate actinide concentrations that are added to the calculated actinide solubility to establish a mobile dissolved concentration for each actinide oxidation state. The overall approach and basis for the calculations currently used in PA are described extensively in the DOE compliance certification application (CCA) [DOE-CCA] and compliance recertification application (CRA) [DOE-CRA/2004; DOE-CRA/2009] documentation in appendix or attachment SOTERM. This dissolved actinide concentration is used to calculate release from the WIPP repository when dissolved brine release (DBR) mechanisms, and to a lesser extent Culebra release pathways (far field), are invoked in PA calculations.

The importance of colloids in the migration and transport of actinide contaminants, although it continues to receive significant attention in the literature, remains somewhat unclear and difficult to define. In this context, the consideration of potential contributions from colloidal actinide species to the dissolved actinide concentrations by WIPP PA is, at least in part, a conservatism that is built into the overall PA approach. The sorption of colloidal actinides onto fixed substrates and their filtration in low-porosity media will also reduce the mobile colloidal actinide source term, but no credit is currently taken for this potentially significant reduction in colloidal concentrations in the source term, although some filtration effects are acknowledged in Culebra release.

The most important reason why it is important to consider the contribution of colloidal actinide species in WIPP PA is that there are processes anticipated in the WIPP that are known to lead to the formation of mobile colloidal species under certain conditions. The most important to these processes are:

- 1) Hydrolysis that is possibly influenced by other anionic species present in brine that leads to the formation of intrinsic colloids
- 2) The formation of pseudo colloids due to the interactions of dissolved actinide species with microbially derived colloids, mineral colloids formed by the corrosion of steel and/or presence of waste constituents (e.g., mineral phases present or MgO), or with humic/fulvic acids that may be present.

The formation of colloids could enhance actinide release in two ways. First, increased actinide concentration will increase the magnitude of DBR release and the effective actinide source term concentration for transport through the Culebra. Second, colloids have very different transport properties than dissolved species, and are predicted to migrate more rapidly in the subsurface. This transport mechanism could enhance the overall actinide release in the WIPP through migration pathways in the Culebra member and the Salado.

An accounting for these processes, supported by some laboratory studies, is the basis of the current WIPP colloid model. This model is based on the data and general understanding that was available at the time of the initial WIPP license application (CCA) and there have been no significant modifications to this model and the associated parameters since that time.

In this report, it is our goal to re-examine the basis of the WIPP PA colloid model and associated parameters for intrinsic, mineral and microbial actinide colloids. These are assessed in the light of new WIPP-specific and literature data. Specifically, in this report, the following are provided:

- An overview summary of the WIPP colloid model and associated peer reviews/EPA documentation over the past certifications
- An updated review of the general colloid literature since the CCA
- A summary of WIPP historic data that supports the current colloid enhancement parameters
- New WIPP-specific colloid data on actinide and actinide analog systems
- Recommendations on proposed changes to the current colloid enhancement parameters

It is important to note that only the enhancement parameter values within the current PA colloid model are considered in this report. An assessment of the overall colloid model is outside the scope of this report and is not being considered for CRA-2014.

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The post-CCA actinide research that pertain to the potential formation of actinide colloids was performed by the Los Alamos Actinide Chemistry and Repository Science Team (ACRSP) under the Los Alamos National Laboratory - Carlsbad Office (LANL-CO) Quality Assurance Program (QAP) as part of following Test Plans: Plutonium (VI) Reduction by Iron: Limited-Scope Confirmatory Study (LCO-ACP-04), Plutonium Speciation and Solubility in the WIPP (LCO-ACP-05), Solubility/Stability of Uranium (VI) in WIPP Brines (LCO-ACP-02), Solubility of Neodymium (III) in WIPP Brines (LCO-ACP-03), WIPP Actinide-Relevant Brine Chemistry (LCO-ACP-11) and Microbial Interactions in the WIPP (LCO-ACP-12). A more extensive description of the results in these Test Plans has already been published [Ams, 2013; Borkowski, 2008, 2012; Lucchini, 2007, 2010, 2013a, 2013b; Reed, 2006, 2007, 2010, 2012; Swanson, 2012a, 2012b, 2013a, 2013b].

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2.0 THE CRA-2009 WIPP COLLOID MODEL: OVERVIEW AND REGULATORY COMMENTS

The potential for colloidal species to have a role in defining the solution concentration and mobility of actinides in the WIPP was recognized early in the WIPP licensing process. For this reason there was a substantial effort to evaluate and establish the nature of colloids that could be present. This led to the development of a colloid model that accounts for these colloidal species. This model was based on an extensive literature review, some WIPP-specific experimental data, and some conservative simplifications that were extensively peer reviewed prior to the first license application (CCA). The EPA found this model to be satisfactory in the WIPP certification and subsequently in the CRA-2004 and CRA-2009 recertification. There has been essentially no change in this model since its initial certification by the EPA.

In this Section, we provide 1) an overview of the current WIPP colloidal actinide source term model and approach, 2) a summary of the simplifications and assumptions in the current model, 3) a description of the parameters used in the current model, and 4) a summary of the reviews and assessments, mostly done by the EPA, of this colloid model.

2.1 CRA-2009 WIPP Mobile Colloidal Actinide Source Term Model

The WIPP colloid model [SOTERM-2009] used in CRA-2009, the last recertification of the WIPP, is the same model that was used in the CCA [SOTERM-CCA, Section 6], and CRA-2004 [SOTERM-2004, Section 6]. The most extensive and essentially identical documentation is in the earlier versions of SOTERM (CCA and CRA-2004). This model was part of the WIPP conceptual model peer review and the results of this peer review are summarized in CCA Appendix PEER3 [PEER-CCA]. There have also been comments provided by the EPA in each of the recertification processes that support the adequacy and continued use of this model, but also flag some recommendations on how to strengthen and support the model.

The key conceptualization in the colloidal actinide source term model is to first recognize that colloids may contribute to the dissolved actinide concentrations and these colloidal species can potentially be transported in the various WIPP release scenarios that are considered. This model describes the concentration of actinides sorbed to or contained in the mobile colloidal particles in the disposal room and the stable colloids that must be quantified for transport in the Culebra. For this reason, it is important to account for colloidal contributions in the PA models in two ways: 1) as a part of the concentration of mobile dissolved actinide species in the source term – important release scenarios where DBR is important, and 2) as transportable actinide species in the far-field (Culebra) for release scenarios where far-field transport may be important. Although we are mostly focused on the contributions of colloidal species to the actinide source

term in this report, some aspects of this report may be useful in addressing colloidal issues associated with actinide migration in the Culebra.

Four potential types of colloids are recognized. These along with their operational definitions are (SOTERM –CCA):

Colloidal particles are classified into the following four types for evaluation of the impact of colloidal particles at the WIPP site:

- 1. Mineral fragments are hydrophobic, hard-sphere particles that are kinetically stabilized or destabilized by electrostatic forces, and may consist of crystalline or amorphous solids. Mineral fragments may be made kinetically stable by coatings with steric stabilizers that prevent close contact. Mineral fragments may act as substrates for sorption of actinides or they may consist of precipitated or coprecipitated actinide solids.*
- 2. Actinide intrinsic colloids are macromolecules of actinides that, at least in some cases, may mature into a mineral-fragment-type of colloidal particle. When immature, they are hydrophilic; when mature, they become hydrophobic.*
- 3. Humic substances are hydrophilic, soft-sphere particles that are stabilized by solvation forces. They are often powerful substrates for uptake of metal cations and are relatively small (less than 100,000 atomic mass units).*
- 4. Microbes are relatively large colloidal particles that are stabilized by hydrophilic coatings on their surfaces, which behave as steric stabilizing compounds. They may act as substrates for extracellular actinide sorption or they may actively bioaccumulate actinides intracellularly.*

The four types of colloids just described include "hard sphere" carrier colloids (mineral fragments), microbes, soft sphere carrier colloids or hydrophilic colloids (humic and fulvic acids), and intrinsic colloids (true colloids). These potentially mobile species develop from a variety of processes in the repository that include waste degradation, host rock decomposition, radiolytic processes, and chemical condensation; all of which can be augmented by microbial activity and processes. Intrinsic colloids are formed by the aggregation of dissolved actinides in the disposal rooms if/when brine is present.

In this context, the concentration of dissolved mobile actinide species is the sum of the solubility of the actinide and the additive contribution of the colloidal species present (Equation SOTERM-79 in SOTERM-2009):

$$\text{Total Mobile} = \text{Dissolved} + \text{Humic} + \text{Microbe} + \text{Mineral} + \text{Intrinsic} \quad (1)$$

This conceptualization, although relatively simple and straightforward, has been successfully applied to the CCA, CRA-2004, CRA-2009 and is the path forward for CRA-2014.

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2.2 Assumptions and Simplifications in the Current Model

There are a number of assumptions and simplifications that were included in the conceptualization of the WIPP colloid mode – mostly at the time of the CCA application. These, along with the source/reference, are given in the following Table:

Table 2-1: Assumptions and Simplifications in the WIPP Colloid Actinide Source Term Conceptual Model		
#	Assumption or Simplification	Reference
1	The potential size of the actinide colloid is not explicitly defined but is generally defined as “particles with at least one dimension between 1 nm and 1 μm, suspended in a liquid”	SOTERM-CCA , section 6.1
2	Colloidal actinides that are not suspended in the aqueous phase are not included	SOTERM-CCA , section 6
3	No credit is being taken for the sorption of colloidal actinides onto fixed substrates – this is a conservatism in the model	SOTERM-CCA , section 6
4	Colloids are instantaneously dissolved, up to their solubility limits when sufficient inventory is present, and mobilized	SOTERM-2009 section 5
5	Simplification 1: competition due to equilibration between the truly dissolved species and the colloid is ignored (so the terms are additive). This overestimates the concentration of mobile actinide species.	PEER1, Section 3.24.1
6	Simplification 2: A conservative partitioning scheme is used when the sum of the colloidal and dissolved actinide species exceed the predicted WIPP inventory. They are preferentially partitioned to the potentially most mobile species.	PEER1, Section 3.24.1
7	Simplification 3: Intrinsic and humic colloids achieve thermodynamic equilibrium. This is judged to be a conservative assumption.	PEER1, Section 3.24.1
8	Simplification 4: Microbes and mineral fragments are present in constant quantities in the aqueous phase. This is judged to be a conservative assumption.	PEER1, Section 3.24.1
9	When the concentration of intrinsic colloids was too low to measure, the actual detection limit was used for concentration of the intrinsic colloids.	PEER1, Section 3.24.2.2
10	When the concentration of mineral colloids was too low to measure, 10X the actual detection limit was used for the concentration of mineral colloids.	PEER1, Section 3.24.2.2

For the sake of historical accuracy, it is important to note that there is much discussion in the earlier documentation (circa mid 1990s) about the fact that there is little/no data that directly addresses the issue of colloidal species under the expected WIPP conditions. In this report, what was available at the time of the CCA is addressed more specifically for each colloid type in section 3. There was also reasonable expectation at the time of the CCA that there would be little/no contribution from colloidal species under WIPP-relevant conditions. The inclusion of colloidal species, as a whole, is a conservatism that is designed to account for future data/evaluations that may be conducted as well as insure that all possible contributions to the mobile actinide species source term are accounted for in the model descriptions. These initial discussions and comments are, for the most part, being corroborated by WIPP-relevant data – something that is discussed in more detail in Sections 4 and 5 of this report.

2.3 Parameters Used in the WIPP Colloidal Actinide Source Term Model

The colloid enhancement parameters currently used in WIPP PA were defined at the time of the initial license application and the colloid model was reviewed and defined in the peer review process. There are, however, new experimental data that pertain to these parameters and, for this reason, there has been a need to re-examine and possibly update the existing colloid enhancement parameters.

In the WIPP colloid model, three types of parameter values were determined: (1) constant concentration values, (2) concentration values proportional to the dissolved actinide concentration, and (3) maximum concentration values. The parameter types are summarized below and were initially described in parameter record packages [Papenguth 1996; Papenguth 1996a, 1996b, and 1996c] and re-summarized for the CRA-2004 Performance Assessment Baseline Calculations (PABC) [Garner, 2005; Leigh, 2005]. For intrinsic actinide colloids and mineral-fragment colloids, associated actinide concentrations were described as constant values. Table 2-2 summarizes the material (e.g., actinide) and associated parameter names and descriptions.

Experiments conducted to quantify actinide concentrations associated with humic substances and microbes provided the basis for a more sophisticated representation, in which colloidal actinide concentrations were related to the dissolved actinide concentration by proportionality constants.

For microbes, the proportionality relationship was made by element. For humic actinides, however, the relationship was made by oxidation state, rather than by element. For microbes and humic substances, the experiments also provided a basis to define upper limits of

the actinide concentration that could be associated with each of those colloid types. For both humic and microbial actinides, the upper limit parameter was defined by element, rather than oxidation state, and is in units of molality. The use of the two upper limit parameters is slightly different, and is described in the sections below discussing humic substances and microbes.

Table 2-2 Material and Property Names for Colloidal Parameters [Table SOTERM-21 in SOTERM-2009]		
Material	Property	Brief Description of Parameter
Th, U, Np, Pu, Am	CONCMIN	Concentration of actinide associated with mobile mineral fragment colloids
Th, U, Np, Pu, Am	CONCINT	Concentration of actinide associated with mobile intrinsic actinide colloids
Th, U, Np, Pu, Am	PROPMIC	Proportionality constant for concentration of actinides associated with mobile microbes
PHUMOX3 ^a PHUMOX4 PHUMOX5 PHUMOX6	PHUMCIM	Proportionality constant for concentration of actinides associated with mobile humic colloids; in Castile brine; actinide solubilities include organics (complexes with man-made organic ligands); solubilities were calculated assuming equilibrium with Mg-bearing minerals (brucite and hydromagnesite)
PHUMOX3 ^a PHUMOX4 PHUMOX5 PHUMOX6	PHUMSIM	Proportionality constant for concentration of actinides associated with mobile humic colloids; in Salado brine; actinide solubilities include organics (complexes with man-made organic ligands); solubilities were calculated assuming equilibrium with Mg-bearing minerals (brucite and hydromagnesite)
Th, U, Np, Pu, Am	CAPMIC	Maximum (cap) concentration of actinide associated with mobile microbes
Th, U, Np, Pu, Am	CAPHUM	Maximum (cap) concentration of actinide associated with mobile humic colloids
<p>^a Proportionality constant for actinide concentrations associated with mobile humic substances for PHUMOX3, for actinide elements with oxidation state <i>III</i> (that is, Pu(III) and Am(III)); PHUMOX4, oxidation state <i>IV</i> (Th(IV), U(IV), Np(IV), and Pu(IV)); PHUMOX5, oxidation state <i>V</i> (Np(V)); and PHUMOX6, oxidation state <i>VI</i> (U(VI)).</p>		

The colloid concentration factors currently used in WIPP PA are summarized in Table 2-3. The general approach used to account for colloidal enhancement of actinide solubilities is described in detail by Garner and Leigh [Garner, 2005]. There were essentially no changes in the approach used since the CCA. The maximum concentrations of actinides predicted for the four types of WIPP colloids are tabulated in Table 2-4. These data show that microbial colloids are likely to have the most significant effect on actinide concentrations, with a smaller but significant contribution from the humic colloidal fraction.

Table 2-3 Colloid Concentration Factors [Table SOTERM-22 in SOTERM-2009]

Actinide	CONCMIN (Concentration on Mineral Fragments ^a)	CONCINT (Concentration as Intrinsic Colloid ^a)	PROPMIC (Proportion Sorbed on Microbes ^{b,c})	CAPMIC (Maximum Sorbed on Microbes ^d)	Proportion Sorbed on Humics ^b		CAPHUM (Maximum Sorbed on Humics ^a)
					PHUMSI M (Salado)	PHUMCI M (Castile)	
Th(IV)	2.6×10^{-8}	0.0	3.1	0.0019	6.3	6.3	1.1×10^{-5}
U(IV)	2.6×10^{-8}	0.0	0.0021	0.0021	6.3	6.3	1.1×10^{-5}
U(VI)	2.6×10^{-8}	0.0	0.0021	0.0021	0.12	0.51	1.1×10^{-5}
Np(IV)	2.6×10^{-8}	0.0	12.0	0.0027	6.3	6.3	1.1×10^{-5}
Np(V)	2.6×10^{-8}	0.0	12.0	0.0027	9.1×10^{-4}	7.4×10^{-3}	1.1×10^{-5}
Pu(III)	2.6×10^{-8}	1.0×10^{-9}	0.3	6.8×10^{-5}	0.19	1.37 ^e	1.1×10^{-5}
Pu(IV)	2.6×10^{-8}	1.0×10^{-9}	0.3	6.8×10^{-5}	6.3	6.3	1.1×10^{-5}
Am(III)	2.6×10^{-8}	0.0	3.6	1.0	0.19	1.37 ^e	1.1×10^{-5}

^a In units of moles colloidal actinide per liter
^b In units of moles colloidal actinide per mole dissolved actinide
^c For the CRA-2004 PABC, all vectors were microbial
^d In units of moles total mobile actinide per liter
^e A cumulative distribution from 0.065 to 1.60 with a median value of 1.37 was used

NOTE: The colloidal source term is added to the dissolved source term to arrive at a total source term. Mineral fragments were provided with distributions, but the maximum was used as described in the CRA-2004, Appendix PA. Humic proportionality constants for the III, IV, and V states were provided with distributions, but only the Castile Am(III) and Pu(III) were sampled.

Table 2-4. Actinide Concentration or Maximum Concentration Due to Colloidal Enhanced Solution Concentrations [Table SOTERM 23 in SOTERM-2009]					
Actinide	CAPHUM Humic colloids	CAPMIC Microbial Colloids	CONCMIN Mineral Colloids	CONCINT Intrinsic Colloids	PROPMIC Microbial Colloids^a
Am	1.1×10^{-5} M	1.0 M	2.6×10^{-8} M	0.0	1.0
Np	1.1×10^{-5} M	0.0027 M	2.6×10^{-8} M	0.0	2.7×10^{-3}
Pu	1.1×10^{-5} M	6.8×10^{-5} M	2.6×10^{-8} M	1.00×10^{-9} M	6.8×10^{-5}
Th	1.1×10^{-5} M	0.0019 M	2.6×10^{-8} M	0.0	1.9×10^{-3}
U	1.1×10^{-5} M	0.0021 M	2.6×10^{-8} M	0.0	2.1×10^{-3}

^aIn units of moles colloidal actinide per mole dissolved actinide

A detailed description of the method and approach used to calculate the dissolved actinide concentrations is given in Section 5 of Appendix SOTERM [SOTERM-2009]. The output of the calculations is a computational database containing the source term and effective inventories. Instantaneous dissolution and colloidal mobilization up to the solubility limit is assumed when sufficient inventory is present. These calculations show the contribution of the dissolved and colloidal fraction for each actinide oxidation state and are given in Table 2-5.

There are a number of observations from these resulting calculations that are critical to the following sections of this report. First, there are significant conservatisms built into the assigned values for the colloid enhancement parameters and in most cases the colloidal contributions are much greater than the dissolved concentration. This, in some cases, leads to inconsistencies where actinide oxidation states that behave similarly have very different parameter values (e.g., PROPMIC values for Am³⁺ and Pu³⁺). Second, the parameter assignments do not follow a consistent pattern. In some cases, they are by oxidation state, and in some cases they are assigned by element and there are disconnects between the supporting arguments and the parameters selected as well as an inconsistency with the known chemistry of each species. This, as will be shown in later sections, is mainly due to the availability of data at the time these model values were compiled/recommended and not based on the solution properties of the actinides which tend to be oxidation-state specific and not element-specific. Lastly, some values are non-physical and, although conservative, cannot be reasonably achieved in a repository scenario.

**Table 2-5 Concentrations (M) of Dissolved, Colloidal, and Total Mobile Actinides
Obtained Using Median Parameter Values for the CCA Performance Assessment
Verification Test (PAVT) and CRA-2004 PABC [Table SOTERM-25 in SOTERM-2009]**

Actinide Oxidation State and Brine	PAVT	CRA-2004 PABC
Pu(III), dissolved, Salado brine	9.75×10^{-8}	3.61×10^{-7}
Pu(III), colloidal, Salado brine	7.48×10^{-8}	2.04×10^{-7}
Pu(III), total mobile, Salado brine	1.72×10^{-7}	5.64×10^{-7}
Pu(III), dissolved, Castile brine	1.06×10^{-8}	2.68×10^{-7}
Pu(III), colloidal, Castile brine	4.46×10^{-8}	4.75×10^{-7}
Pu(III), total mobile, Castile brine	5.52×10^{-8}	7.44×10^{-7}
Am(III), dissolved, Salado brine	9.75×10^{-8}	3.61×10^{-7}
Am(III), colloidal, Salado brine	3.96×10^{-7}	1.39×10^{-6}
Am(III), total mobile, Salado brine	4.93×10^{-7}	1.75×10^{-6}
Am(III), dissolved, Castile brine	1.06×10^{-8}	2.68×10^{-7}
Am(III), colloidal, Castile brine	7.78×10^{-8}	1.34×10^{-6}
Am(III), total mobile, Castile brine	8.83×10^{-8}	1.61×10^{-6}
Th(IV), dissolved, Salado brine	1.06×10^{-8}	6.70×10^{-8}
Th(IV), colloidal, Salado brine	1.25×10^{-7}	6.56×10^{-7}
Th(IV), total mobile, Salado brine	1.36×10^{-7}	7.23×10^{-7}
Th(IV), dissolved, Castile brine	3.33×10^{-8}	8.07×10^{-8}
Th(IV), colloidal, Castile brine	3.39×10^{-7}	7.85×10^{-7}
Th(IV), total mobile, Castile brine	3.73×10^{-7}	8.65×10^{-7}
U(IV), dissolved, Salado brine	1.06×10^{-8}	6.70×10^{-8}
U(IV), colloidal, Salado brine	9.26×10^{-8}	4.48×10^{-7}
U(IV), total mobile, Salado brine	1.03×10^{-7}	5.15×10^{-7}
U(IV), dissolved, Castile brine	3.33×10^{-8}	8.07×10^{-8}
U(IV), colloidal, Castile brine	2.36×10^{-7}	5.35×10^{-7}
U(IV), total mobile, Castile brine	2.69×10^{-7}	6.15×10^{-7}
Pu(IV), dissolved, Salado brine	1.06×10^{-8}	6.70×10^{-8}
Pu(IV), colloidal, Salado brine	9.67×10^{-8}	4.69×10^{-7}
Pu(IV), total mobile, Salado brine	1.07×10^{-7}	5.36×10^{-7}
Pu(IV), dissolved, Castile brine	3.33×10^{-8}	8.07×10^{-8}

Information Only

Table 2-5 Concentrations (M) of Dissolved, Colloidal, and Total Mobile Actinides Obtained Using Median Parameter Values for the CCA Performance Assessment Verification Test (PAVT) and CRA-2004 PABC [Table SOTERM-25 in SOTERM-2009]

Actinide Oxidation State and Brine	PAVT	CRA-2004 PABC
Pu(IV), colloidal, Castile brine	2.47×10^{-7}	5.60×10^{-7}
Pu(IV), total mobile, Castile brine	2.80×10^{-7}	6.40×10^{-7}
U(VI), dissolved, Salado brine	7.07×10^{-6}	1.00×10^{-3}
U(VI), colloidal, Salado brine	8.89×10^{-7}	1.31×10^{-5}
U(VI), total mobile, Salado brine	7.96×10^{-6}	1.01×10^{-3}
U(VI), dissolved, Castile brine	7.15×10^{-6}	1.00×10^{-3}
U(VI), colloidal, Castile brine	3.69×10^{-6}	1.31×10^{-5}
U(VI), total mobile, Castile brine	1.08×10^{-5}	1.01×10^{-3}

2.4 Summary of EPA Comments and Assessments

The WIPP Mobile Colloidal Actinide Source Term Conceptual Model was extensively reviewed prior to the CCA as part of the peer review on all conceptual models for the WIPP [PEER1-CCA]. For the sake of completeness, the part of this review that directly pertains to the colloid model is included as Attachment 1 in this report. The overwhelmingly important conclusion from this review is the observation that the colloid model was satisfactory, comprehensive, appropriate and conservatively implemented. This observation is supported and further confirmed in the technical support documentation of the CRA-2004 [DOE, 2004], and CRA-2009 [DOE, 2009].

There have been, however, some comments and concerns documented over the past 15 years or so that this model was reviewed and assessed. The importance of capturing these comments is to provide a context for the new data summarized in Sections 4 and 5, help guide research direction and emphasis, and continue to demonstrate that the key criteria are being met. These comments are summarized, along with a reference to their source, in table 2-6.

Table 2-6 Comments/concerns expressed in review documentation of the WIPP Colloidal Actinide Source Term Conceptual Model		
#	Comment/Concern	Reference
CCA, ~ 1996		
1	Four key assumptions (see Table 2-1) are conservative, perhaps overly so and are most probably valid	PEER1 3.24.1/2.2/9
2	The colloid conceptual model makes liberal use of literature publications that are also used to drive the experimental program	PEER1 3.24.2.1
3	Non-compete assumption between colloidal and truly dissolved species is “certainly conservative and will overestimate the total actinide source term.” There is however lack of integration between the various experimental results and it is unclear how well the potential interdependencies were addressed.	PEER1 3.24.2.2 PEER3 4.1.3.1
4	Partitioning scheme when inventory is exceeded is “reasonable and again conservative”	PEER1 3.24.2.2
5	Thermodynamic equilibrium assumption for intrinsic and humic colloids is “valid”	PEER1 3.24.2.2
6	Assumption of steady state mineral and microbial colloids “allows for conservatism”	PEER1 3.24.2.2
7	Using detection limits for bounding colloidal fractions is “probably adequate, possibly overly conservative ... and can be considered adequate”	PEER1 3.24.2.2
8	Decision to not consider colloids absorbed to immobile substrates is “conservative and allows for the possibility of more actinides being transported by colloids”	PEER1 3.24.2.3
9	There is no experimental proof that Pu(IV) intrinsic colloids will act as a mineral colloid in time. There is no understanding of the mechanistic operation of this colloid. (this must be dealt with)	PEER1 3.24.2.4/5/9
10	The site densities available for actinide sorption onto microbes has not been established (this must be dealt with)	PEER1 3.24.2.4/5/9
11	The assumption that humic colloids behave like dissolved species is not supported with data (this must be dealt with)	PEER1 3.24.2.4/5/9
12	Conservative bounding values for intrinsic and mineral fragment concentrations should be abandoned in favor of real-system measurements (this however overall seems an insignificant issue). Using order of magnitude above the detection limit is “probably extreme and not truly representative”	PEER1 3.24.2.5/7
13	True unknowns in the model are 1) rapidity of equilibrium, 2) nature of microbes, and 3) waste uniformity – these are “most probably adequate and reasonable”	PEER1 3.24.2.6

14	A key concern with the estimation of numerical values for the colloid parameters is the manner in which uncertainty was determined. This is mainly an issue with the lack of extensive repository-specific data. Experimental methods seem adequate but the limitation is the number of experiments performed.	PEER3 4.1.3.1 PEER3 4.1.3.2
CRA-2004, ~ 2005		
1	No significant new data on colloid model. Model is previously reviewed as “adequate for use in PA.” No specific issues on the colloid model itself are raised.	CRA-2004 TSD Section 8.1.2 and 8.7 [EPA-2006]
2	Model change in application of microbial colloids (to only be in microbial vectors) was noted. This was changed per EPA recommendation in the CRA-2004 PABC (to include microbial degradation in all vectors)	CRA-2004 TSD section 4.2.2 and 8.1.2 [EPA-2006]
CRA-2009, ~ 2010		
1	Overall adequacy and conservatism of the model is confirmed.	CRA-2009 TSD (Docket: A-98-49) – Section 7 [EPA-2010]
2	There is a literature observation that Th(IV) intrinsic colloids may persist in high ionic-strength systems [Neck 2002; Altmaier 2004]. This contradicts the statements in SOTERM that only Pu(IV) colloids are discussed in the literature. Also the mobilized thorium represented by these data are greater than currently predicted values for An(IV) in WIPP PA. In this context “DOE should address the possible effects of the formation of intrinsic thorium colloids on repository performance”	CRA-2009 TSD (Docket: A-98-49) – Section 7 [EPA- 2010]
3	Statements in Xiong 2012 were criticized. It incorrectly states that WIPP research to support the CCA did not identify intrinsic or mineral fragment colloids [Xiong 2010]. This is contradicted by the results in Papenguth [1996] when iron and bentonite mineral fragments were present. Also the argument that the Altmaier and Neck experiments were not performed in WIPP brine is not persuasive.	CRA-2009 TSD (Docket: A-98-49) – Section 7 [EPA- 2010]
4	The issue of plutonium nano-colloids, raised in public comment, is adequate “DOE has adequately accounted for the potential formation of plutonium nano-colloids in PABC-2009.”	CRA-2009 TSD (Docket: A-98-49) – Section 7. [EPA-2010]
5	Pre-CCA mineral fragment experiments did not account for the presence of MgO. This possibility is however raised by the Altmaier data [Altmaier 2004] and DOE needs to address this. Explanations provided by the DOE based on the likelihood of korschunovskite phase formation need to be supported.	CRA-2009 TSD (Docket: A-98-49) – Section 7 [EPA- 2010]

3.0 ENVIRONMENTAL ACTINIDE COLLOID LITERATURE REVIEW: IMPACT ON WIPP COLLOID MODEL

The extent and potential formation of actinide colloids continues to be debated by researchers in the field. Since the CCA, there have been over 100 publications on actinide colloid chemistry that range in topics from real-system transport studies to the structure and inherent stability of actinide colloids. These remain largely focused on plutonium and its associated and very complex subsurface chemistry, but there are also studies on neptunium, americium, thorium and curium reported in the literature. It is also important to note that relatively few of these studies specifically address ionic-strength effects on colloid formation, stability and mobility. In this context, there are very few studies that in high ionic-strength systems ($I > 5 \text{ M}$) and only a small fraction of these studies have direct application to the WIPP repository safety case.

There are essentially five themes in the colloid research reported. These, along with a brief summary of the results of relevant publications are given in this section.

Theme 1: A wide variety of actinide intrinsic and mineral colloids form in natural systems

A key role of colloids in actinide transport has been proposed to explain actinide migration at Rocky Flats [LoPresti, 2007], the Nevada Test Site [Kersting 1999; Zavarin, 2003], Hanford [Dai, 2005; Cantrell, 2012], the Savannah River Site [Dai, 2002], the Sellafield site [Alexander, 2011; May 2012; Asbury, 2001], natural and clay materials [Huittinen, 2012; Zavarin, 2012; Wang, 2012], and the Mayak site [Novikov, 2006; Novikov, 2009]. Colloidal transport at these sites provides an explanation for subsurface actinide migration that exceeds the rates predicted for dissolved actinide species.

An important theme to recent field observations of actinide colloids is the tendency of Pu, as Pu(IV), to form iron and manganese (Mn) oxide pseudocolloids [Khasanova, 2007]. The colloidal transport of Pu in the far-field was investigated by Novikov et al. [Novikov, 2006; Novikov, 2009] at the Mayak site in Russia. They found that the mobility of Pu in groundwater was facilitated by submicron-sized colloids. Pu(IV) hydroxides or carbonates adsorbed on amorphous iron oxide colloids were most transported. These Pu colloids were essentially removed from groundwater, leading to a decrease in the Pu concentration from 1000 becquerel (Bq)/L to 0.16 Bq/L over a distance of 3 km.

The field observations are supported by laboratory studies that show a high tendency of lower-valent actinides to form iron and Mn pseudocolloids in environmentally relevant systems. Zavarin et al. [Zavarin, 2003] shows that, at pH 8, there is a strong sorption of Pu(IV) in

groundwater to birnessite (Mn-oxide) and goethite (Fe-oxide) rather than clinoptilolite (a zeolite) and calcite. Sorption was rapid and equilibrium was reached after 24 hours. Complexation with carbonate reduced Pu(IV) sorption to clinoptilolite about 15%. For iron and Mn oxides, Pu(V) sorption was also rapid, but led to the reduction of Pu(V) to Pu(IV). Khasanova et al. [Khasanova, 2007] also studied iron and Mn oxide interactions with actinides and saw a strong association between the dissolved actinide species and the oxides.

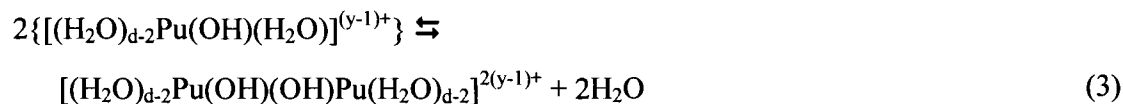
The potential formation of actinide pseudocolloids by association of dissolved actinides with biogenic and humic (natural) organics has also been established in the laboratory and the field. Santschi et al. [Santschi, 2002], Asbury et al. [Asbury, 2001], and Orlandini, Penrose, and Nelson [Orlandini, 1986] all show that actinides associate strongly with natural organics. These have been implicated as a potential explanation for actinide migration at Rocky Flats and in near-surface groundwater transport as a result of fallout.

Theme 2: Colloidal contributions are not properly accounted for in many solubility studies meaning that the true solubility is lower than what is measured.

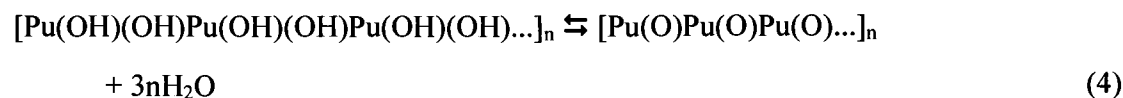
The formation of intrinsic colloids (colloids that are polymers of actinides) are important because they potentially add to the concentration of actinides in groundwater, but also because they potentially contribute to measured solubilities if care is not taken to properly account for their formation. The tendency of actinides to hydrolyze and to polymerize to form intrinsic colloids follows the order [Cleveland, 1979; Choppin, 1983; Kim, 1991; Lieser, 1991]



The most well known and well studied actinide intrinsic colloid is the Pu(IV) intrinsic colloid, which has been used as a basis of comparison for investigating intrinsic colloids of other actinides. The most convincing and consistent explanation for the chemistry of these Pu(IV) intrinsic colloids is presented by Johnson and Toth [Johnson, 1978]. Pu polymerization occurs nearly immediately after the first hydrolysis occurs. The following reaction involving polymerization of two hydrolyzed species by loss of H₂O (olation) is proposed:



Aging or maturation of the polymer then occurs by loss of H₂O (olation) as follows:



A key insight into the important role of Pu polymer formation was reported by Neck et al. (2003), which investigated the solubility of Pu hydroxides/hydrous oxides under reducing

conditions and in the presence of oxygen. The experimental data and thermodynamic calculations show that, under reducing conditions in the stability field of water, $\text{Pu}(\text{OH})_3(\text{s})$ is not stable and it converts to $\text{PuO}_2(\text{s,hyd})$. It also found that small Pu(IV) colloids/polymers, present in neutral to alkaline solutions at the constant level of $\log[\text{Pu}(\text{IV})]_{\text{coll}} = -8.3 \pm 1.0$, play an important role in defining the redox potentials in these systems. The experimental results in these systems including colloid species can be described in terms of equilibrium thermodynamics. These data argue for a thermodynamically stable Pu(IV) oxidation state in the WIPP.

Actinides in the IV oxidation state, because of the complexity of their solution chemistry and very high tendency towards hydrolysis, form colloidal species in groundwater. The potential effect of colloid formation on the solubility of Th(IV) in concentrated NaCl and MgCl_2 solutions was recently published by Altmaier, Neck, and Fanghänel [Altmaier, 2004]. These data indicate relatively high colloidal contributions to the measured thorium solubility. According to the authors, ultracentrifugation of these samples for 60 minutes at 90,000 rpm ($500,000 \times g$) indicated that the total dissolved thorium in solution was ~99% colloidal. Only ~1% or less was the thorium hydroxide complex. It was also observed that the % of thorium colloids is not constant and changes from ~90% to ~99.9% as the ionic strength is decreased. In solutions at high magnesium concentration and conditions conducive to colloid generation, mineral colloids can also form (i.e., Th(IV) sorbed onto $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{coll})$). This led to an apparent increase of the total thorium concentration up to 10^{-5} M [Altmaier, 2004; Walther, 2003; Degueldre and Kline, 2007; Bundschuh, 2000].

Lastly, there is a growing debate about the care needed in solubility studies to account for colloids in the solubilities measured—which is not a trivial problem, as the colloids are often very small (< 20 nm) and difficult to detect experimentally. The role of colloid formation, especially for An(IV) solubilities, was discussed by Fanghänel and Neck [Fanghänel, 2002], who state, “The formation of amorphous and crystalline solids and the discrepancies between the corresponding experimental solubility data may be explained as an effect of particle size. ... the predicted solubilities are often significantly lower than experimental data indicating that the solubility is controlled by the surface properties” [Fanghänel, 2002]. In this context, existing solubility data in the literature may include significant colloidal enhancement and overestimate the corresponding solubility.

Theme 3: There is an increased emphasis in the potential colloidal transport of actinides in site-specific assessments of contaminant transport

The increased focus on colloidal transport of actinides is consistently being identified as a potential issue in site-specific contaminant assessments. This is a focus of the recent assessments at Hanford [Cantell, 2012], Sellifield [Alexander, 2011; May 2012; Asbury, 2001], and Mayak [Novikov, 2006; Novikov, 2009]. The concentration of intrinsic colloids is often

comparable to the solubilities of the actinide. Significant enhancement can be observed when actinides associate with oxide mineral colloids and natural and biogenic organic species. However, there remains high uncertainty in the ability of these colloidal species to migrate in the subsurface. This key issue was raised by Kersting et al. [Kersting, 1999] for the Nevada Test site, Dai et al. for the Hanford and Savannah River site [Dai, 2002; Dai, 2005], and strong attenuation was noted at the Mayak site [Novikov, 2006]. In the near-field of the WIPP (e.g., Salado Formation), with its very low porosity, it is reasonable to predict that the transport of colloids is likely to be negligible; the only significant concern would be the colloidal contribution to dissolved concentrations for DBR-type release. This is less certain for the release scenarios where transport in the Culebra (far-field) may be important.

Theme 4: There is a growing understanding of the structure and nature of plutonium colloidal species

There is a growing understanding of the structure of some nano-colloidal species, particularly those of plutonium (IV) [Soderholm, 2008; Powell, 2011; Schmidt, 2012] but also reported extensively for uranium systems [Duval, 2001; Burns, 2005]. These nano-colloids are formed under a range of laboratory conditions and are typically <10 nm in size. Their published structure is based on nanoclusters with a very specific size and structure that are formed by oxolation reactions (Pu-O-Pu bonding), rather than the more conventionally accepted ololation (Pu-OH-Pu bonding) reactions. In this context, the colloids proposed have a much more rigid/defined structure that contrasts with the more generally accepted view that they are amorphous and less rigidly structured under environmentally-relevant conditions. Examples of highly specific structures were provided for colloids formed in alkali hydroxide media and reconstituted under highly acidic conditions in hydrochloric and nitric acid where high-energy X-ray scattering (HEXS) was used to establish their structure. The long-term stability of these colloids, their relevance to the much higher pH systems typically of concern in groundwater/brine systems, and transport properties were not addressed – so the overall relevance of these preliminary results to the WIPP case is not clearly established. Although these studies raise an important question about the possible structure of plutonium colloids, it does not, in fact, raise an issue that will significantly impact current WIPP PA calculations of plutonium release.

Theme 5: Actinide-microbial sorption behavior is shown to follow a surface complexation model

The biosorption of actinides towards microorganisms has been investigated for low ionic strength groundwater systems [Songkasiri, 2002; Gorman-Lewis, 2005; Fein, 1997; Fein 2005; Deo, 2011]. In organic-rich natural systems, significant bioassociation should be expected that can lead to immobilization (by filtration or incorporation into biofilms) or mobile colloid

formation. The surface properties of soil bacteria in these systems do not vary significantly and correspond to the known surface complexants (e.g., sulfate, phosphate, carboxylates).

We, in our own studies [Ams, 2013] have extended this to halophilic bacteria at moderately high ionic-strength brine systems (2 and 4 M). The surface complexation fit to a four-complexant surface is shown in Figure 3-1 and the sorption observed as a function of pH is shown in Figure 3-2. In this study, it was shown that the surfaces complexation properties of these halophilic bacteria are not much different than those of the soil bacteria (low ionic-strength groundwater). These studies, were all performed with Np(V), which is an almost ideally behaved actinide species due to its very low tendency towards hydrolysis, high solubility and low charge. For this well-behaved system, the sorption observed depends on the speciation and can be described using the surface complexation model (i.e., reversible surface and site-specific sorption). In Section 5 of this report we provide some initial data on archaeal systems in high ionic-strength brine systems. Sorption, for the archaea, when compared to bacteria under similar conditions is considerably lower and likely linked to a very different surface site density and composition of complexants.

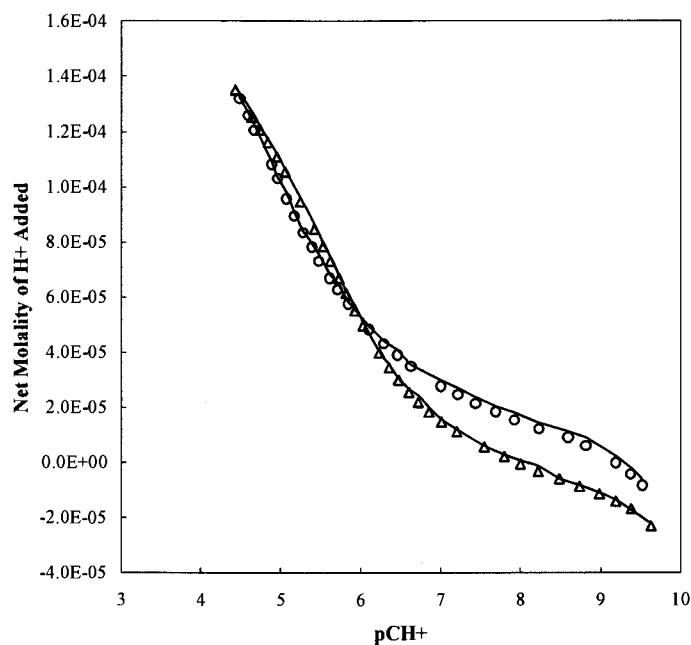


Figure 3-1 Best-fit calculated 4-site surface complexation model curves (solid curves) to representative titration data in 2 (open circles) and 4 (open triangles) M NaClO₄.

Overall Impact of literature publications on the WIPP Colloid Model

Although there continues to be some progress made in the assessment of the colloidal issue as it applies to the potential subsurface migration of actinide species, there remains a great

deal that is not well understood and substantive progress in this area is not likely in the very near future. Because of this focus, the following general recommendations remain:

- 1) It remains critical that the WIPP model continue to address the colloid issue.
- 2) There is no literature evidence that the current four-colloid type model is inadequate, if anything it continues to be a conservative assumption built into the model.
- 3) Current literature shows that colloidal species, intrinsic and mineral, of a number of actinides, not just plutonium is observed – this is somewhat of a departure from the initial CCA literature survey conducted. These literature data, however, still do not explicitly address high ionic-strength systems.
- 4) The structural data point towards intrinsic colloids that persist as very small (typically < 10nm) species.
- 5) Biosorption data show that increased ionic-strength increased the extent of sorption and the overall trend with pH was to go through a maximum at about pH 8 and then decrease with increasing pH. At the predicted pC_{H^+} of ~ 9.4 in the WIPP site, biosorption is in the range of ~ 40 -65%.

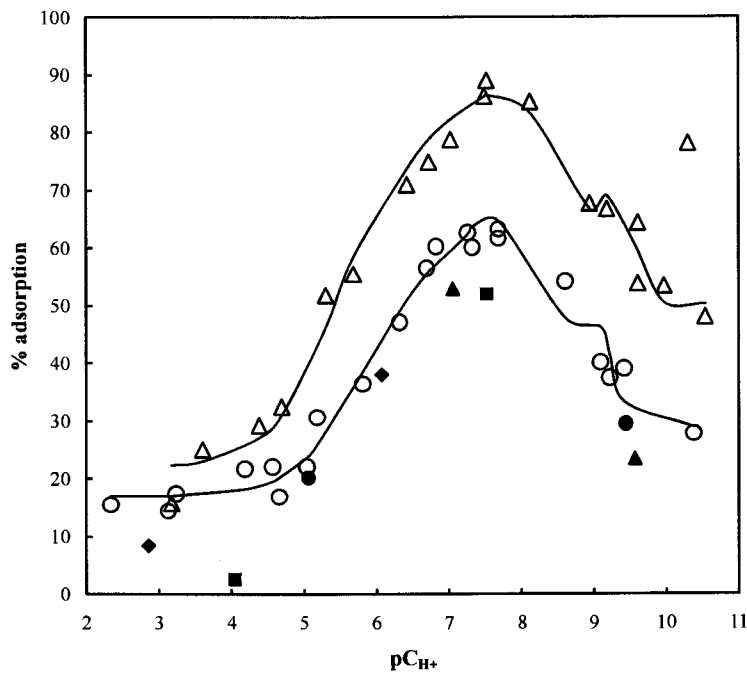


Figure 3-2 Experimental data for neptunium (V) adsorption onto *Chromohalobacter* sp. as a function of pH in 2 (open circles) and 4 (open triangles) M NaClO₄. Adsorption experiments were performed with 5 x 10⁻⁶ M total neptunium (V) and 5 g/L (wet weight) bacteria [Ams, 2013]. Solid curves represent best-fit calculated surface complexation models. Solid diamonds, squares, triangles, and circles represent the results of desorption experiments performed with 5 x 10⁻⁶ M total neptunium (V) and 5 g/L (wet weight) bacteria in 2 M NaClO₄.

4.0 EXPERIMENTAL BASIS OF WIPP-RELEVANT INTRINSIC AND MINERAL COLLOIDS

The nature and long-term stability of actinide intrinsic and mineral colloidal species continues to be the subject of debate and is especially not understood in the high ionic-strength brines and conditions expected in the WIPP. In this Section, a summary of the current basis for the intrinsic colloid parameters is provided, new WIPP-specific data obtained since the CCA are summarized, and an overall assessment, including recommendations, of the current PA parameters is provided.

The colloidal contributions due to mineral and intrinsic colloids remain a relatively insignificant contribution to the mobile actinide concentration. The justification for updating these parameters is to maintain consistency with recent WIPP-specific actinide data and improve the alignment of these parameters with the known solution chemistry of the actinides. The overall conceptual model, as it will be implemented in PA, remains unchanged.

4.1 Summary of Past Experimental Work and Recommendations

An extensive literature review and analysis of what is critically important in defining an actinide intrinsic colloid was performed prior to the CCA and is well documented [Papenguth, 1996; Papenguth, 1996c; Papenguth, 1996d]. The results of this literature review are summarized in both the CCA and CRA-2004 SOTERM appendix/attachment. The most important conclusions and observations from this review, along with a summary of the data that support the CCA recommendations are given in this Section.

4.1.1 Intrinsic Actinide Colloids

The key results and observations of the pre-CCA literature summary related to intrinsic actinide colloids were:

- Intrinsic colloid literature is most centered on the properties of Pu(IV) where oxolation and oxalation processes, coupled with polymerization reactions, can lead to the formation of stable colloids. Although this is widely observed and studied, there are still questions about the structure and mechanism of their formation.
- The overall stability of the plutonium polymer is dependent on the presence and effects of anions (e.g., halides, nitrates, phosphate, perchlorate, and many organic ligands).

- The overall structure of the Pu(IV) polymer is between Pu(OH)₄ and PuO₂. There is an aging effect that leads to greater stability with time and is possibly explained as having an increased PuO₂ nature.
- A wide range of sizes were reported for the plutonium polymer – between 1 nm and 370 nm. Most however are < 10 nm in size.
- There are many references to a variety of intrinsic colloids for other actinides – but there is not a systematic study of this in the literature and the plutonium colloids appear to be unique in this regard.
- The tendency towards hydrolysis and polymerization to form intrinsic colloids is dependent on oxidation state and is expected to be:
$$\text{An}^{4+} \gg \text{An(VI)O}_2^{2+} > \text{An}^{3+} > \text{An(V)O}_2^+$$
- There are mixed reports in the literature about the existence/formation of Am colloids (trivalent)

Some WIPP-related experiments, as described in the Test Plan [Papenguth, 1996], were conducted. The results of these experiments are summarized in the parameter record package [Papenguth, 1996d] and SOTERM write-ups [CCA and CRA-2005].

The short term (few weeks duration) experiments conducted were performed under the following conditions: ~ 0.1 mM Pu(IV) as a function of ionic strength (0.001 to 5 M) in NaCl and in the pC_{H+} range of 3-10. Potential inhibition of colloid formation by organic complexants and carbonate was also investigated. These experiments were done from under and oversaturation approach and were compared to the results of solubility studies done with amorphous and crystalline PuO₂ [Rai, 1980; Rai, 1981].

The experiments completed did not resolve the issue of thermodynamic vs. kinetic control on the question of colloid formation/stability. They did indicate that relatively few colloids were observed over the range of conditions investigated. The solubility of the plutonium polymer, under the most repository-relevant conditions (I= 5M, and pC_{H+} ~ 9) was below the detection limit of 1 x 10⁻⁹ M. This result, along with the lack of literature on colloids for the other actinides, is the basis of the current PA values for intrinsic colloids that are shown in Table 4-1.

Table 4-1 PA Values for the Intrinsic Actinide Colloid Contribution	
Actinide and Oxidation State	CONCINT (Concentration as Intrinsic Colloid)
Th(IV)	0.0
U(IV)	0.0
U(VI)	0.0
Np(IV)	0.0
Np(V)	0.0
Pu(III)	1.0×10^{-9} M
Pu(IV)	1.0×10^{-9} M
Am(III)	0.0

4.1.2 Mineral Actinide Colloids

The key results and observations of the pre-CCA literature summary related to mineral actinide colloids were:

- Actinide mineral pseudo-colloids are observed in natural systems and need to be accounted for in the WIPP model.
- In the WIPP model, the additive contribution of mineral fragments is defined by the CONCMIN parameter which is the concentration of each actinide oxidation state associated with the mobile mineral fragment colloids present in brine.
- Mineral fragments are expected in the WIPP horizon due to the interactions of the brine with the iron and alkali minerals predicted in WIPP waste, can be already present in the brine that flows into the repository during an intrusion scenario, and can be generated in the Culebra due to mixing of repository and Culebra brines.
- A bounding approach, rather than mineral-specific one, is used to account for the possible concentration of actinides associated with minerals. This is done by the measurement of residual concentrations of colloidal particles in brine coupled with reasonable assumptions on the maximum of actinides that could be sorbed to the mineral fraction.

The experimental basis of the current mineral fragment parameters in the WIPP model are a set of experiments where colloidal suspensions were prepared and placed in brine to evaluate their long-term stability. A wide range of potentially repository-relevant phases that could lead to the formation of mineral colloids were evaluated in general “screening” experiments [SOTERM-CCA – see Section 6]: this included bentonite, kaolinite, montmorillonite, vermiculite, illite, anhydrite, calcium carbonate, magnesite, hematite, limonite, goethite, magnetite, quartz, siderite, brucite, strontianite, diatomaceous earth, pyrite and cellulosic materials. This was conducted as a function of brine composition and pH. More detailed studies were conducted using bentonite, goethite and hematite in low ionic strength (0.1 M) sodium chloride. Particle concentrations were measured using a particle spectrometer. In the majority of the screening experiments the colloids added rapidly settled out of solution – typically > 99%.

For the longer-term studies, the iron oxides investigated (hematite and goethite) had the most significant potential for the formation of actinide mineral colloids with estimated solution concentration of 1.6×10^{-8} M and 9.5×10^{-10} M respectively. A significantly smaller effect was estimated for bentonite with a predicted concentration of 1.3×10^{-9} M. The geometric mean of these results was 1.3×10^{-9} M and it was recommended that a value that is twice this amount, 2.6×10^{-9} M be used for the value of CONCMIN for all actinide oxidation states. In the end, this value was multiplied by a factor of ten for the sake of conservatism and a value of 2.6×10^{-8} M has been used in WIPP PA since the CCA.

4.2 WIPP-Relevant Data since the CCA

The presence of colloidal species, defined as species with a filterable size of > 2.5 nm, was evaluated for a series of long-term actinide solubility studies in WIPP brine. These 3-6 year solubility studies used redox-invariant analogs and were performed to provide a baseline for the solubility of the An (III, IV, and VI) actinides. Additionally, the long-term colloidal speciation was evaluated in ~ six-year plutonium-iron interaction studies where Pu(III), in the end, was the predominant aqueous species. A more extensive description of these results and experiments are given elsewhere [Borkowski, 2008 and 2012; Lucchini, 2007, 2010 and 2013a; Reed, 2010].

Although, mechanistic studies were not performed, these results, as shown in the following sections, indicate that there are nano-colloidal species for all the actinides and analogs investigated. These tend to be very small in size (<20 nm) and appear to be in equilibrium with the truly dissolved species, although this is not completely proven. This was somewhat of a surprise and contradicts some of the literature observations reported initially in the CCA documentation. Regardless, the colloidal fraction remains a relatively small effect in WIPP PA

calculations, but it may be conservative to include a broader set of colloidal contributions in the colloid enhancement parameter set (e.g., CONCINT values).

4.2.1 Experimental Approach

Solubility experiments were performed in GWB and ERDA-6 brine for Nd(III), Th(IV) and U(VI), using both an undersaturation and oversaturation approach at room temperature (25 ± 3 °C) and a pC_{H^+} range of ~ 7 to 12. These were performed in a nitrogen glovebox to control the carbonate content and were performed in the presence and absence of carbonate and organic complexants. The typical duration of these experiments was 2-6 years and the concentration of the actinide/analog was tracked and routinely filtered by 100kDa (~ 20 nm) filtration prior to analysis. Routinely, there were no filtration effects noted in much of these studies meaning that there was not a large difference between the unfiltered and filtered samples when this was evaluated.

To more completely evaluate the colloidal fraction of the actinide/analog in these long-term studies sequential ultrafiltration and, in some cases, ultracentrifugation was performed after long-term equilibration. This was achieved by consecutively filtering the same volume of solution through different pore size filters (Fisher Amicon[®] ultrafilters), starting with the largest pore size and ending with the smallest. The following pore size filters were used (in the order of filtration): $0.45\mu\text{m}$, $0.22\mu\text{m}$, $\sim 20\text{nm}$ (100kDa), $\sim 10\text{nm}$ (30kDa), $\sim 5\text{nm}$ (10kDa), and $\sim 2.5\text{nm}$ (3kDa).

The applicability of this filtration approach was established in two ways: First, the time of filtration for each filter size was evaluated to insure that all the brine was going through the filter. Our long-established protocol is to centrifuge brine solutions for ~ 15 minutes for filters with a pore size of 10 nm or greater. Longer centrifugation times were needed for the smaller pore-size filters (see data for 2.5 and 5 nm in Table 4-2). This led to a procedure that was somewhat system-specific but was typically 15 minute filtration times for the 20 nm or greater size filtration ranging up to 1 hour for the smallest filter size used.

Second, systems that were “truly” dissolved were prepared in the actual brines and filtered to confirm that there was no filtration effect on the samples. The results for plutonium(VI) under acidic conditions are summarized in Table 4-2. A slight increase in the plutonium concentration due to brine volume retention in the filter (the heavier plutonium goes through, a small amount of the brine is retained in the filter) was noted. This increase, rather than decrease, suggests that significant filtration effects are not present. An additional set of experiments was performed with Nd(III)-EDTA, Th(IV)-EDTA, Np(V)-carbonato, and U(VI) – carbonato complexes in 95% GWB brine at $pC_{H^+} \sim 9$. These results are shown in Figure 4-1. The time data and sequential filtration data show that, within $\sim 5\%$ or less, we get complete

recovery of the truly dissolved actinide/analog and confirmed the filtration technique used. In the case of thorium, a truly dissolved species was not present and filtration effects were noted even in the presence of EDTA. For this system, ultracentrifugation was also performed (Beckmann-Coulter ultracentrifuge at 100 kDa for ~ 2 hours) and shown to be effectively comparable to ~ 10 nm sequential filtration.

Table 4-2 Protocol Development: Filtration of 95% GWB brine for the 3 K and 10K (smallest pore size) amicon ultrafilters		
Duration and RPM for Centrifugation		
Filter	Centrifugation Time and RPM	Result
Amicon Ultra 10K Filter (~ 5 nm)	5 minutes / 10 K	~ 60% through the filter
	10 minutes / 10 K	~ 90% through the filter
	10 minutes / 13.3 K	~ 100% through filter
	10 minutes / 13.3 K (repeat)	~ 100% through filter
	20 minutes / 13.3 K	~ 100% through filter
Amicon Ultra 3 K Filter (~2.5 nm)	5 minutes / 10 K	~ 10% through the filter
	10 minutes / 10 K	~ 20% through the filter
	10 minutes / 13.3 K	~ 50% through filter
	10 minutes / 13.3 K (repeat)	~ 75% through filter
	20 minutes / 13.3 K	~ 90% through filter
	60 minutes / 13.3 K	~ 100% through filter
Recovery of “truly” dissolved Pu(VI) under acidic conditions		
Filter	Centrifugation Time and RPM	Result*
Amicon Ultra 10K Filter (~ 5 nm)	30 minutes at 13.3 K	Trial 1: 5.8% increase in [Pu]
		Trial 2: 7.2% increase in [Pu]
Amicon Ultra 3 K Filter (~2.5 nm)	60 minutes at 13.3 K	Trial 1: 11.3% increase in [Pu]
		Trial 2: 10.4% increase in [Pu]
		Trial 3: 11.3% increase in [Pu]
*a reproducible increase, not decrease, in [Pu] is indicative of all/most of the Pu going through the filter and a small brine volume retention by the filter – so the concentration is effectively increased. These data establish minimal interaction between filter and Pu.		

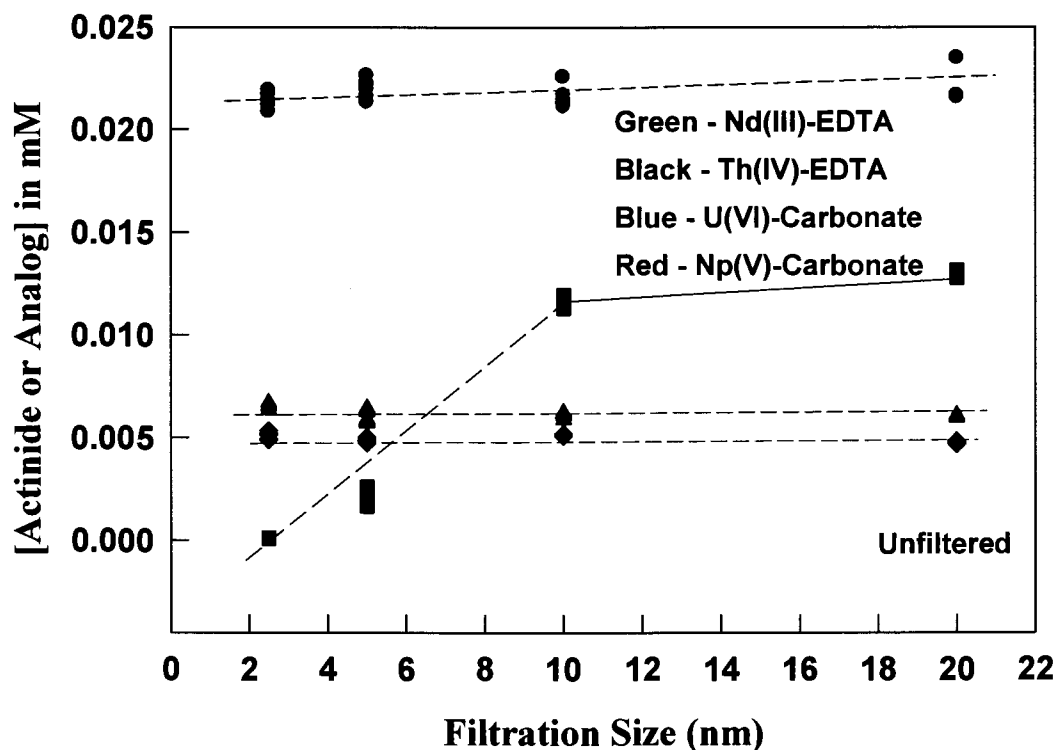


Figure 4-1 Effect of the sequential filtration approach on dissolved actinide species in GWB brine at $pC_{H^+} \sim 9$. For the Nd-EDTA, U-carbonate, and Np(V)-carbonate systems essentially full recovery of the actinide/analog was obtained. A significant filtration effect is noted for Th-EDTA in an analogous brine system where truly dissolved species were not expected. These results support the validity of the filtration approach used.

Following filtration, the brine samples were quantitatively diluted 100 times prior to analysis using Ion Coupled Plasma-Mass Spectrometry (ICP-MS Agilent 7500), per our analytical procedure ACP-EXP-011, Analysis of Solutes in Brine Using the Agilent ICP-MS. This dilution was needed to minimize analytical effects due to the highly concentrated brines being used. In some cases, the concentration of the actinide/analog was at or below the detection limit. In these cases, either a 10X, not 100 X, dilution was used or a reverse extraction using HDEHP was used to pre-concentrate the actinide/analog so that it could be detected. The limit of detection for the concentration of actinide/analog measured in this way were typically $\sim 5 \times 10^{-10} M$ for the 100X dilutions and up to an order of magnitude better in the cases where pre-concentration or 10X dilutions were performed.

4.2.2 Neodymium Sequential Filtration Results

The sequential filtration results for the neodymium solubility studies in brine [Borkowski, 2008] are shown in Figure 4-2. These experimental results reflect GWB (high magnesium) and ERDA-6 brine formulations, and a pC_{H^+} that ranges from 7.94 to 9.14. As has been previously noted, there is little/no filtration effect on the neodymium concentration down to a filter size of ~ 10 nm (30 kDa). Below 10 nm, however, the filtration effect leaves between 17% and 70% of the measured concentration in solution indicating the presence of nano-sized colloidal neodymium.

Some nano-colloidal fraction was noted in all the long-term solutions that were analyzed. This colloidal fraction was typically in the range of 30% to as high at 83% and varied with pH, the solubility approach used (e.g., over vs. undersaturation) and the brine composition. For the most WIPP-related conditions, defined as a pC_{H^+} of 9-10, the observed colloidal fraction for ERDA-6 brine was 33% corresponding to a solution concentration of a solution concentration of $4 \pm 1 \times 10^{-9}$ M. In GWB, at lower pC_{H^+} , the colloidal contribution was somewhat higher at 33% to 77%, with an average of 65% which lead to an effective concentration that is about an order of magnitude higher.

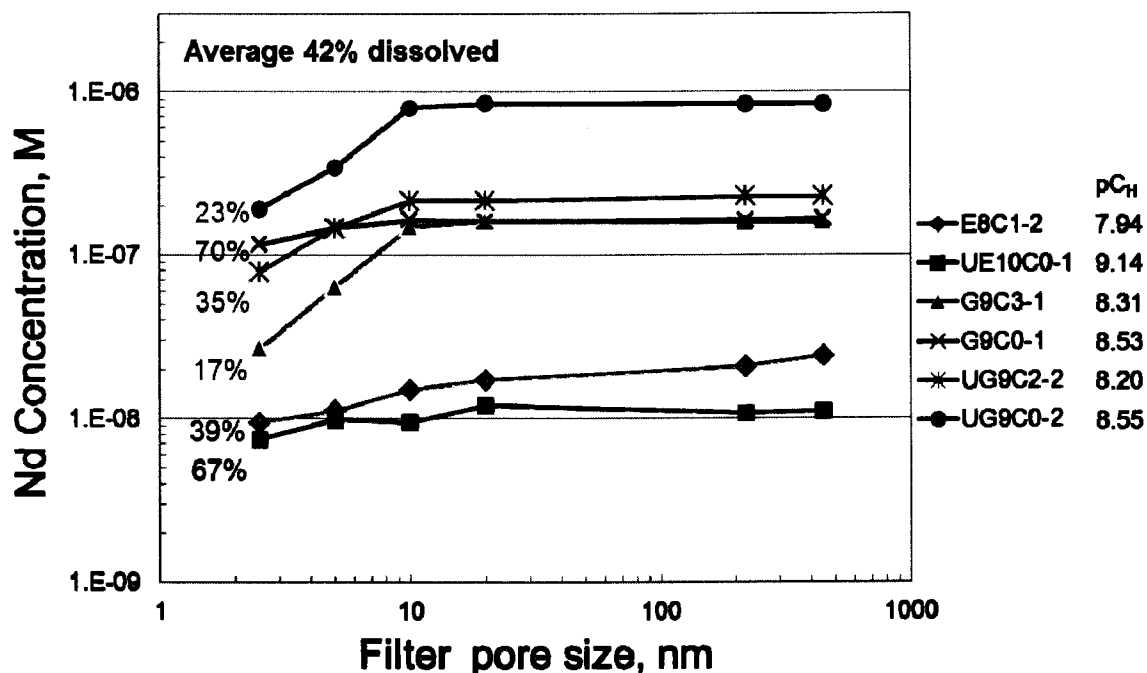


Figure 4-2 Sequential filtration results for the long-term neodymium solubility studies in brine (E = ERDA-6; G = GWB) as a function of pC_{H^+} . Significant filtration effects are only noted for filters that are 10 nm or smaller in size.

4.2.3 Plutonium Sequential Filtration Results

The experimental details of the plutonium-iron experiments are described elsewhere [Reed, 2010]. These redox experiments were left to sit unperturbed in a nitrogen glovebox for almost six years and selected experiments were re-analyzed to establish oxidation state and colloidal fraction of the plutonium (see section 2.3, in the LANL-CO Test Plan LCO-ACP-011). A description of the experiments analyzed is given in Table 4-3. In all of these experiments, the iron underwent anoxic corrosion and generated some colloidal iron in solution. In this context, information on both the association of plutonium with the iron and the potential formation of plutonium intrinsic colloids was obtained. Oxidation state analyses of the sorbed and dissolved aqueous plutonium showed that mostly Pu(III) was present in this system given the strongly reducing conditions established by the iron. These results are also summarized in Table 4-3. A plot of the concentration of plutonium as a function of pC_{H^+} and filtration is shown in Figure 4-3 as a function of pC_{H^+} and in Figure 4-4 as a function of filtration size.

Table 4-3 Redox Indicators for Iron Interactions with Plutonium under Anoxic Conditions				
Experiment	Description	^a Oxidation State of Pu Solid	^b [Fe]_{total} in mM (%Fe²⁺ in solution)	^c E_h Measured (± 3 mV)
PuFeCE8	ERDA-6 brine at $pC_{H^+} = 8.34$ with Fe coupon	~100 % Pu(III)	ND	ND
PuFeCE10	ERDA-6 brine at $pC_{H^+} = 9.54$ with Fe coupon	~100% Pu(III)	0.27 (100%)	ND
PuFeC	ERDA-6 brine at $pC_{H^+} = 9.11$ with Fe coupon	~90% Pu(III), rest Pu(IV)	0.18 (58%)	-110 mV
PuFeG7	GWB brine at $pC_{H^+} = 7.71$ 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

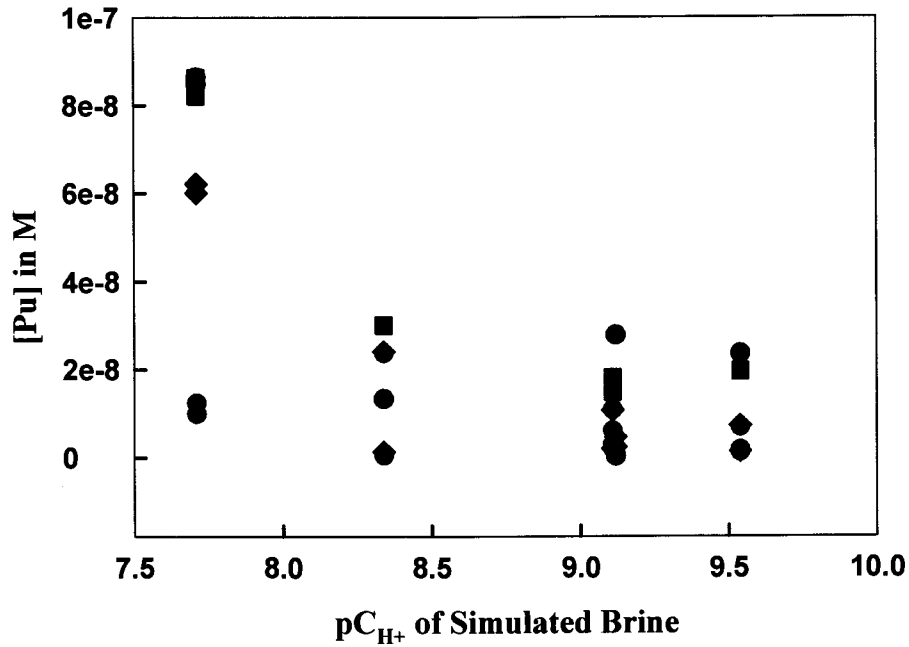


Figure 4-3 Effect of filtration on the measured concentration of plutonium as a function of pC_{H^+} . Data shown are 0.45 μ m (black squares), 0.22 μ m (green circles), 20 nm (blue diamonds) and 10 nm (red circles) filtrations. Uncertainty in the filtration data, based on ICP-MS analyses, is estimated to be $\pm 20\%$.

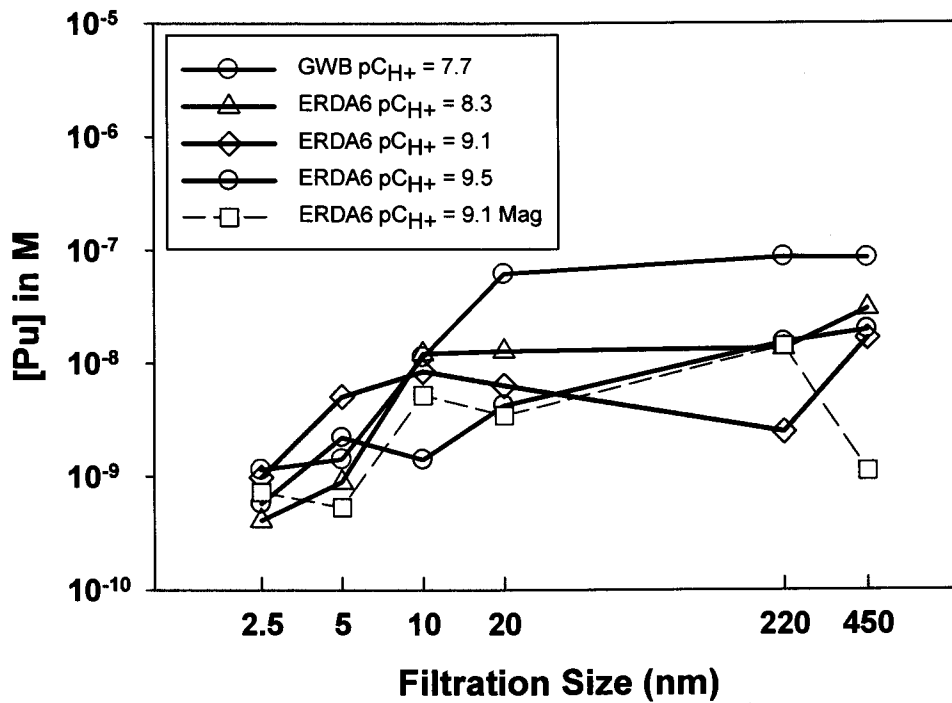


Figure 4-4 Sequential Filtration Data for the Pu-Fe Experiments as a function of pC_{H^+} , Brine Composition and Filtration Size

Collectively, these data show that we are seeing fairly low plutonium concentrations across the pC_{H^+} range investigated (7.7 to 9.5) but significant “colloidal” solubilization was also evident. The contribution of the mineral, intrinsic and truly dissolved fraction is summarized in Table 4-4. For the most repository-relevant $pC_{H^+} = 9.2$ and 9.6, the mobile concentration was an average of 1.7×10^{-8} M, and the dissolved concentration, defined as the concentration of plutonium that passed through a 2.5 nm filter, was an average of 7.7×10^{-10} M. The mineral fraction in these two experiments, defined as the concentration filterable by a 10 nm filter and associated with the iron particulates in solution, ranged from 43 to 86% with an average concentration of 1.8×10^{-8} M. The intrinsic colloidal fraction, defined as the concentration of plutonium between 2.5 and 10 nm in size, was 11 to 50% with an average concentration of 4.8×10^{-9} M. The intrinsic colloidal fraction is comparable to what was observed for Nd^{3+} and supports these data.

Table 4-4 Colloidal Fractionation in the Plutonium-Iron Interaction Experiments Mineral Fraction = [Pu] that is filtered by 10 nm filter Intrinsic Fraction = [Pu] between 10 and 2.5 nm Truly Dissolved = [Pu] after filtration by 2.5 nm filter					
Brine and pC_{H^+}	Total [Pu] in M	[Pu] @ 10 nm Filtration in M	[Mineral] in M and (%of total)	[Intrinsic] in M and (%of total)	[Dissolved] in M and (%of total)
GWB at pC_{H^+} 7.7	8.4×10^{-8} M	1.1×10^{-8} M	7.3×10^{-8} M (87%)	1.0×10^{-8} M (12%)	1.1×10^{-9} M (1%)
ERDA-6 at pC_{H^+} 8.4	3.0×10^{-8} M	1.2×10^{-8} M	1.8×10^{-8} M (60%)	1.2×10^{-8} M (40%)	4.1×10^{-10} M (1%)
ERDA-6 at pC_{H^+} 9.1	1.7×10^{-8} M	8.4×10^{-9} M	8.6×10^{-9} M (51%)	7.4×10^{-9} M (43%)	9.7×10^{-10} M (6%)
*ERDA-6 at pC_{H^+} 9.1	2.8×10^{-8} M	5.2×10^{-9} M	2.3×10^{-8} M (82%)	4.5×10^{-9} M (16%)	7.3×10^{-10} M (3%)
ERDA-6 at pC_{H^+} 9.5	2.0×10^{-8} M	1.5×10^{-9} M	1.9×10^{-8} M (95%)	9.3×10^{-10} M (5%)	5.7×10^{-10} M (3%)
*this experiment contained magnetite, all others contained an iron coupon					

4.2.4 Thorium Sequential Filtration Results

A number of the thorium long-term solubility experiments were sampled to establish their colloidal fraction. This was done at various times throughout the ~ 4 year experiments, as a function of brine composition, over/under saturation approach and the presence/absence of carbonate. A detailed summary of these experiments is given in Borkowski et al., 2012 [Borkowski, 2012]. The colloidal fraction was established by ultracentrifugation and sequential filtration.

Ultracentrifugation Results: Thorium Solubility in Brine Studies

In the ultracentrifugation studies, a representative number of samples from the carbonate-free experiments were further analyzed to establish the colloidal fraction of the thorium concentrations measured. In our procedure, ultracentrifugation was performed for 2 hours at 120,000 rpm (~ 1,000,000 × g) with a Beckmann-Coulter model Optima max-XP ultracentrifuge. This protocol exceeded the degree of separation used by Altmaier et al. [Altmaier, 2004], where 90,000 rpm for 60 minutes was used. Thorium concentrations measured before and after ultracentrifugation are reported in Figure 4-5, along with the initial total concentration data.

Although our total thorium concentration data are in agreement with Altmaier et al. [Altmaier, 2004], our results show a different partitioning between the thorium colloidal and dissolved fractions. In our samples, the highest colloidal fraction was ~40%, while Altmaier et al. reports a high colloidal fraction of at least ~99%. We do not yet fully understand what is causing this difference, but their samples were equilibrated for a much shorter period of time. The newest information provided by German scientists [Altmaier, 2012] is more consistent with

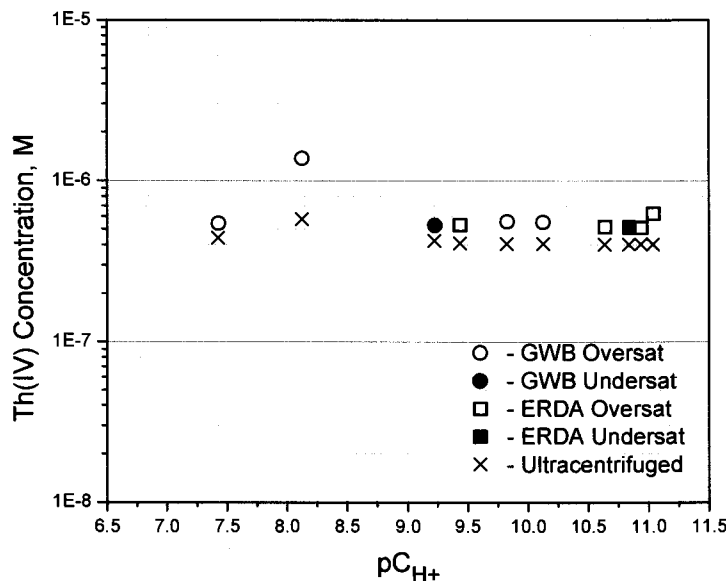


Figure 4-5

Concentration of thorium measured before and after ultracentrifugation in representative ERDA-6 and GWB samples.

our current results and makes the previously-published results somewhat unclear. Research to establish the colloidal fraction of the measured thorium concentrations as a function of time was continued for carbonate-containing samples using sequential filtration.

Sequential Filtration Results: Thorium Solubility in Brine Studies

Selected brine samples from the thorium solubility experiments were used to determine the thorium particle size distribution. The same sequential filtration approach as described in Section 4.2.1 was used. The sequential filtration results are shown in Figures 4-6 and 4-7. The highest colloidal fraction was observed for sample G8C2-1 which also had the highest total thorium concentration. The dissolved thorium concentration in all the GWB samples was in the range of $2-6 \times 10^{-8}$ M. In the ERDA-6 sample the dissolved thorium concentration was about 10 fold greater, but steady state concentrations were not yet achieved. At the most WIPP-relevant pC_{H^+} of 9.1 and 9.2 there is no evidence for mineral colloidal enhancement and the intrinsic colloidal contribution ranges from 9 to 58%. As shown in Borkowski et al., 2012, there is a slow time equilibration in the thorium system where the colloidal fraction and total concentration evolve with time. For this reason, the pC_{H^+} 9.1 data, which is at a lower concentration and closest to its long-term equilibrium, should be used to establish the intrinsic colloidal contribution. This is a colloidal fraction of 21-45% (average of 33%) and an intrinsic colloidal contribution of approximately 2×10^{-8} M.

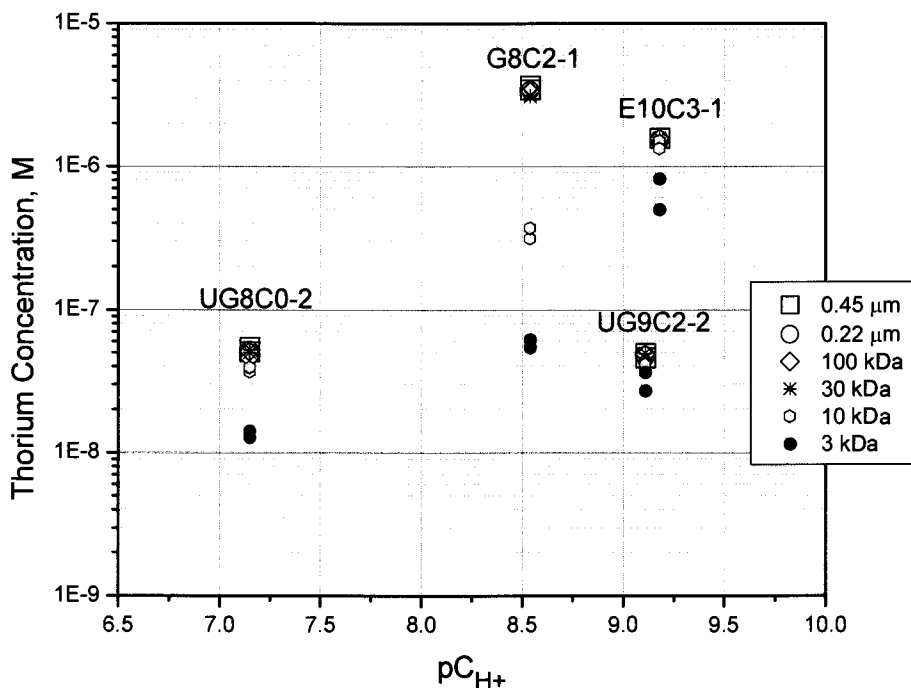


Figure 4-6 Thorium concentrations measured by sequential filtration as a function of pore size for brine samples with varied pC_{H^+} .

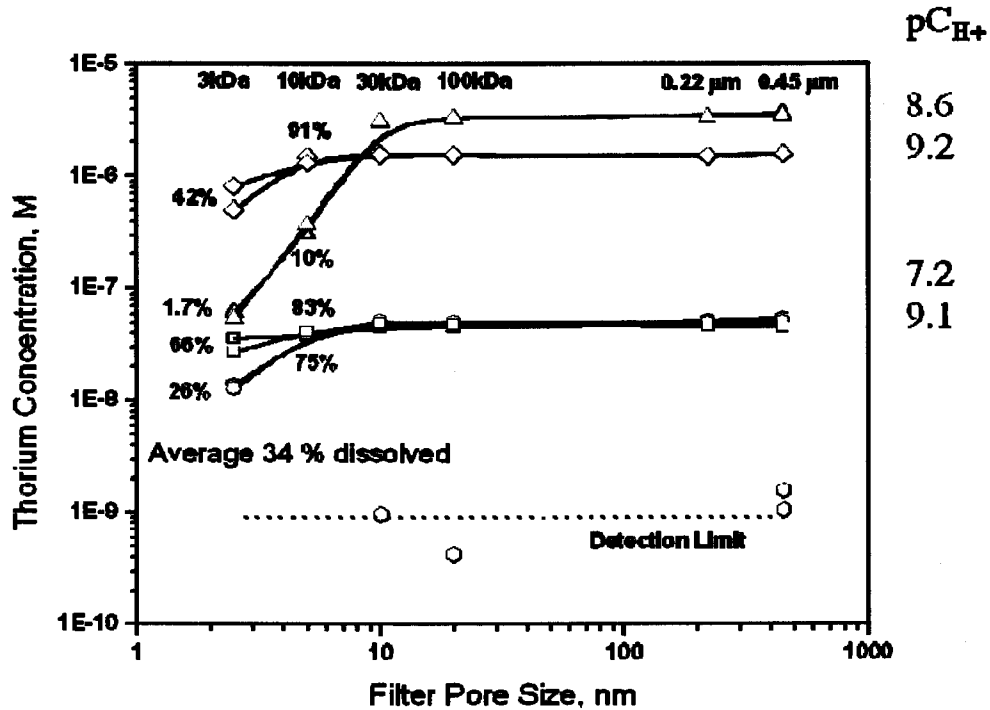


Figure 4-7 Distribution of the measured concentration of thorium as a function of filter pore size for the brine samples.

4.2.5 Uranium Sequential Filtration Results

Sequential filtration was performed on six selected solutions from the U(VI) solubility experiments to determine the size distribution of colloids of uranium possibly present. These experiments were initiated more than 5 years ago, and the experimental solutions were kept in closed vessels in nitrogen-controlled atmosphere. More experimental detail for these experiments can be found in the ACRSP report LCO-ACP-14, “Uranium (VI) Solubility in WIPP Brine” [Lucchini, 2013a]. The selected solutions and their properties (description, pC_{H^+} , and age) are presented in Table 4-5.

Sequential filtration was performed according to the overall procedure described in Section 4.2.1. The sequential filtration results for the selected uranium solutions are plotted in Figure 4-8, as a function of the filter pore size. Colloidal species were observed but are small; typically below 20nm and mostly below 10nm. Only in the case of the under-saturation experiment in carbonate-free ERDA-6 brine at high pC_{H^+} is there measurable uranium colloids of all sizes. This verifies the assumption made in the LCO-ACP-14 report concerning this specific system [Lucchini, 2013a]. For this carbonate-free ERDA-6 solution generated at pC_{H^+} 9.8, despite the 2022 days of the experiment, it is evident that there are small colloidal U(VI) species in the various brine solutions.

Table 4-5 Properties of the selected uranium solutions for the sequential filtration experiments.			
Solution ID	Description	pC _{H+}	Age (days)
T1-GW-9.1	U(VI) solubility in initially carbonate-free GWB brine (over-saturation)	8.9	2678
T1-ER-10.1	U(VI) solubility in initially carbonate-free ERDA-6 brine (over-saturation)	9.3	2678
T3-GW-C3-9.1	U(VI) solubility in GWB brine in the presence of 2×10^{-3} M initially (over-saturation)	8.9	2422
T3-ER-C3-9.1	U(VI) solubility in ERDA-6 brine in the presence of 2×10^{-3} M initially (over-saturation)	8.6	2422
T8-GWE-9.1	U(VI) solubility in initially carbonate-free GWB brine (under-saturation)	8.6	2022
T8-ERE-10.1	U(VI) solubility in initially carbonate-free ERDA-6 brine (under-saturation)	9.8	2022

In high ionic strength WIPP simulated brine, at pC_{H+} between 8.6 and 9.8, in the presence or in the absence of carbonate, the percentage of uranium intrinsic colloids is greater. Our study shows that uranium is present in an average of 47% as dissolved species (≤ 2.5 nm), and in ~53% as intrinsic colloidal fraction (between 2.5nm and 10nm in size). The speciation of these colloids was not experimentally determined. It is possible that these colloids are precursors of the schoepite-type phase (UO₃·xH₂O(s)) or uranate phase (clarkeite, NaUO₂O(OH)·H₂O) precipitates that form when uranium reaches saturation in solution [Diaz-Arocas, 1998; Yamazaki, 1992]. Alternatively uranium nanoclusters in this size range are also reported in the literature [Burns, 2005; Duval, 2001].

Based on these experimental data for U(VI), we expect essentially no mineral fragment colloids. At the most repository-relevant pC_{H+} (9.3 and 9.8), the intrinsic colloid fraction is 2% and 3% respectively. This leads to an average colloidal concentration of 1×10^{-8} M that corresponds to an average total aqueous uranyl concentration of 4×10^{-7} M.

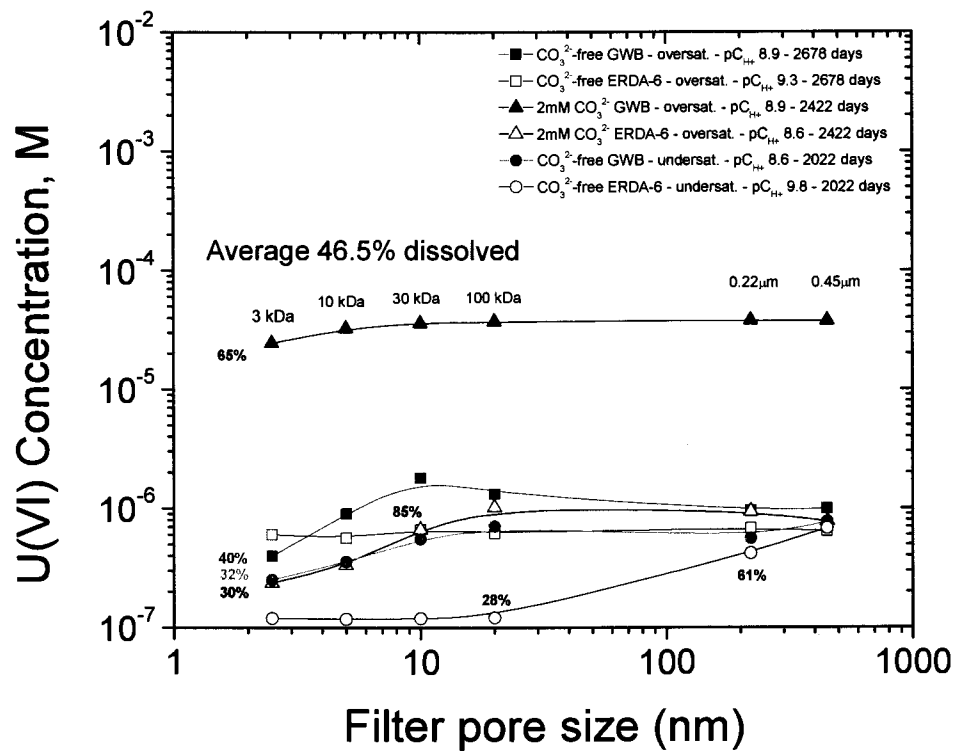


Figure 4-8 Concentrations of uranium measured during sequential filtration as a function of different pore size filters for different brine solutions at different pC_{H^+} .

4.3 Mineral Colloids: Summary of Observations and Recommendations

There was not an explicit goal to re-establish and replace the mineral colloid enhancement parameters in the post-CCA research summarized in this report. These data, however, do support and indirectly reflect on the pre-CCA data and conclusions used to establish the existing colloid enhancement parameters. The long-term actinide/analog solubility results reported in section 4.2, in this context, can be used to re-assess the mineral colloid enhancement parameters.

Magnesium-based mineral colloid effects

The effect of colloidal mineral species on the mobile actinide concentration is not simply a function of the concentration of mineral species, but also depends on the oxidation-state-specific affinity of the actinides towards these mineral species. It is also likely that relatively small concentrations, probably in many cases too difficult to measure, can influence the

formation of actinide mineral colloids. In the specific case of magnesium colloids, which is the EPA-raised issue in this CRA, the measurement of magnesium colloidal species is made problematic by the very high concentrations of magnesium in the GWB-like brine formulation and the inherent uncertainty in measuring these very high concentrations (e.g., an uncertainty of 0.1% in a 1 M concentration is still 1 mM which is almost four orders of magnitude higher than the predicted actinide concentrations). In this context, we believe that the best information on the potential for actinide mineral colloid formation are the sequential filtration data from the long-term actinide/analog studies performed in GWB brine where small increases in actinide/analog concentrations are easily measured and observed.

As indicated in the data presented in Section 4.2, there was essentially no significant increase in actinide/analog concentration above the 10 nm particle size threshold used to define intrinsic colloids. This was especially true in the case of the GWB brines that were typically at a lower pH. These data extend the conclusion in the CCA colloid model that only iron oxide mineral formation led to an increase in actinide/analog solution concentrations. Our data, although indirect, do not support an additional concentration adjustment (higher mineral colloid parameter value) due to the formation of magnesium colloids. We continue to believe that the colloidal enhancements reported by Altmaier et al. [Altmaier, 2004] were transient and specific to their experimental conditions. This is also the current position of the authors of this research [Altmaier, 2012]. For this reason, they do not apply/extend to the WIPP-specific case.

Iron oxide mineral colloids

The initial conclusions and observations that led to the current mineral colloid enhancement parameters [SOTERM-CCA] were that only iron oxides, specifically goethite and magnetite, formed actinide mineral colloids in the systems investigated. The sequential data from the plutonium-iron experiments summarized in this report (see Table 4-4) re-confirm this observation and show that iron oxides generated due to anoxic corrosion in WIPP brine led to some mineral colloid formation. As reported in Table 4-4 for the most repository-relevant pC_{H+} experiments, 51-95% of the aqueous Pu^{3+} was associated with the iron in solution corresponding to additional plutonium concentrations of 8.6×10^{-9} M to 2.3×10^{-8} M respectively. This is consistent with the 2.6×10^{-8} M that is currently in the WIPP model.

Overall Recommendations on Actinide Mineral Colloids

The results we report herein confirm and re-affirm the current WIPP PA model for mineral colloidal enhancement in two ways:

- 1) We show, albeit, indirectly that there is no evidence for magnesium-derived mineral colloidal enhancement.

- 2) We re-affirm that iron oxides can lead to long-term and relatively small plutonium mineral colloids in these brine systems and that the concentrations observed are within the current enhancement parameter values. That iron oxides are important in this process is also confirmed by literature observations.

Since there is no WIPP-specific iron mineral colloid data for actinides other than plutonium, there is no justification to change the ubiquity of the colloidal enhancement parameter and it is recommended that it continues to be extended to all the WIPP-relevant actinide oxidation states. It stands to reason that this interaction, at some level, will be oxidation-state specific, but there are no data at this time to justify this distinction.

4.4 Intrinsic Colloids: Summary of Observations and Recommendations

The sequential filtration data reported in Section 4.2 are directly relevant to the actinide intrinsic colloid parameters in WIPP PA. Based on the pre-CCA literature review and data collected it was concluded that only plutonium was likely to form intrinsic colloids although there was a recognition of scattered results in the literature that other actinides form intrinsic colloids. That other actinides may also form intrinsic colloids is suggested by our sequential data results and is consistent with published literature [Kim, 1991] that “all oxidation states of actinides generate intrinsic colloids in groundwater systems”. Specifically, in the Gohy-1012 groundwater investigated (from the Gorleben site, pH 8.2, NaCl-dominated brine ~ 10mM), Kim found that uranium colloids smaller than 15nm account for ~11% of the total uranium concentration. There are also literature-reports of thorium, americium, and neptunium colloidal species.

In the actinide/analog brine solubility studies that were analyzed by sequential filtration, we observed <10 nm species in all cases investigated – specifically for the Nd(III), Pu(III), Th(IV) and U(VI) systems. These observations are tabulated in Table 4-6 along with a comparison to the current enhancement parameter and a recommended change (if applicable). The proposed changes make the current parameter set consistent with the supporting CCA documentation that intrinsic colloids are correlated with the oxidation state of the actinide. This also addresses the several observations in the literature that actinides other than plutonium can also form intrinsic colloids. These changes, taken together, continue to show that the intrinsic colloidal contributions do not significantly impact calculated actinide concentrations and increase the robustness of the current WIPP PA position on all actinides that contribute to the potential for actinide release from the WIPP.

Table 4-6 Summary of Observed Intrinsic Colloidal Fraction and Comparison to Existing CRA-2009 Parameters			
Actinide/Analog	% Intrinsic Colloidal Fraction (<10 nm)	Equivalent [Actinide/analog] in M and % of WIPP PA calculated or assumed actinide/analog solubility*	Current CRA-2009 Intrinsic colloid enhancement parameter (M)
Nd(III)	~ 33%	~4 x 10 ⁻⁹ M (0.2%)	0
Pu(III)	~ 79%	~ 4 x 10 ⁻⁹ M (0.2%)	1 x 10 ⁻⁹ M
Th(IV)	~ 33%	~2 x 10 ⁻⁸ M (34%)	0
U(VI)	~ 2.5%	~1 x 10 ⁻⁸ M (0.1%)	0
*Solubilities used were those calculated for the CRA-2009 PABC			

The experiments on which the results just summarized in Table 4-6 were performed in simulated WIPP brine in the absence of organics and iron minerals (except for the Pu data). For this reason, these should be viewed as conservatively high numbers since the addition of organics, carbonate, and other colloids should result in a lowering of the steady-state intrinsic colloidal concentration. In the case of the organics and carbonate, these will complex the actinide to shift the equilibrium toward truly dissolved complexes. The presence of other colloids, e.g., mineral colloids or biocolloids should result in the association or further aggregation of the intrinsic colloids lowering their solution concentration.

5.0 WIPP-RELEVANT MICROBIAL COLLOIDS

There are two processes that contribute to the microbial colloidal factor used in WIPP PA: 1) the available mobile biomass in solution and 2) the sorption/uptake of actinides by this biomass. This was approached historically by performing oxidation-state specific biosorption experiments on microorganisms and using a combination of the toxicity threshold and highest estimates of growth under optimal conditions. The colloid enhancement parameters in the current WIPP PA model, relative to the other colloidal parameters, have the greatest effect on the concentration of mobile actinides due to their high level of conservatism. In this section we restate the literature and experimental basis for the current model, summarize new growth and biosorption data on WIPP-indigenous microorganisms, and give recommendations for updating the current microbial colloid enhancement parameters.

5.1 Basis of the CRA-2009 Microbial Colloid Enhancement Parameters

In order to generate values for the microbial contribution to the colloid source term [SOTERM, 2009], a set of experiments was conducted by A.J. Francis and colleagues [Papenguth, 1996; Francis, 1998]. This early work used a bacterium isolated from the WIPP environs (*Halomonas* sp. WIPP-1A) and a mixed culture enriched in a high-magnesium medium (BAB). These organisms were inoculated into growth media containing complexed actinides and incubated until stationary phase. Samples were then withdrawn from the fluid column and fractionated by filtration. The 0.03 μm (30 nm) filtrate represented the total dissolved actinide concentration; while, the fraction between 0.4 -10 μm was measured as the mobile, microbially-associated actinide concentration.

Growth inhibition studies were also conducted in which cultures of *Halomonas* and BAB were exposed to different concentrations of complexed actinides. The toxic dose was defined as the concentration at which growth was no longer observed.

The BAB culture was never characterized, but based on its description (survival only at high ionic strength, pink-red pigmentation, slow growth) and the likelihood that a large number of transfers had occurred since the origin of the culture that would “weed” out any Bacteria, it is assumed that it contained mostly haloarchaea. This distinction is important as only bacterial data (*Halomonas* WIPP-1A) were used to generate the microbial source term contribution, given that the faster growth rate of these organisms permitted more experiments.

A proportionality constant (PROPMIC) was generated by dividing the moles of microbially-associated actinide (0.4 μm retentate) by the moles of dissolved actinide (0.03 μm filtrate). The PROPMIC is multiplied by the expected dissolved concentration (“dissolved” term in SOTERM.79) of actinide in brine to determine the microbial contribution of the total mobile

actinide. Additionally, the toxicity data were used to generate a CAPMIC value, or the maximum concentration of actinide that can be associated with mobile (viable) microbes. If the total mobile actinide concentration is less than the CAPMIC value, then the microbial contribution equals the dissolved actinide concentration times the PROP MIC value. Otherwise, the microbial contribution equals the CAPMIC value, thus constraining the mobile actinide concentration to its association with viable biomass (see SOTERM 2009, p. 90).

A summary of PROP MIC values listed in SOTERM [originally from Papenguth, 1996a] and those published in the peer-reviewed literature by Francis et al. [Francis, 1998] are shown in Table 5-1. For SOTERM, the measurements obtained at different time points were averaged (2 for thorium, 2 for americium, and 13 for plutonium, regardless of complexant); while Francis et al. included only measurements taken at the latest sampling point. Measurements for neptunium and uranium were only considered valid at one time point, so the Francis and SOTERM values for these are the same. The same PROP MIC value is assigned for all oxidation states of each actinide in SOTERM, although where available, data are included below by oxidation state.

Table 5-1 Comparison of SOTERM-2009 and Francis et al. (1998) PROP MIC values

Actinide	Francis et al. PROP MIC (based on mean values from one time point)		SOTERM PROP MIC (mean ± sd values from >1 time points)
	Hmn*	BAB	Hmn only
Th(IV)-EDTA	4.48	0	3.1 ± 1.9
U(VI)-nitrate	0.0022	0.0019	0.0021
U(VI)-citrate	0.0039	0.0034	---
Np(IV)	nd	nd	12
Np(V)-EDTA	11.8	2.45	12
Pu(III)	nd	nd	0.3 ± 0.544**
Pu(IV)	nd	nd	0.3 ± 0.544**
Pu(V)-EDTA	0.146	0.022	0.142 ± 0.146
Pu(V)-perchlorate	--	--	0.475 ± 0.791
Am(III)-EDTA	7.67***	0.824	3.6 ± 2.45

nd = not done; *Hmn = *Halomonas* sp. WIPP-1A; **average of all Pu values for EDTA and perchlorate complexes;
***discrepancy in Francis vs. Papenguth raw data used to calculate PROP MIC

Table 5-2 provides a comparison of the listed SOTERM CAPMIC values (based on toxicity data), values calculated from the sum of Francis' data in Papenguth 1996a (3rd column), maximum adsorbed concentrations of actinides from Francis' data 1998 ("CAPMIC", 1st column), and toxicity values from Francis 1998 (2nd column).

Table 5-2 Comparison of the maximum concentrations of actinide adsorbed onto microbes (theoretical "CAPMIC", column 2) and of toxicity data from Francis et al. (1998, column 3) to the SOTERM listing of toxicity values (column 4) and the SOTERM choice of CAPMIC values (column 5).

Actinide	Francis et al. "CAPMIC" (maximum M An sorbed)*		Francis Toxicity Data (minimum concentration affecting growth)		SOTERM Toxicity Data (growth cessation)	SOTERM CAPMIC (M)
	Hmn	BAB	Hmn	BAB		
Th(IV)-EDTA	6.95 x 10 ⁻⁴	N/A	1.01 x 10 ⁻³	ne	1.90 x 10 ⁻³	0.0019
U(VI)-nitrate	2.11 x 10 ⁻⁶	2.22 x 10 ⁻⁶	2.1 x 10 ⁻³	ne	2.1 x 10 ⁻³	0.0021
U(VI)-citrate	3.78 x 10 ⁻⁶	4.20 x 10 ⁻⁶	1.05 x 10 ⁻³	ne	---	---
Np(IV)	nd	nd	nd	nd	---	0.0027
Np(V)-EDTA	2.33 x 10 ⁻⁶	2.74 x 10 ⁻⁸	5 x 10 ⁻⁵	ne	*2.65 x 10 ⁻⁴	0.0027
Pu(III)	nd	nd	nd	nd	nd	†6.8 x 10 ⁻⁵
Pu(IV)	nd	nd	nd	nd	nd	†6.8 x 10 ⁻⁵
Pu(V)-EDTA	9.24 x 10 ⁻¹⁰	1.22 x 10 ⁻⁹	ne**	1 x 10 ⁻⁵	*8 x 10 ⁻⁶	---
Pu(V)-perchlorate	---	---	---	---	8.8 x 10 ⁻⁶	---
Am(III)-EDTA	1.22 x 10 ⁻⁸	4.72 x 10 ⁻⁸	5 x 10 ⁻⁶	5 x 10 ⁻⁶	*2.65 x 10 ⁻⁶	1.0

ne = no effect; nd = not done; *concentration at which slight effect on growth observed; **discrepancy between Francis' published data and Papenguth; †source of value unconfirmed

The CAPMIC approach was problematic for americium, where restrictions on the amount that could be used prevented a toxic concentration from being reached. Therefore, no Am CAPMIC value was assigned in SOTERM 2004, but SOTERM 2009 assigns a value of 1M. In the case of Np, where growth cessation was not observed, an order of magnitude was added onto the highest measured dissolved concentration. In the case of Pu, the source of the toxic concentration value was reportedly extrapolated from cell number data with an order of magnitude added, although this number cannot be confirmed from the raw data [Papenguth, 1996a].

5.2 Assessment of Current Microbial Enhancement Parameters

SOTERM Assumptions

Because little was understood about WIPP microbial ecology at that time, assumptions were made in PA regarding microbe-actinide associations. Given our current level of understanding, it is evident that these assumptions lend a large amount of conservatism to the model. As such, it is appropriate to revisit these assumptions. The three chief assumptions are: 1) all microbial cells are viable and growing optimally; 2) all viable cells are fully saturated with biosorbed actinides; and 3) all cells are mobile.

The first two assumptions will be addressed in more detail below. Assumption 1 requires a review of microbial halophilism and what is currently known of the microbial ecology at the WIPP site. This review will explain how the microbes themselves inherently lend an incredible amount of conservatism to the model without anthropogenic input. Assumption 2 requires a continued microbiology review and a review of the sorption-related data generated to date. The third assumption will be addressed briefly

Review of Assumption 1: all cells are viable and growing optimally

Several factors will influence microbial survival in the WIPP, including ionic strength, pH, atmospheric conditions, moisture, and substrate and nutrient type and availability. However, the chief determinant of microbial survival and diversity in the WIPP environs is ionic strength; more specifically [Na] and [Mg] in the brine.

In order to survive in hypersaline systems, microorganisms must maintain osmotic balance between their internal and external environments. This is done in one of two ways: 1) by importing K^+ and often Cl^- into the cell interior and 2) by a combination of K^+ import and the synthesis or uptake of small organic molecules known as “compatible” solutes. The first mode is used by halophilic *Archaea* of the Family *Halobacteriaceae* and some few *Bacteria* and is much less costly energetically than the second mode, used by eukaryotes and all other *Bacteria*. Because of the high cost of the second mode, *Bacteria* are less likely to survive at high ionic strengths (i.e. > 2.5 M NaCl) [Oren, 2011].

In light of this, significant differences are expected between the microbial populations in the WIPP near-field (delineated by the immediate repository “soup”) versus intermediate-field (herein defined as the area of mixing of repository “soup” and Culebra groundwaters) versus far-field environments (Culebra groundwaters) that reflect the variation in ionic strength in these spaces. This is supported by the current microbial characterization data.

It is important to make the distinction between haloarchaea and *Bacteria* because they utilize different substrates and exhibit different modes of metabolism, thus affecting their ability

to grow. Haloarchaea are predominantly aerobic organisms, although the ability to ferment small molecules, such as amino acids, and the ability to reduce nitrate has also been shown. WIPP haloarchaea have been shown to utilize acetate, oxalate, and citrate under aerobic conditions; and while a *Halomonas* culture was also able to utilize acetate and citrate aerobically, it could only do so in diluted brines [Swanson, 2012b]. *Halomonas* WIPP-1A was capable of nitrate reduction; however, its ability to utilize complexing agents was not tested. Halophilic bacteria from the Culebra have a larger repertoire of metabolic capabilities, including aerobic respiration, nitrate-reduction, iron-reduction, sulfate-reduction, and fermentation (Swanson, 2013a). However, as ionic strength increases in these groundwaters, the structural and functional diversity of *Bacteria* decreases.

Additionally, there is the question of whether microorganisms introduced into the WIPP in emplaced waste should be considered as potential sorbents. While sampling actual waste has not been possible, earlier studies were conducted on organisms cultivated from “laboratory environs” [Francis, 1994]. None of these organisms was able to survive in briny media, and for the purposes of PA, these organisms will not be considered. Most will lyse and serve as a finite nutrient source for grazing halophiles. Those resistant to lysis will likely be spore-formers that can admittedly be capable of long-term survival in harsh environments. Still, it is highly unlikely that they will germinate and grow under the given conditions. For example, a halophilic *Virgibacillus* sp. isolated from a shallow WIPP well preferred [NaCl] of 1.3 M and sporulated at concentrations above 3.4 M and under anaerobic conditions.

In conclusion, conditions will not be optimal for haloarchaeal growth in the WIPP and will be destructive to most *Bacteria*. Haloarchaeal longevity is well-documented, but once anaerobic conditions prevail, biomass concentrations will decrease. Even in the worst case scenario, assuming all cells are viable and growing, biomass concentrations cannot increase indefinitely. In optimal growth media, numbers of haloarchaea reached between 10^8 - 10^9 cells per mL, an increase of only two orders of magnitude from the original inoculum concentration. Given that most halite sampled contains no cells [McGenity, 2000; current work] and interstitial brines contain between 10^4 - 10^7 cells/mL [Francis, 1994], chances are slim that numbers will go above 10^9 cells/mL.

Review of Assumption 2: Viable cells are fully saturated with biosorbed actinides

Another reason to distinguish between halophilic *Archaea* and *Bacteria* is the difference in their cell wall structures and the impact that may have on actinide sorption. As cells die, cell wall integrity is compromised. This change in wall structure changes the potentially reactive surface area presented to the actinide in bulk solution. Second, *Archaea* do not possess the same cell wall structure as *Bacteria*, and this may present a different type of surface with different

functional groups to metals. This difference is clearly reflected in the available data [Francis, 1998; and current data), where *Archaea* sorb less actinides than *Bacteria*.

A second, and larger, reason to readdress assumption 2 is actinide solubility. PA assumes that undissolved actinides will become part of the colloidal fraction, hence CAPMIC values for both humics and microbes may exceed actual solubility (see Table 5-3). While it is possible for precipitating metals to impinge upon microbial surfaces and for microbes to become nucleation sites, it is also likely that once that happens, the resulting colloid will be precipitate from solution and/or the cell will die. In reality, metal biosorption is dependent upon the actual solution concentration presented to microbial surfaces.

Actinide solubility in WIPP brines is low (see Table 5-3), thus decreasing the amount of potential exposure to microorganisms either for sorption or to elicit a toxic response. As with lowering biomass concentrations, the solubility itself may limit the amount of actinides that can be biosorbed and this limitation may be more constraining than the CAPMIC value.

Thus, actinide solubilities are important to consider for assumption 2 and for CAPMIC values. Table 5-3 shows calculated actinide solubilities in both Salado and Castile brines (Brush et al., 2009) as compared to SOTERM CAPMIC values.

Table 5-3 Actinide solubilities as compared to SOTERM CAPMIC values.

ACTINIDE	BRINE	PAVT 1999	PABC 2004	PABC 2009	SOTERM CAPMIC (M)
An(III)	Salado (high Mg)	1.2×10^{-7}	3.9×10^{-7}	1.7×10^{-6}	6.8×10^{-5} (Pu) 1 (Am)
An(III)	Castile (NaCl)	1.3×10^{-8}	2.9×10^{-7}	1.5×10^{-6}	
An(IV)	Salado (high Mg)	1.3×10^{-8}	5.6×10^{-8}	5.6×10^{-8}	1.9×10^{-3} (Th) 2.7×10^{-3} (Np) 6.8×10^{-5} (Pu)
An(IV)	Castile (NaCl)	4.1×10^{-9}	6.8×10^{-8}	6.98×10^{-8}	

Two questions should be addressed: 1) is the actual soluble concentration of the actinide species toxic to the microorganisms, and 2) is it reasonable to assign a CAPMIC value that exceeds actinide solubility? The first question is difficult to answer with the current data, since toxicity tests were not performed based on oxidation state, and oxidation state-specific toxicity has been shown previously [Banaszak, 1998]. In general, strongly hydrolyzed or complexed

species, which is the predicted speciation of most actinides at WIPP-related conditions, are not chemically toxic. Furthermore, the system used to generate CAPMIC data was lower in ionic strength than actual WIPP brines, such that solubilities may have actually been higher.

In the case of americium, a slight decrease in growth was elicited at 2.7×10^{-6} M, a concentration slightly higher than americium solubility in WIPP brine. This is likely the result of radiolytic and not chemical activity due to the relatively high activity of americium. In the case of thorium, soluble concentrations are five orders of magnitude lower than those found to affect cell growth. The plutonium CAPMIC was increased by an order of magnitude in SOTERM to account for uncertainty. Finally, precipitation was observed in the uranium studies, suggesting that the CAPMIC (0.0021) exceeds solubility significantly.

Review of Assumption 3: all cells are mobile

Although cells are predominantly found attached to surfaces in nature, very little research has been done on biofilm formation by halophilic microorganisms, especially haloarchaea [Fröls, 2012]. Should haloarchaea be mobilized in the event of an intrusion, it is probable that most of them will lyse as they reach lower ionic strength groundwaters (e.g. *Halobacterium noricense* cannot survive below 2.1 M; [Gruber, 2004]). It is likely that Culebra groundwater organisms form biofilms, a common strategy that allows microorganisms to retain substrates and nutrients while offering protection from the external environment (e.g. increased salt concentrations). However, because this has not been studied extensively, it is probably prudent to keep this assumption and its associated level of conservatism.

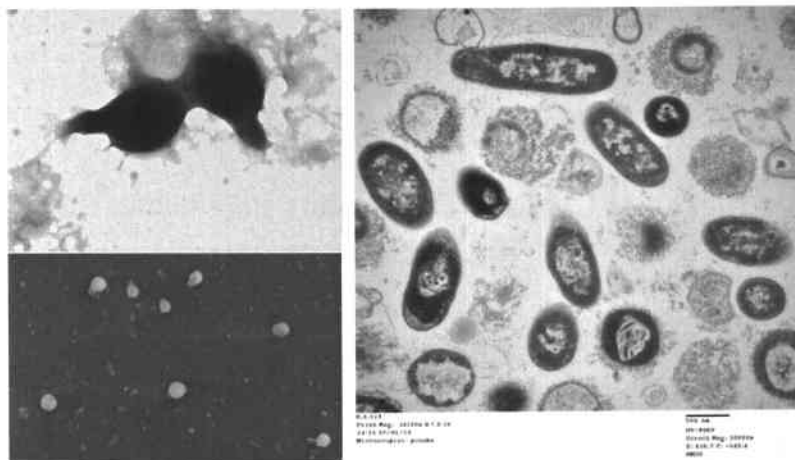
5.3 Microbial Colloid Experiments Performed Since the CCA

Experiments performed by the LANL-CO ACRSP team under the Test Plan entitled “Microbial Interactions in the Waste Isolation Pilot Plant” and designated LCO-ACP-12 are summarized in this Section. These experiments were focused on the biosorption of the two most important actinide oxidation states, Nd(III) for An(III) and Th(IV) for An(IV), towards a representative halophilic bacteria and archaea. Redox-invariant analogs were used so that there was no question about the oxidation state being sorbed. These biosorption data are used to recalculate the PROPMIC microbial colloid enhancement parameter, and, when combined with laboratory observations of microbial growth under WIPP-relevant conditions, a biomass-based CAPMIC value (see Section 5.4).

5.3.1 Experimental Approach

Selection of Microorganisms

The microorganisms used in the LANL-CO biosorption experiments are indigenous to the WIPP area and are shown in Figure 5-1. The bacterium used, *Chromohalobacter* sp., was isolated from brine retrieved from a shallow subsurface monitoring well incubated under aerobic conditions [Swanson, 2012a; Ams, 2013]. The origins of this water are believed to be a mixture of seepage from an above-ground, but capped, mine tailings salt pile and actual groundwater flow through the Santa Rosa and Dewey Lake contact (WIPP ASER, 2010). Since then, this bacterium has also been isolated from incubations of WIPP halite at lower salt concentrations, and a Culebra groundwater incubated under aerobic, transitional, and nitrate-reducing conditions. It grows in media containing between 0.9-4.3 M NaCl and will not grow in the absence of salt, classifying this organism as a borderline extreme halophile (Oren, 2008). *Chromohalobacter* sp. tolerates pH between 5-9 with an optimum between 6-8. For the experiments, *Chromohalobacter* sp. is grown aerobically in trypticase soy broth (30g/L) with yeast extract (5 g/L) and NaCl (200 g/L) in an incubator-shaker (37°C, 200 rpm). Cells are harvested at early stationary phase (day 4). This organism is considered representative of the far-field environment.



Halobacterium noricense

Chromohalobacter sp.

Figure 5-1 TEM micrographs for selected microorganisms:

Chromohalobacter sp.: a bacteria isolated from area groundwater, borehole seep, and halite; strain used tolerates pH 5-9, 0.9-4.3 M NaCl; 0.3-0.5 x 1.5-2 µm size.

Halobacterium noricense: archaea 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 pH 6-10; 0.3-1.5 x 0.3-1.5 µm size

The archaeon used for the LANL-CO biosorption experiments, *Halobacterium noricense*, was isolated from WIPP halite incubated under aerobic conditions [Swanson, 2012a]. This same organism has also been isolated from subsurface halites in Austria, Germany, Poland, the United Kingdom, Brazil, and Turkey. It is an extreme halophile, requiring 2.5-5 M NaCl for growth. It tolerates a pH of 6-10, and lysis has been noted below pH 5. *Hbt. noricense* is grown in a semi-defined medium containing the following in g/L: NaCl, 200; yeast extract, 2.5; casamino acids, 2.5; soluble starch, 0.2; MgCl₂·6H₂O, 20; KCl, 2.0; CaCl₂·2H₂O, 0.2; sodium pyruvate, 0.08; and trizma base, 0.24. Cells are harvested at early stationary phase (day 7). This organism is considered representative of the near-field environment.

Both organisms were identified based on a comparison of their small subunit (16S) ribosomal RNA-encoding gene sequence to those in international databases.

WIPP Brine Chemistry

Historically, ACRSP experiments were performed using the WIPP “bracketing” brines, GWB and ERDA-6 at 95% of their saturated formulation [Borkowski, 2008/2012; Lucchini 2010/2013a; Reed, 2010]. In the biosorption experiments, however, transitional pH-specific brine formulations were used. These transitional brines are WIPP-relevant simulated brines that were established based on the results of the brine titration experiments reported in the WIPP Actinide-Relevant Brine Chemistry report [Lucchini, 2013b]. An average composition of the WIPP-relevant simulated brine was determined at each pC_{H+} value in the range of 8-13, with a 100% saturated formulation.

The four WIPP-relevant simulated brines selected for the biosorption experiments were: pC_{H+} 8.5, 9, 9.5 and 9.7. These brines were prepared at 90% of the saturated formulation, in order to avoid any possible precipitation effect during the biosorption experiments. The composition of these 90% saturated formulation brines are shown in Table 5-4 for each pC_{H+} value. The preparation of the brines was done according to the ACRSP procedure ACP-EXP-001, “Brine Preparation”. The biosorption experiments were conducted in a nitrogen controlled-atmosphere glovebox, at 25±3°C.

Overall Approach: Biosorption Studies

A few days prior to the biosorption experiments, metal (Nd³⁺ or Th⁴⁺) stock solutions were prepared in the desire pC_{H+} brines to allow equilibration. The concentrations of the stock solutions were 4×10⁻⁸M for Nd³⁺ and expected to be below the solubility limits based on previous studies in similar systems [Borkowski, 2008]. The initial concentration used in the Th⁴⁺ experiments was less straightforward and varied with pH. For thorium, as described in Borkowski et al. [Borkowski, 2012], the thorium system is dominated by small (<10 nm)

colloidal species that take months to equilibrate. The experimental approach was to add an excess of thorium, typically to 0.1 mM concentrations in each pC_{H^+} -specific brine, allow this to pre-equilibrate, and then filter with a 100 kDalton (~20 nm) filter prior to use. With this approach the initial concentration was typically in the range of 10^{-6} to 10^{-7} M and decreased with increasing pH.

Table 5-4 Compositions of the WIPP-relevant brine used in the biosorption experiments as a function of pC_{H^+} . These brines were prepared at 90% of their saturated formulations determined [Lucchini, 2013].

pC_{H^+}	Element/Species - Measured Concentrations (M)								
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Li ⁺	B ₄ O ₇ ²⁻	Cl ⁻	SO ₄ ²⁻	Br ⁻
8.5	3.18E+00	4.20E-01	9.18E-01	1.24E-02	4.03E-03	3.56E-02	5.04E+00	1.59E-01	2.39E-02
9.0	3.15E+00	4.12E-01	9.27E-01	1.22E-02	3.38E-03	3.50E-02	4.89E+00	1.58E-01	2.12E-02
9.5	3.35E+00	4.13E-01	7.65E-01	1.18E-02	3.33E-03	1.48E-02	5.00E+00	1.58E-01	2.18E-02
9.7	4.12E+00	4.01E-01	1.16E-01	1.20E-02	3.20E-03	2.52E-03	4.84E+00	1.51E-01	2.07E-02

Metal- EDTA stock solutions were also prepared the same way, with an excess of EDTA ligand equal or greater than 2. Prior to the beginning of the experiments, the metal stock solutions and/or metal-ligand stock solutions were filtered using 0.22 μ m filtration for the neodymium experiments or ~20nm (100kDa) pore size filtration for the thorium studies to remove pre-existing colloids. For the neodymium experiments, the presence of EDTA formed a complex that did not alter the total concentration of neodymium in solution – so only the speciation was changed. In the case of thorium, a metastable EDTA complex persisted for weeks in time at a concentration of ~ 0.01 mM in the lower pH stock solutions (pC_{H^+} 8.5 and 9) but was unstable and slowly precipitated in the two highest pH brines (pC_{H^+} 9.5 and 9.7). This instability could not be avoided and made some of the data interpretation somewhat difficult as both sorption and precipitation was occurring simultaneously at the highest pH values. For this reason, the lower-pH data was preferentially used to evaluate the extent of biosorption.

Microorganisms (*Halobacterium noricense* or *Chromohalobacter sp.*) were pelleted by centrifugation at 9000 revolutions per minute (rpm), and rinsed three times with 4M NaCl. They were then pelleted by centrifugation at 9000rpm for 30 minutes to remove excess of water to obtain a wet weight. Suspension of the microorganisms in the desired pC_{H^+} brines was done to get a concentration of 20g/L (wet weight).

The biosorption experiments were initiated when defined volumes of metal (or metal-ligand) stock solutions and microorganisms solutions (and possibly brine) of the same pC_{H^+} were mixed together to achieve the following conditions: $\sim 2 \times 10^{-8} M$ for Nd^{3+} , or 0.5 to 0.005 micromolar amounts of Th^{4+} (depending on pH), and approximately 10g/L at maximum (wet weigh) of microorganism concentration. The reaction vessels were slowly agitated for 2 hours to ensure homogenization of the mixture and to reach equilibrium. Duplicate samples were then centrifuged and filtered using $\sim 20nm$ (100kDa) pore size filters, to remove the microorganisms from the systems. The filtered supernatants were diluted $\times 100$ times in 2% HNO_3 for Nd/Th analysis using ICP-MS, according to procedure ACP-EXP-011, Analysis of Solutes in Brine Using the Agilent ICP-MS. The precision and accuracy of the ICP-MS analyses were determined by having replicate samples and analyzing check standards throughout the analyses (every 10 samples analyzed). An internal standard (indium) was used to account for variations in matrix effects. Overall, the error in the ICP-MS analyses was about $\pm 15\%$ for the Nd^{3+} studies, and $\pm 15-25\%$ for the Th^{4+} studies, depending on the pH. All of these experiments were performed under the LANL-CO Quality Assurance Program as Quality Level 1 experiments.

The pH of the experimental solutions was also measured using the procedure ACP-EXP-010, Determination of Hydrogen ion Concentrations in Brine. The measured pH values, typically with a Ross semi-micro combination electrode, were corrected to obtain the corresponding pC_{H^+} values, using the correction factors based on the ionic strength calculated from the measured concentration of the brine components and the correction factors determined experimentally by ACSP for WIPP-simulated brines [Lucchini, 2013b]. The pC_{H^+} values were measured with an uncertainty of ± 0.1 pH unit and corrected for ionic strength.

Abiotic control experiments, analogous to the biosorption experiments, were performed to account for all possible other losses of metal in solutions (retention on the filters, sorption on vessel walls, etc.).

5.4 Biosorption of Nd(III) and Th(IV) Towards Halophilic Microorganisms

Experiments performed with Nd(III) and Th(IV) are summarized in this Section. Similar experiments with the halophilic bacterium *Chromohalobacter sp.* were also completed and are published [Ams, 2013].

5.4.1 Biosorption of Nd(III)

The biosorption experiments for An(III) were performed using neodymium as the redox-invariant analog. They were performed in WIPP relevant brines (90% of saturated formulation

determined in the Brine Chemistry experiments – see Table 5-4) at different pC_{H^+} values between 8.5 and 9.7, using an initial concentration of neodymium of 20nM and 10g/L of microorganisms (*Chromohalobacter* sp. or *Halobacterium noricense*).

The experimental data related to the *Chromohalobacter* sp. systems are plotted in Figure 5-2 and Figure 5-3. The experimental data obtained in the *Halobacterium noricense* systems are plotted in Figure 5-4 and Figure 5-5. Figure 5-2 and Figure 5-4 give the concentrations of neodymium (in μM) measured in the presence or the absence of EDTA as a function of measured pC_{H^+} , in biotic and abiotic conditions after 2 hours of equilibration. The difference in the results between the biotic and the abiotic conditions at a certain pC_{H^+} gives the contribution of the micro-organisms on the adsorption of neodymium. In Figure 5-3 and Figure 5-5, the percent of adsorption of neodymium is depicted versus measured pC_{H^+} . The numerical values of the concentrations of neodymium measured in these experiments are given in Table 5-5.

***Chromohalobacter* sp. Biosorption**

The adsorption of neodymium on the *Chromohalobacter* sp. surface increases as pC_{H^+} increases: from ~33% at $pC_{H^+} \sim 8.7$ to ~66% at $pC_{H^+} \sim 9.4$. The same trend is observed in the presence of EDTA: from ~16% at $pC_{H^+} \sim 8.7$ to ~40% at $pC_{H^+} \sim 9.4$. Even though the strong complexation expected between Nd(III) and EDTA should have out-competed the sorption of the metal on the microorganisms, we are still observing a loss of neodymium in solution when EDTA is present in excess. It is highly possible that hydrolysis of neodymium (leading to colloidal precipitation) is still significantly influencing the speciation of neodymium during the 2-hour period of the experiments, in the presence or the absence of the microorganisms, despite the pre- and post-filtrations performed on the solutions to remove colloids. The effect of the biomass load was investigated, in the absence or in the presence of an excess of EDTA (Figure 5-6, Figure 5-7 and Figure 5-8). When the biomass decreases, the loss of Nd in solution is less important, particularly in the presence of complexant. The extrapolation of the data to zero biomass show that hydrolysis can account for ~35% of the Nd loss at $pC_{H^+} \sim 9.4$ in the absence of EDTA, and for ~12% of the Nd loss at $pC_{H^+} \sim 8.9$ in the presence of an excess of EDTA. Overall, whatever the contribution of Nd precipitation can be, the present data on the adsorption of neodymium on *Chromohalobacter* sp. are very conservative, in a WIPP PA point of view.

***Halobacterium noricense* Biosorption**

As expected, the adsorption of neodymium on the *Halobacterium noricense* surface also increases as pC_{H^+} increases, but this effect is less important than with the *Chromohalobacter* sp. : from ~22% at $pC_{H^+} \sim 8.5$ to ~48% at $pC_{H^+} \sim 9.3$. The same trend is observed in the presence of EDTA, but only for $pC_{H^+} \geq 9.1$: ~5% at $pC_{H^+} \leq 9.1$ and ~23% at $pC_{H^+} \sim 9.2$. The EDTA complex

of Nd is here clearly out-competing the sorption of the metal on the microorganisms, at least at $pC_{H^+} \leq 9.1$. In the absence of a strong complexant, further hydrolysis could lead to precipitation of some neodymium causing a decrease in the neodymium concentration during the 2-hour period of the experiments. This can occur in the presence or the absence of the microorganisms and despite the pre- and post-filtrations performed on the solutions to remove colloids. If we take into consideration the data obtained during the biomass load investigation (see *Chromohalobacter* sp. systems section), the biosorption of Nd onto *Halobacterium noricense* appears relatively minor (less than 15%).

Table 5-5 Concentration of neodymium measured in carbonate-free brines (90% saturated composition) at different pC_{H^+} values, in the absence or the presence of an excess of EDTA, in biotic and abiotic conditions after 2 hours of equilibration. These data are plotted in Figure 5-2, Figure 5-3, Figure 5-4 and Figure 5-5.						
Ligand	<i>Chromohalobacter</i> sp. (bacteria)			<i>Halobacterium noricense</i> (archaea)		
	pC_{H^+}	Average measured concentrations of Nd in solutions (M)		pC_{H^+}	Average measured concentrations of Nd in solutions (M)	
		Abiotic (Controls)	Biotic		Abiotic (Controls)	Biotic
Cl ⁻	8.7	2.6E-08	1.76E-08	8.5	4.0E-08	3.1E-08
Cl ⁻	9.4	3.1E-08	1.03E-08	9.1	1.09E-07	6.29E-08
Cl ⁻	9.7 → 9.4	2.3E-08	1.1E-08	9.3	4.2E-08	2.19E-08
EDTA	8.7	2.6E-08	2.15E-08	8.5	2.5E-08	2.42E-08
EDTA	9.4	2.7E-08	1.59E-08	9.1	2.5E-08	2.43E-08
EDTA	9.7 → 9.3	2.4E-08	1.44E-08	9.2	2.4E-08	1.86E-08

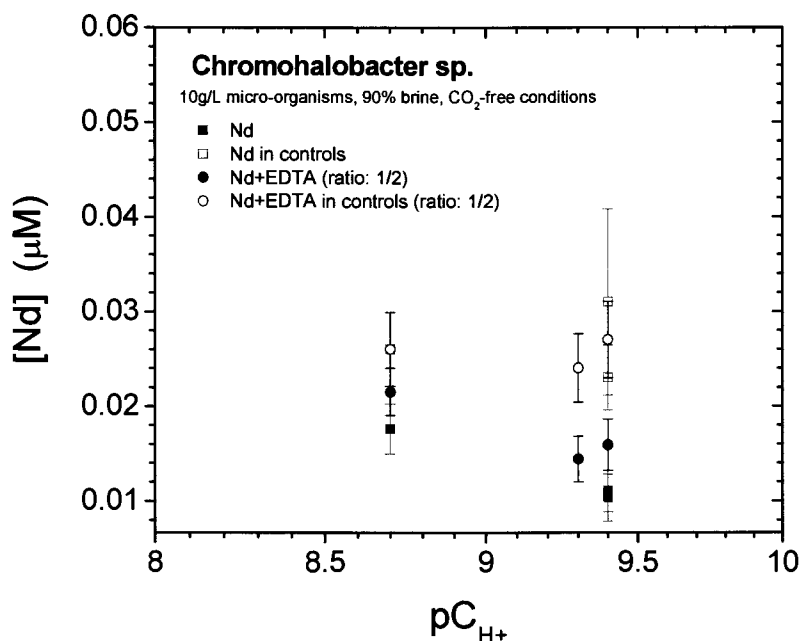


Figure 5-2 Concentration of neodymium measured in carbonate-free brines (90% saturated composition) at different pC_{H+} values, in the presence (green symbols) or the absence (pink symbols) of EDTA, in biotic (full symbols) and abiotic (open symbols) conditions after 2 hours of equilibration.

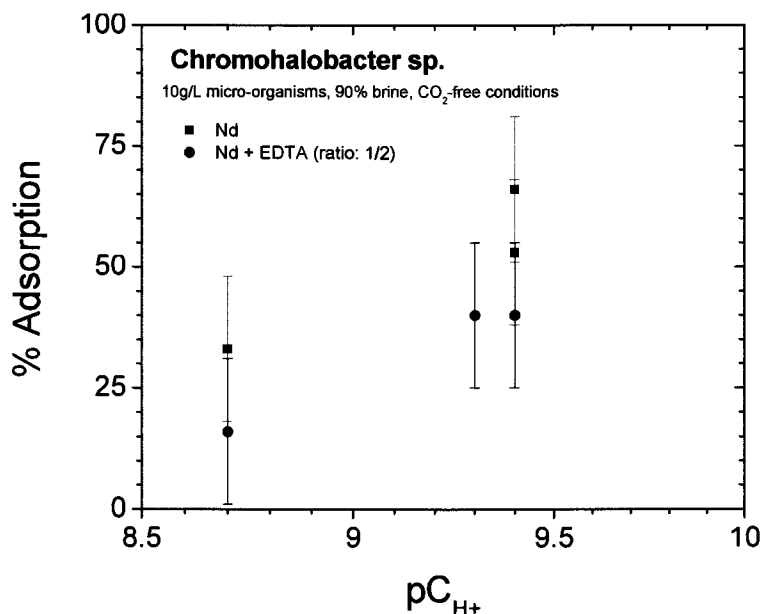


Figure 5-3 Adsorption of neodymium (in %) measured in carbonate-free brines (90% saturated composition) at different pC_{H+} values, in the presence (green symbols) or the absence (pink symbols) of EDTA.

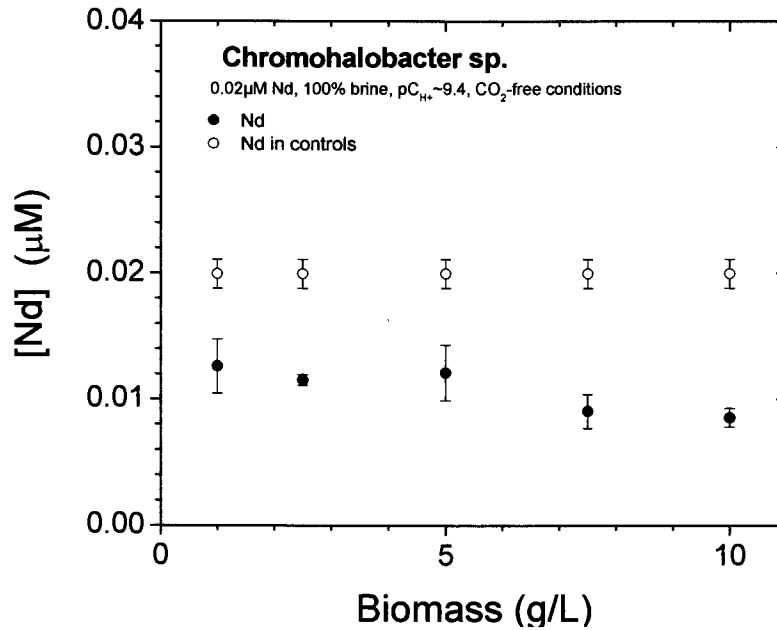


Figure 5-4 Concentrations of neodymium measured in carbonate-free brines (90% saturated composition) as a function of biomass at $pC_{H^+} \sim 9.4$, in the absence of EDTA, in biotic (full symbols) and abiotic (open symbols) conditions after 2 hours of equilibration.

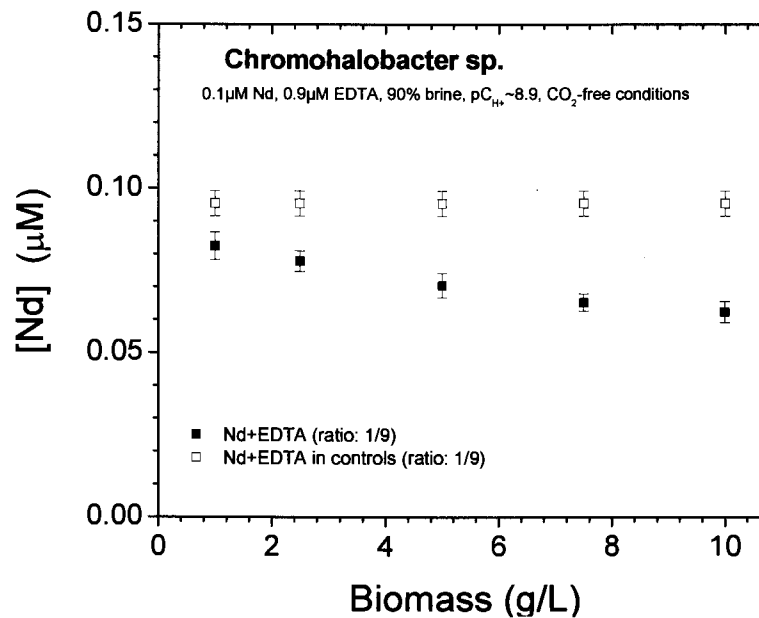


Figure 5-5 Concentrations of neodymium measured in carbonate-free brines (90% saturated composition) as a function of biomass at $pC_{H^+} \sim 8.9$, in the presence of EDTA, in biotic (full symbols) and abiotic (open symbols) conditions after 2 hours of equilibration.

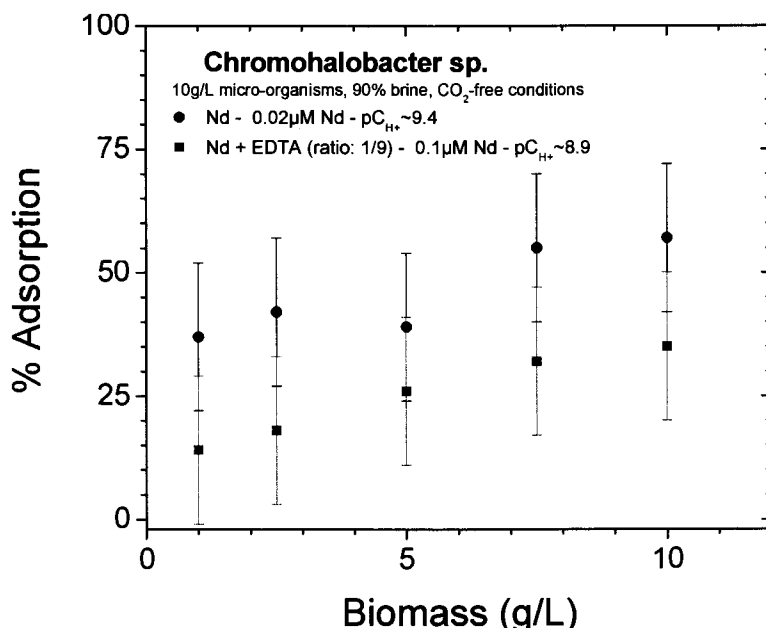


Figure 5-6 Adsorption of neodymium (in %) measured in carbonate-free brines (90% saturated composition) as a function of biomass, in the presence (pink symbols) or the absence (green symbols) of EDTA.

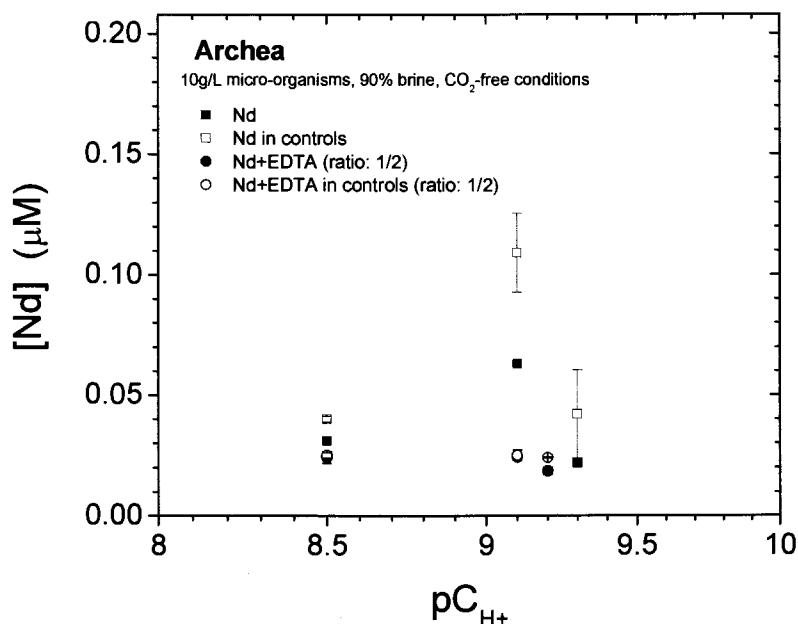


Figure 5-7 Concentrations of neodymium measured in carbonate-free brines (90% saturated composition) at different pC_{H+} values, in the presence (green symbols) or the absence (pink symbols) of EDTA, in biotic (full symbols) and abiotic (open symbols) conditions after 2 hours of equilibration.

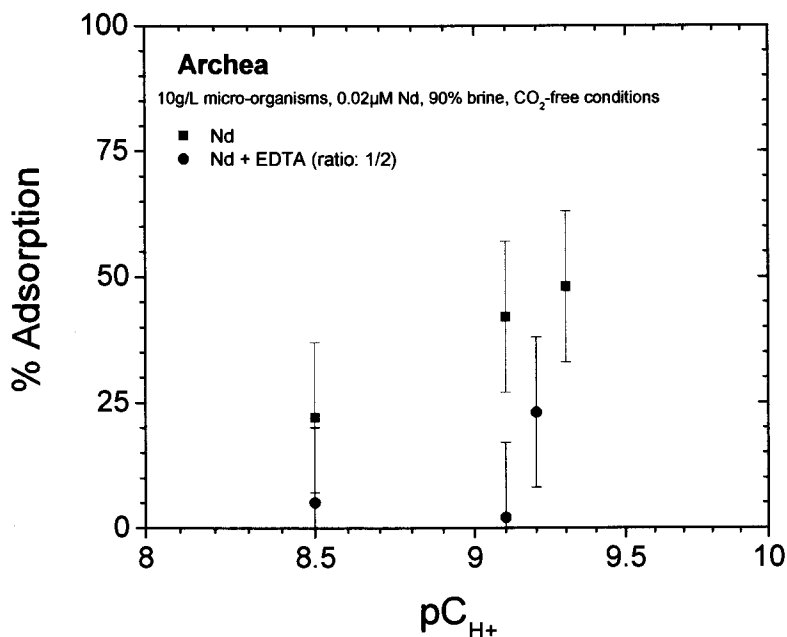


Figure 5-8 Adsorption of neodymium (in %) measured in carbonate-free brines (90% saturated composition) at different pC_{H+} values, in the presence (green symbols) or the absence (pink symbols) of EDTA.

5.4.2 Biosorption of Th(IV) as an Analog for An(IV)

The An(IV) oxidation state is critical to WIPP PA and, for this reason, it was important to re-assess the biocolloid enhancement parameter for this oxidation state. Microbial surfaces, especially under anoxic conditions, can induce redox reactions in multivalent actinides so it is important to use redox-invariant analogs, as is the case in our solubility studies. In this context, both Np(IV) and Th(IV) were evaluated for the planned biosorption experiments, but in the end Th(IV) was selected due to its somewhat higher, albeit metastable, solubility at the higher pH range of interest. It was also not possible to eliminate the oxidation of Np(IV) to Np(V) even under anoxic conditions making the interpretation of the results obtained difficult. Overall, the experimental approach used for these experiments is the same as that used for the +3 actinide analog just described.

The experimental matrices for the thorium biosorption experiments are shown in Tables 5-6 and 5-7. In many cases only one of the higher pH values were used (either pC_{H+} 9.5 or 9.7) - not both. These experiments will be performed in pH-specific brines with a representative halobacteria (*Chromohalobacter sp.*) and archaea (*Halobacterium noricense*). The general procedure is to mix equal amounts of pre-filtered thorium and high biomass brine, shake for ~ 2 hours, filter, and re-measure the thorium concentration. The amount sorbed is the difference between the starting concentration and the amount left in solution after sorption has occurred.

Table 5-6 Experimental Matrix: Biosorption of Th(IV) onto Bacteria (<i>Chromohalobacter sp.</i>)		
Experiment Designation	Description	Comment
B-Th4-85-1,2,B	Thorium (IV) in $pC_{H^+} \sim 8.5$ Brine	1,2 are replicates, B is bio-blank
B-Th4-9-1,2,B	Thorium (IV) in $pC_{H^+} \sim 9$ Brine	1,2 are replicates, B is bio-blank
B-Th4-97-1,2,B	Thorium (IV) in $pC_{H^+} \sim 9.7$ Brine	1,2 are replicates, B is bio-blank
B-Th4-E85-1,2,B	Thorium (IV) in $pC_{H^+} \sim 8.5$ Brine with $\sim 10^{-5}$ M EDTA	1,2 are replicates, B is bio-blank
B-Th4-E9-1,2,B	Thorium (IV) in $pC_{H^+} \sim 9$ Brine with $\sim 10^{-5}$ M EDTA	1,2 are replicates, B is bio-blank
B-Th4-E97-1,2,B	Thorium (IV) in $pC_{H^+} \sim 9.7$ Brine with $\sim 10^{-5}$ M EDTA	1,2 are replicates, B is bio-blank

Table 5-7 Experimental Matrix: Biosorption of Th(IV) onto Archaea (<i>Halobacterium noricense</i>)		
Experiment Designation	Description	Comment
A-Th-85-1,2,B	Thorium (IV) in $pC_{H^+} \sim 8.5$ Brine	1,2 are replicates, B is bio-blank
A-Th-9-1,2,B	Thorium (IV) in $pC_{H^+} \sim 9$ Brine	1,2 are replicates, B is bio-blank
A-Th-95-1,2,B	Thorium (IV) in $pC_{H^+} \sim 9.5$ Brine	1,2 are replicates, B is bio-blank
A-Th-97-1,2,B	Thorium (IV) in $pC_{H^+} \sim 9.7$ Brine	1,2 are replicates, B is bio-blank
A-Th-E85-1,2,B	Thorium (IV) in $pC_{H^+} \sim 8.5$ Brine with $\sim 10^{-5}$ M EDTA	1,2 are replicates, B is bio-blank
A-Th-E9-1,2,B	Thorium (IV) in $pC_{H^+} \sim 9$ Brine with $\sim 10^{-5}$ M EDTA	1,2 are replicates, B is bio-blank
A-Th-E95-1,2,B	Thorium (IV) in $pC_{H^+} \sim 9.5$ Brine with $\sim 10^{-5}$ M EDTA	1,2 are replicates, B is bio-blank
A-Th-E97-1,2,B	Thorium (IV) in $pC_{H^+} \sim 9.7$ Brine with $\sim 10^{-5}$ M EDTA	1,2 are replicates, B is bio-blank

Dependency of Th(IV) Sorption on Biomass

The dependency of the measured sorption of Th(IV) on biomass and stability of the post-filtration control for thorium was determined for *Chromohalobacter sp.* and *Halobacterium noricense*. These data are shown in Figures 5-9 and 5-10.

The stability of the thorium in the controls is shown in Figure 5-9. Even with pre-equilibration and pre-filtration with a 100 kDa filter (~20 nm), the thorium controls were not well-behaved and continued to precipitate at the highest pH brines evaluated. This is consistent with the long-term studies of the thorium system [Borkowski, 2012] and appears to be an unavoidable complication of this experimental approach. This was also observed in the Np(IV) system that was initially evaluated for these studies along with thorium, and will likely extend to all of the An(IV) species in the higher pH brine systems. This issue was re-examined, as a function of initial and final filtration for *Halobacterium noricense*. These data are summarized in Table 5-8 and show that even with 2.5 nm pre-filtration there is a continued precipitation of the thorium. This instability complicates the interpretation of the biosorption data at the higher pH brine systems investigated and supports a heavier weighting of the lower-pH data where the system is better behaved.

To further establish the prevalence of sorption vs. precipitation the biomass dependency was determined for the bacteria and archaea at various pC_{H+} values. In these cases, same- pC_{H+} experiments were performed where the only variable was the biomass loading of the system. These data are shown in Figure 5-10 for both *Chromohalobacter sp.* and *Halobacterium noricense*. These are two important observations from these data. First, the biomass dependency trends of the archaea, but not the bacteria, are well-behaved. This interesting result appears to indicate that the interaction between residual colloidal Th(IV) in these systems is stronger for the bacteria than in the case of the archaeon. We do not have enough data to fully explain these results. The second observation is that there is evidence of continued precipitation at the higher pH experiments leading, in some cases, to lower sorption with increased biomass. These are, in this context, consistent with the concentration data that show unavoidable coupling at the higher pH conditions evaluated.

The combined effect of the concentration and biomass dependency data is that increased reliance should be on the lower- pC_{H+} data and, to a lesser extent, on the archaea rather than bacteria data. This focus sufficiently minimizes, but does not eliminate, the coupling of precipitation and sorption as well as the differences in the interactions of colloidal vs. dissolved thorium species.

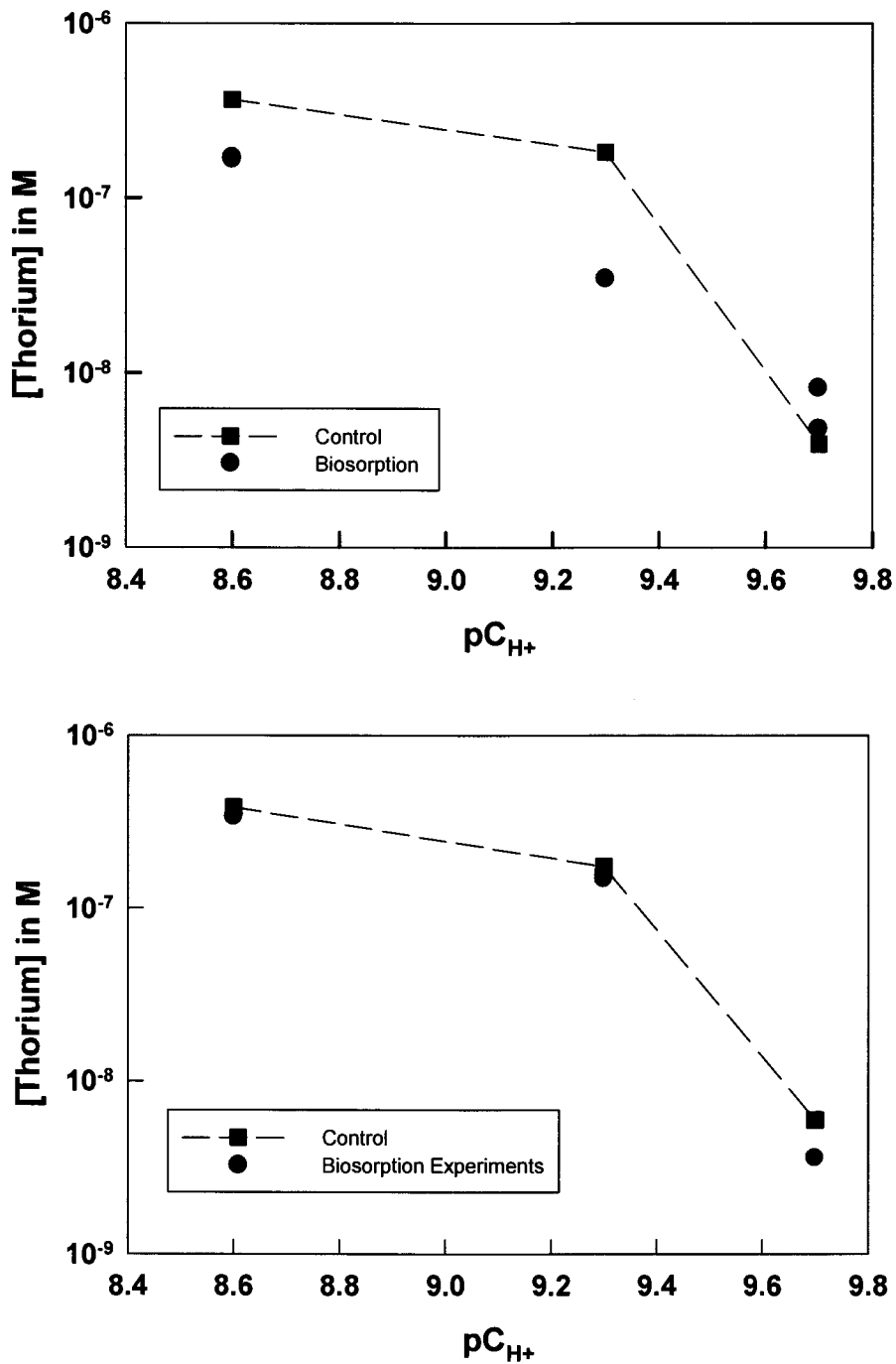


Figure 5-9 Concentration of thorium in the control and sorption experiments as a function of pC_{H+} for *Chromohalobacter sp.* (top) and *Halobacterium noricense* (bottom). More scatter and “inversion” was noted at the highest pH indicating coupled precipitation and sorption.

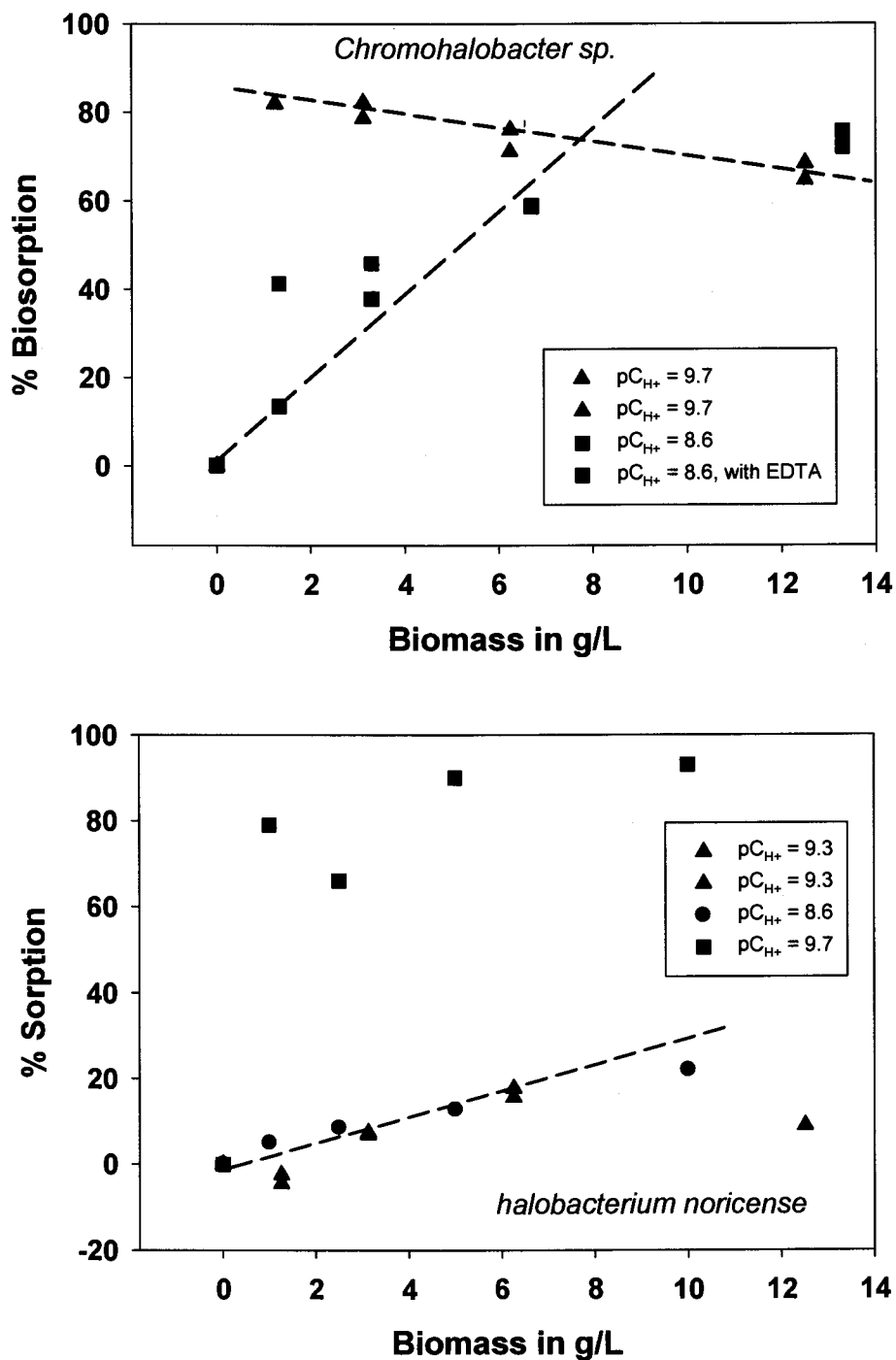


Figure 5-10 Dependency of thorium (IV) sorption on the biomass of *Chromohalobacter sp.* (top) and *Halobacterium noricense* (bottom). For the highest pC_{H+} evaluated precipitation of thorium, even after filtration, was dominant over sorptive processes.

Biosorption of Th(IV) towards Chromohalobacter Sp. (Bacteria)

The biosorption of thorium(IV) species towards *Chromohalobacter sp.* was evaluated as a function of pC_{H^+} and the presence/absence of EDTA at a relatively high (~10 g/L) biomass loading. These data are shown in Figure 5-11.

The sorption of thorium depended on pH and the presence and absence of EDTA. When a metastable Th-EDTA complex was present, significantly higher concentrations persisted for the 2-3 week duration that the stock solution was monitored. Sorption, under these conditions was approximately 33% and 57% at pC_{H^+} 8.6 and 9.3 respectively. In the absence of EDTA, which is the model-predicted and expected long-term speciation of the thorium even with EDTA present, considerably higher sorption was observed. Under these conditions the 54% and 81% of the thorium was sorbed at pC_{H^+} 8.6 and 9.3 respectively. These are likely upper limits and bound the extent of biosorption since it is not possible to completely discount the presence of thorium precipitation.

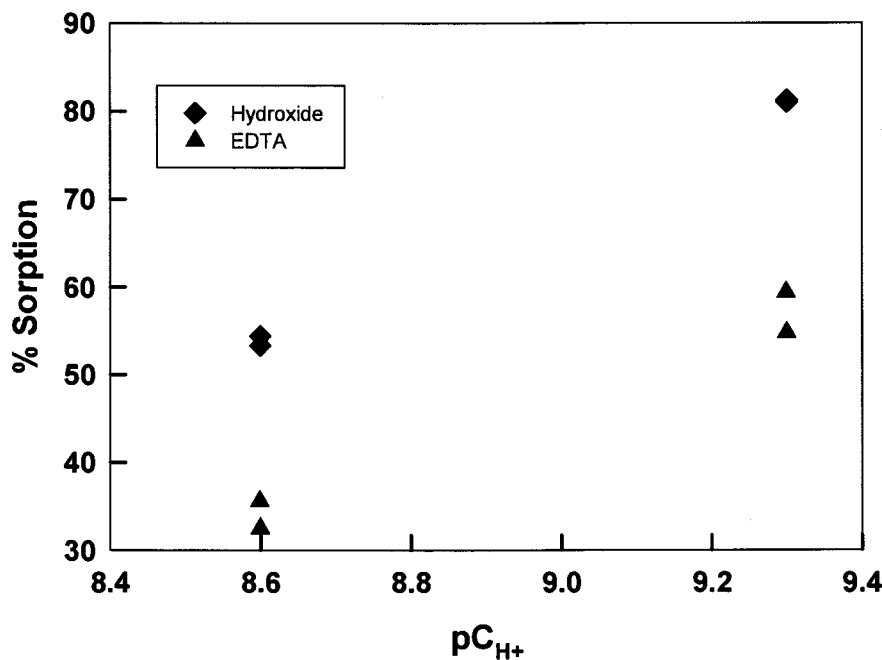


Figure 5-11 Biosorption of thorium (IV) towards *Chromohalobacter sp.* as a function of pC_{H^+} and the presence and absence of EDTA. Highest pH data is not shown since precipitation processes predominated over sorption.

Biosorption of Th(IV) towards *Halobacterium noricense* (archaea)

The biosorption of thorium(IV) towards *Halobacterium noricense* was determined as a function of pC_{H^+} and the presence and absence of EDTA; also at a very high (10g/L) biomass loading. These data are shown in Figure 5-12.

The biosorption of thorium (IV) towards *Halobacterium noricense* under the conditions of the experiments depended on the pC_{H^+} and was complicated by the precipitation of thorium even though pre-filtration was used in these experiments (100 kDa or ~ 20 nm). In the presence of EDTA, a metastable complex persisted and no sorption was observed ($0 \pm 5\%$). In the absence of EDTA, which is the model-predicted speciation, the sorption observed was 12.1%, 13.5% and 40-66% at pC_{H^+} 8.6, 9.3 and 9.7 respectively. The highest pH is not considered because of the very high coupling of sorption and precipitation processes. There is likely some precipitation at the lower pH values as well but these are better behaved systems (see Figure 5-8 for biomass dependency). Overall, the biosorption towards the archaeon was considerably less than that observed for the bacteria by a factor of almost 4-6. This difference cannot be fully explained based on the data presented. It is likely that there are contributing factors due to differences in the cell surface (archaea vs. bacteria) and differences in the way the microorganisms interact with the colloidal thorium species present.

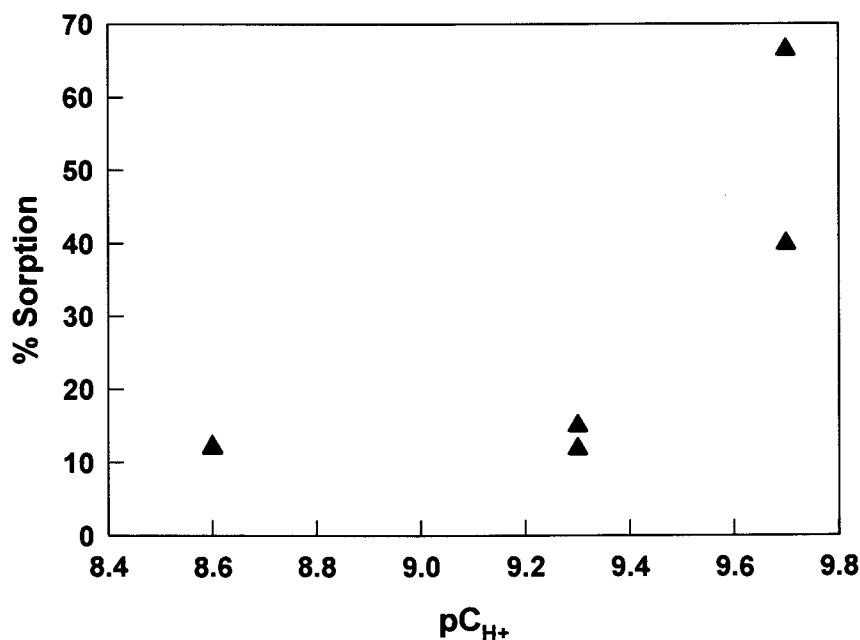


Figure 5-12 Biosorption of thorium(IV) towards *Halobacterium noricense* as a function of pC_{H^+} when EDTA is not present. The highest pH data should be excluded given the strong coupling of precipitation.

5.5 Modeling of Neodymium and Thorium in the Presence and Absence of EDTA

There were two somewhat unexpected results in the biosorption experiments performed with Nd^{3+} and Th^{4+} . In the case of neodymium, there was a non-zero intercept when EDTA was present in the biomass dependency experiments indicating that, even in the presence of 2:1 ligand-metal ratios that a significant amount of neodymium was not complexed. In the case of thorium, the Th-EDTA complex persisted at $\text{pC}_{\text{H}^+} \sim 8.6$ and 9.3 – something that appears to contradict our previous multi-year solubility studies with thorium where no effect of EDTA was noted. For this reason, some non-QL1 (qualitative) modeling was performed to help guide the interpretation of the biosorption results. In particular, we wanted to verify that we were below the solubility limits in the experiments and explain the effect of EDTA in our system on the speciation of the two analogs.

Thomas Wolery's EQ3/6 thermodynamic modeling program version 8.0a was used in conjunction with the Sandia FMT thermodynamic database to model the behavior of neodymium and thorium in high-ionic-strength brine with EDTA to determine trend behavior as pC_{H^+} increases from the nominal ~ 8.5 repository value to $\text{pC}_{\text{H}^+} = 10$. The thorium case was modeled directly. As americium and neodymium are used as analogs of each other and the FMT database contains americium data only (no Nd), americium was used as the stand-in for neodymium.

A nominal EDTA concentration of 1×10^{-5} M was used. Americium was set at 4×10^{-6} M, thorium at 1×10^{-6} M. Experimentally determined values of the various important cations and anions of the WIPP brine were used as the model input basis at each pC_{H^+} point (see Table 5-4).

After attempting to model these systems, and after having previously performed a model titration of the GWB WIPP brine system, it has become apparent that the FMT database, as constructed, does not completely capture the behavior of the real system, i.e. the model shows magnesium-based species precipitating considerably more quickly between $\text{pC}_{\text{H}^+} = 9-10$ than the experimental data. The carbonate-containing magnesium species are by far the worst offenders. Not surprisingly, the FMT dataset has no Pitzer parameter data for magnesium species and as such, does not completely track the behavior of the real system. We are therefore forced to look mainly at limiting cases, such as $\text{pC}_{\text{H}^+} = 8.5$, where the model and experiment match and the behavior of the brine is, for all intents and purposes, that of GWB, and $\text{pC}_{\text{H}^+} = 10$, where the brine is fairly close to the behavior of ERDA-6 and where the model-predicted magnesium values do undershoot somewhat, but not so much so that a comparison cannot be made. To aid this comparison, the model system was treated as being nearly carbonate free and any magnesium/calcium carbonate species, using the analogy to sea water systems, were treated as being metastable and therefore non-precipitating.

Partitioning of americium (analog for neodymium) in EDTA-containing brine

Conditions of the calculations were:

$$\text{Log } f_{\text{CO}_2} = -7.5$$

$$\text{Log } f_{\text{O}_2} = -15$$

$$[\text{Am}] = 4 \times 10^{-6} \text{ M}, [\text{EDTA}] = 1 \times 10^{-5} \text{ M}, \text{pC}_{\text{H}^+} = 8.5 \text{ or } 10$$

Results are shown in Table 5-8.

Table 5-8 Partitioning of Am and EDTA in pH-specific brines		
<i>Am or EDTA Species</i>	<i>% of Species at pC_{H+} = 8.5 with 100% Am in solution</i>	<i>% of Species at pC_{H+} = 10 %americium in solution = 2.030% (remainder precipitated as Am(OH)₃(s))</i>
<i>Am Species</i>		
<i>AmEDTA⁻</i>	81	68
<i>Am(OH)₂⁺</i>	17	31
<i>AmOH²⁺</i>	1.3	<0.1
<i>EDTA Species</i>		
<i>MgEDTA²⁻</i>	67	73
<i>AmEDTA⁻</i>	32	26

Partitioning of Thorium in EDTA-containing brine

Conditions of the calculation performed were:

$$\text{Log } f_{\text{CO}_2} = -7.5$$

$$\text{Log } f_{\text{O}_2} = -15$$

$$[\text{Th}] = 1 \times 10^{-6} \text{ M}, [\text{EDTA}] = 1 \times 10^{-5} \text{ M}, \text{pC}_{\text{H}^+} = 8.5, 10$$

Results are shown in Table 5-9.

Table 5-9 Partitioning of thorium and EDTA in pH-specific brines		
<i>Am or EDTA Species</i>	<i>% of Species at pC_{H+} = 8.5 4.42% Th in solution (remainder precipitated as amorphous ThO₂)</i>	<i>% of Species at pC_{H+} = 10 5.50% Th in solution (remainder precipitated as amorphous ThO₂)</i>
<i>Th Species</i>		
<i>Th(OH)₄(aq)</i>	100.0	95
<i>Th(OH)₃(CO₃)⁻</i>	~0	5.3
<i>EDTA Species</i>		
<i>MgEDTA²⁻</i>	100.0	74
<i>CaEDTA²⁻</i>	~0	26
<i>ThEDTA⁻</i>	~0	~0

These modeling results were very helpful and provided insight to both the Nd and Th systems investigated. For neodymium, that we were below the solubility limit in the EDTA-free system was confirmed. In the presence of EDTA, as much as 20% of the neodymium was not complexed by the EDTA present which explains the non-zero intercept obtained in the biomass dependency (so some precipitation was likely occurring). For thorium, there is no EDTA complexation predicted across the range of conditions investigated although this complexation was experimentally evident and the complex had a strong effect on the sorptive behavior. These modeling results, along with the long-term solubility data, justify the reliance on the EDTA-free experimental results since the EDTA complex although meta-stable for the short 2 hour duration of the experiments, should not contribute in the longer-term to the observed biosorption processes. Regardless, taking the higher sorption values for the non-EDTA case is conservative from the point of view of the formation of biocolloids under WIPP-relevant conditions.

5.6 Overall Results and Assessment for the Biosorption of Nd(III) and Th(IV) Towards Halophilic Microorganisms

PROPMIC values generated from the current work are compared to values generated at the single time point used in Francis et al. (1998) and the averaged multiple time points listed in SOTERM (see Tables 5-10 and 5-11). The tables are separated by actinide oxidation state (Table 5-10, +3; Table 5-11, +4).

Table 5-10. PROPMIC values calculated for +3 actinides; comparison of values generated from Francis' data (columns 2 and 3) and current data (columns 4 and 5) and how these compare to SOTERM PROPMIC values.

+3 Actinide	Francis et al. PROPMIC (based on mean values)		Current Work PROPMIC				SOTERM PROPMIC
			Highest Value		Recommended value (lowest pH experiments)		
	Hmn	BAB	Chromo*	Hbt*	Chromo*	Hbt*	
Am(III)-EDTA	7.673	0.824	nd	nd	nd	nd	3.6
Nd(III)-EDTA	nd	nd	0.70	0.29	0.21	0.033	nd
Nd(III)-chloride	nd	nd	2.0	0.92	0.48	0.29	nd
Pu(III)†	nd	nd	nd	nd	nd	nd	0.3

*Chromo = *Chromohalobacter*, Hbt = *Halobacterium*; †SOTERM PROPMIC for Pu(III) is same as Pu(V); Francis et al. PROPMIC for Pu(V) = 0.15 for Hmn and 0.02 for BAB

Table 5-11. PROPMIC values calculated for +4 actinides; comparison of values generated from Francis' data (columns 2 and 3) and current data (columns 4 and 5) and how these compare to SOTERM PROPMIC values.

+4 Actinide	Francis et al. PROPMIC (based on mean values)		Current Work PROPMIC				SOTERM PROPMIC
			(highest value)		Recommended value (lowest pH experiments)		
	Hmn	BAB	Chromo	Hbt	Chromo	Hbt	
Th(IV)-EDTA	4.48	nd	1.3	0.14	0.52	~0	3.1
Th(IV)-hydroxide	--	--	4.3	1.1	1.2	0.14	--
Np(IV)	nd	nd	nd	nd	nd	nd	12
Pu(IV)*	nd	nd	nd	nd	nd	nd	0.3

*SOTERM PROPMIC for Pu(IV) is same as Pu(V); Francis et al. PROPMIC for Pu(V) = 0.15 for Hmn and 0.02 for BAB

The biosorption of actinides towards microorganisms should correlate with their aqueous speciation. For this reason, it would be expected that similar oxidation states would exhibit similar biosorption behavior, at least to the extent that their aqueous speciation is similar. The large differences noted in SOTERM for these bio-enhancement parameters, in this context, are not consistent with the current understanding and were likely assigned in the absence of significant oxidation-state specific data.

It is also notable that the biosorption data are different for bacteria and archaea. In both +3 and +4 cases and in both Francis' and LANL-CO work, the PROPMIC values obtained for *Archaea* are less than those for *Bacteria*. Currently, SOTERM takes into account only the bacterial data, as it was easier to generate at the time. However, since *Archaea* are likely to predominate in the near-field, it would be more realistic to use those data instead. Additionally, the BAB culture in Francis' experiments tended to show less of a toxic response (with the exception of Pu) than the *Halomonas* culture. This could lead to a lower CAPMIC value, in which case the CAPMIC may actually be invoked.

Recommendations for An(III/IV) Biosorption Enhancement Parameters

Based on the current understanding of halophilism and microbial ecology at the WIPP site, recommendations can be made for the implementation of biosorption data. This requires weighing the desire to remain ultra-conservative with the need to be realistic.

First, if PA can separate near-field from far-field, then both bacterial and archaeal data should be incorporated, each modeled in its respective space. If not, we recommend that archaeal data, rather than bacterial data be used. For the near field, this presents the most realistic scenario of which organisms will be present, since the majority of *Bacteria* will not be capable of survival at the projected ionic strength. However, this will not cover the far-field, in which *Bacteria* will predominate.

Second, the biosorption data obtained at the lowest pH values investigated ($\sim pC_{H^+} = 8.5$) are most reliable and should be the basis of the PROPMIC calculation. These have well correlated biomass dependencies (so sorption is the predominant process) and overall concentration stability. The higher pH data for both thorium and neodymium appear to have significant contributions from precipitation pathways, although this is clearly more evident in the thorium data. The pH correction to get to repository-relevant conditions ($pC_{H^+} \sim 9.5$) should not be large based on the expected changes with pH in the surface complexation of the microorganisms and the solution speciation.

Third, it is more consistent with the overall WIPP actinide model to use actinide oxidation state rather than element to assign biosorption enhancement parameters – although element-specific values are also provided. This would imply that the biosorption of U(IV), Np(IV), and Pu(IV) will correlate with the Th(IV) system and should be based on the Th(IV) biosorption data. Consistent with this, the Nd(III) data should be the basis of the Pu(III), Am(III) and Cm(III) biosorption. These correlations are consistent with the solution properties of An(III) and An(IV) actinides.

Fourth, it is recommended that the CAPMIC values be changed for all elements to a concentration based on microbial biomass and sorption capacity. The reason for this recommendation is threefold: 1) the new numbers are more realistic from a solubility perspective, 2) the toxicity data differed significantly between bacterial and archaeal cultures such that one CAPMIC value does not fit all organisms, and 3) it does not change the calculation for the microbial contribution, except in the cases of americium and plutonium where the new CAPMIC would be less than the total mobile concentration.

Regardless of whether this change is implemented, the values for americium and plutonium should be revisited. Because of limitations in the amount of americium that could be used during the Francis study, sufficiently toxic concentrations could not be reached. Thus, there

is no data-based CAPMIC for this element, and the value of 1M was chosen in the absence of these data. In the case of Pu, the toxicity data are inconclusive, and in addition, the source of the value used cannot be verified [Papenguth 1996a, Table 2].

Fifth, it is recommended that a biomass-based number be used as a CAPMIC. One reason is because the soluble concentrations of actinides are not toxic. A second reason is that to achieve a CAPMIC of 1 M americium, given an association of 4.88×10^{-18} moles of americium per cell (see Table 5-12), would require an unrealistic number of over 10^{14} cells/mL. Using an optimistic biomass concentration (10^9 cells/mL), the concentration associated with cells becomes 4.88×10^{-9} moles Am/L. The far right column of Table 5-13 provides biomass-based CAPMIC values generated using a constant biomass of 10^9 cells/mL multiplied by the moles An/cell (Francis et al., 1998, single value; current data averaged). These values are separated by organism to highlight the difference between bacterial and archaeal sorption tendencies.

The new biomass-based CAPMICs are less than the total mobile values in the case of the +3 oxidation state. Additionally, all archaeal CAPMIC values are less than the total mobile value; however, it is difficult to compare these numbers, since the total mobile value is originally based on bacterial numbers. Thus, it appears that the CAPMIC should be invoked when modeling Pu and Am. Uranium(VI) values are similar, and the +4 cases are less than the biomass-based CAPMIC.

Table 5-12. Moles of actinide per cell, comparison of Francis (1998) data and current data.

Actinide	Moles An/cell (Francis et al., 1998)		Moles An/cell (current work)	
	Hmn	BAB	Chromo	Hbt
An+4- (EDTA)	1.88×10^{-12}	nd	$2.4-4.1 \times 10^{-18}$	~ 0 to 7.1×10^{-20}
An+3- (EDTA)	4.88×10^{-18}	1.57×10^{-19}	$3.1-7.7 \times 10^{-21}$	$0.3-2.6 \times 10^{-22}$

Table 5-13. Comparison of the Total Mobile actinide concentration and SOTERM CAPMIC values. Note CAPMIC values always exceed Total Mobile, such that the microbial contribution = PROPMIC*total dissolved actinide. Contrast to columns containing biomass-based CAPMIC values, where these values are less than the Total Mobile concentration in the case of all archaeal data and in the case of current +3 data.

Actinide (CRA-2004 PABC)	Total Mobile (M)*	CAPMIC (M)	BIOMASS-BASED CAPMIC (M)			
			Francis' data		current data	
			Hmn	BAB	Chromo	Hbt
Pu(III) in Salado	5.64×10^{-7}	6.80×10^{-5}	No data for this oxidation state			
Pu(III) in Castile	7.44×10^{-7}	6.80×10^{-5}	No data for this oxidation state			
Am(III) in Salado	1.75×10^{-6}	1	No data for this oxidation state			
Am(III) in Castile	1.61×10^{-6}	1	4.88×10^{-6}	1.57×10^{-10}	7.6×10^{-9}	6.7×10^{-10}
Th(IV) in Salado	7.23×10^{-7}	1.90×10^{-3}	No data for this oxidation state			
Th(IV) in Castile	8.65×10^{-7}	1.90×10^{-3}	3.12×10^{-6}	No data	No data for this oxidation state	
U(IV) in Salado	5.15×10^{-7}	2.10×10^{-3}	No data for this oxidation state			
U(IV) in Castile	6.15×10^{-7}	2.10×10^{-3}	No data for this oxidation state			
Pu(IV) in Salado	5.36×10^{-7}	6.80×10^{-5}	No data for this oxidation state			
Pu(IV) in Castile	6.40×10^{-7}	6.80×10^{-5}	No data for this oxidation state			
U(VI) in Salado	1.01×10^{-3}	2.10×10^{-3}	No data for this oxidation state			
U(VI) in Castile	1.01×10^{-3}	2.10×10^{-3}	1.14×10^{-3}	2.58×10^{-8}	No data for this oxidation state	

*from Table SOTERM-25 (2009)

6.0 SUMMARY OF OBSERVATIONS AND RECOMMENDATIONS

The literature publications, WIPP-specific work performed prior to the CCA, reviews, and newly obtained data pertaining to the WIPP colloid model were summarized in this report. Although the WIPP colloid model, from many perspectives, remains conservative, there are new literature results and WIPP-specific data that should be considered and used to update the colloid enhancement parameters within the current model.

Colloid Literature Review

The literature review shows colloidal transport and the structure and nature of colloidal species to be an ongoing area of study in the environmental actinide field. Specific issues identified that directly impact the WIPP colloid model include:

- The prevalence of colloidal species in a number of actinide systems. This is not consistent with the pre-CCA literature review that concluded that only plutonium colloids are relevant to the WIPP.
- Nano-structures for some actinide intrinsic colloids have been observed for plutonium and uranium. The extent that these apply to the WIPP case has not been established, but these may explain the very small, typically < 10 nm, colloidal species that are being observed in WIPP brine.
- There is still an overall uncertainty in the literature as to the role of colloidal species in the transport of actinide contaminants in the subsurface. This remains an active area of study and there are data that show colloidal species contribute to immobilization as well as the mobilization of actinides. In this context, the presence of a WIPP colloid model is needed to address this uncertainty and should be considered as a conservatism that is part of the actinide source-term model.

New WIPP-specific Data on Actinide Colloids

One of the consistent criticisms over the years in the regulatory reviews of the WIPP colloid model was that it was based on very little and often incomplete data. There remain some gaps in the data but there are new results, based on WIPP-specific actinide solubility studies that help address this regulatory issue. Specifically, the following results were summarized in this report and significantly increase the data sets which form the basis for the WIPP colloid enhancement parameters:

- Greater and more extensive understanding of the microbial ecology under WIPP-relevant conditions. This gives a better understanding of the expected microbial community that will be present and isolates from this community were utilized in the colloid studies.

This understanding also provided a better basis for the biocolloid enhancement parameters.

- A better and more comprehensive understanding of the brine chemistry and its linkages to the formation of colloids and actinide speciation/solubility has been achieved.
- Iron mineral and, indirectly, Mg-derived mineral data on the bio-sorption of actinides. These confirm the initial pre-CCA observation that only iron oxide minerals led to substantial formation of mineral colloids. It also helps answer the recent questions about Mg-derived effects that were not initially considered in the CCA and were potentially flagged as a problem by published thorium data in high ionic-strength systems.
- Biosorption experiments for the An (III, IV and V) oxidation states were performed with WIPP-relevant microorganisms in pH-specific brines at the expected repository pH. These provide a basis for the PROPMIC enhancement parameters.
- Detailed analyses were performed on a number of long-term actinide/analog solubility studies to establish the size distribution of the aqueous species present using sequential filtration. These data gave significant insight into the mineral and intrinsic colloidal contributions to the mobile actinide concentrations and are the basis of the recommendation for updates to the intrinsic colloid enhancement parameter.

Summary of Recommendations on Colloid Enhancement Parameter Updates

Based on the results discussed in Sections 4 and 5 of this report, the following specific recommendations are made to update the mineral, intrinsic and microbial enhancement parameters in the WIPP colloid model:

Mineral Colloid Enhancement Parameters

No change is recommended. It is not likely that Mg-derived mineral colloids are important in WIPP. It is however confirmed that iron oxide mineral colloids do form in plutonium systems. There is not sufficient data to show the oxidation-state-specific actinide relationships.

Intrinsic Colloid Enhancement Parameters

Change to newly determined parameters is recommended. The literature review and new WIPP-specific data indicate that small (<10 nm) intrinsic colloids are likely being formed for all actinide oxidation states. These, although correlated with oxidation state and not the actinide element, can be phrased as either oxidation-state specific or element-specific values. Their overall impact on the dissolved mobile actinide concentration remains, however, relatively small.

**Microbial Colloid
Enhancement
Parameters**

Change to newly derived/measured parameters is recommended. The pre-CCA data in this area is the most incomplete leading to substantial conservatism in the current parameters. Oxidation-state specific values were obtained for An(III/IV/V). These can be phrased as either oxidation-state specific or element-specific values.

A summary of the recommended mineral and intrinsic colloid enhancement parameters is given in Table 6-1. The recommended microbial colloid enhancement parameters are given in Table 6-2. These recommendations are based on the data summarized in Sections 4 and 5 of this report. The specific details that show the logic and rationale for the values recommended are summarized in Attachment 2.

Table 6-1 Summary of CRA-2009 and recommended/updated enhancement parameters for mineral and intrinsic colloids					
Actinide Oxidation State	Mineral Colloid Enhancement Parameter		Intrinsic Colloid Enhancement Parameter		
	CRA-2009	Proposed	¹ CRA-2009	Proposed Oxidation- State Specific	² Proposed Element- Specific
Th(IV)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	2 x 10 ⁻⁸ M	2 x 10 ⁻⁸ M
U(IV)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	2 x 10 ⁻⁸ M	3 x 10 ⁻⁸ M
U(VI)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	3 x 10 ⁻⁸ M	
Np(IV)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	2 x 10 ⁻⁸ M	2 x 10 ⁻⁸ M
Np(V)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	ND	
Pu(III)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	1 x 10 ⁻⁹ M	4 x 10 ⁻⁹ M	2 x 10 ⁻⁸ M
Pu(IV)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	1 x 10 ⁻⁹ M	2 x 10 ⁻⁸ M	
Am(III)	2.6 x 10 ⁻⁸ M	2.6 x 10 ⁻⁸ M	0	4 x 10 ⁻⁹ M	4 x 10 ⁻⁹ M
1 - for CRA-2009, only plutonium intrinsic colloids are considered 2 - for the element-specific case, the highest value is proposed ND - not determined					

Table 6-2 Summary of CRA-2009 and recommended/updated oxidation-state specific enhancement parameters for microbial colloids

Actinide Oxidation State	PROPMIC			CAPMIC (M)		
	CRA-2009 (M)	Proposed (M)		CRA-2009	Proposed	
		Archaea	Bacteria		Archaea	Bacteria
Th(IV)	3.1	0.21	1.76	0.0019	3.8 E-8	2.3 E-6
U(IV)	0.0021	0.21	1.76	0.0021	3.8 E-8	2.3 E-6
U(VI)	0.0021	ND	ND	0.0021	ND	ND
Np(IV)	12	0.21	1.76	0.0027	3.8 E-8	2.3 E-6
Np(V)	12	ND	1.4	0.0027	ND	4 E-6
Pu(III)	0.3	0.05	0.32	6.8E-5	3.9 E-10	3.1 E-8
Pu(IV)	0.3	0.21	1.76	6.8E-5	3.8 E-8	2.3 E-6
Am(III)	3.6	0.05	0.32	1.0	3.9 E-10	3.1 E-8

ND – not determined, no new recommendation

Table 6-3 Summary of CRA-2009 and recommended/updated element-specific enhancement parameters for microbial colloids

Actinide Oxidation State	¹ PROPMIC			¹ CAPMIC (M)		
	CRA-2009 (M)	Proposed (M)		CRA-2009	Proposed (M)	
		Archaea	Bacteria		Archaea	Bacteria
Th(IV)	3.1	0.21	1.76	0.0019	3.8 E-8	2.3 E-6
U(IV)	0.0021	0.21	1.76	0.0021	3.8 E-8	2.3 E-6
U(VI)	0.0021			0.0021		
Np(IV)	12	0.21	1.76	0.0027	3.8 E-8	2.3 E-6
Np(V)	12			0.0027		
Pu(III)	0.3	0.21	1.76	6.8E-5	3.8 E-8	2.3 E-6
Pu(IV)	0.3			6.8E-5		
Am(III)	3.6	0.05	0.32	1.0	3.9 E-10	3.1 E-8

ND – not determined, no new recommendation
1 – highest value for a particular element is recommended for the element, this is extended to all oxidation states even if they are “ND”

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Attachment 1

July 1996 Peer Review: Conceptual Models Peer Review (for WIPP)

Excerpt pertaining to the WIPP Colloid Model

3.24. Colloidal Actinide Source Term

3.24.1. Model Description

The Colloidal Actinide Source Term conceptual model describes the concentration of actinides sorbed to or contained in mobile colloidal particles in the disposal rooms and also describes the stable colloids that must be quantified for transport in the Culebra. The actinides addressed with this model are thorium (Th), uranium (U), neptunium (Np), plutonium (Pu), americium (Am), and curium (Cm). Presently, transport of colloids in the Culebra have not been rigorously modeled because of the complexities of coupling hydrogeology, geochemistry, and colloid chemistry. Because of the chemical complexities of the integrated system and high ionic strength brines present, an attempt has been made to characterize the major colloid types believed to be present in the repository.

The four types described are "hard sphere" carrier colloids (mineral fragments), microbes, soft sphere carrier colloids or hydrophilic colloids (humic and fulvic acids) , and intrinsic colloids (true colloids). These particles develop from a variety of processes in the repository, including waste degradation, microbial activity, rock decomposition, and chemical condensation. Intrinsic colloids form by condensation of dissolved actinides in the disposal rooms. Mineral fragments and humic substances provide surfaces that dissolved actinides may sorb to. Microbes actively bioaccumulate actinides intracellularly and also act as substrates for surficially extracellular sorption (Francis 1985).

Four major decisions have been made that greatly simplify this conceptual model. First, DOE has elected to disregard the effects of competition associated with the equilibrium between dissolved actinides and actinides associated with colloidal particles. Therefore, the two source terms are not inexorably linked, resulting in an overestimation of the total concentration of mobile actinides that may leave the repository. Second, in the event that the sum of the concentrations of the dissolved actinide and colloidal actinide source terms for a particular element exceed the inventory limited concentration of that element, then a partitioning scheme is utilized. Instead of basing the partitioning on an equilibrium approach, DOE has decided to use an approach based on conservatism. The concentration of a particular actinide in the inventory is first made available to the most efficient transport mode. If the inventory is not used up, then the next most efficient transport mechanism is filled. This rationale is continued until the inventory

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- is exhausted by assignment to the five groups of transpon vehicles (four colloidal and dissolved actinide source terms). Third, thermodynamic equilibrium is achieved by actinide intrinsic and humic colloids. And fourth, DOE has assumed that microbes and mineral fragments are present in constant quantities in the aqueous phase. This allows a steady state quantity on which the actinides can sorb. Because of the effect of high ionic strength brines on mineral fragment colloids, which collapses the electric double layer surrounding the colloid, Van der Waals forces can cause agglomeration and settling of such colloids. Laboratory experiments using WIPP brines indicate that this settling effect largely negates mineral fragments as an effective transport mechanism. Thus, DOE has conservatively assigned a mineral fragment concentration for each actinide to be 1×10^{-11} miL, one order of magnitude higher than the detection limit of the experiments.

Microbes have a large study base at WIPP, primarily to provide data for the gas generation program. This information has also been helpful in the Colloidal Actinide Source Term model. The source term concentrations associated with microbes are based on actinide uptake experimentally determined from experiments with relevant bacteria cultures. Source term values range from 1×10^{-1} to 10^{11} miL.

Humic and fulvic acids are of particular concern because of their well known capability to complex metal cations, including actinides. These soft sphere carrier colloids are not affected by high ionic strength brines, so they may be important in the transport of actinides at WIPP. To determine humic substance concentrations, actinide complexation constants from WIPP experiments or from literature are coupled with site binding densities and solubilities of humic substances in WIPP brines. Source term values range from 10^{-5} to 10^{-9} miL.

Intrinsic colloids are well represented by the Pu(N) polymer. The mechanism of formation of this polymer has not yet been identified; however, it is known to be stable in high concentrations in highly acidic environments. There is some evidence that the polymerization is strongly linked to hydrolysis, and that it produces an amorphous macromolecule that becomes crystalline with time. This polymer is typically on the order of nanometer size range. Hence, it is assumed to act like a hard sphere carrier colloid. Experiments were conducted by over- and undersaturation at a range of pH values to determine concentrations of Pu intrinsic colloids. The source term value of this polymer is 1×10^{-1} miL. Other actinide intrinsic colloids (especially Am) were found to have negligible importance.

The computer code that will describe the transport of the Actinide Source Term model is called NUTS. NUTS is dependent on BRAGFLO (chemical conditions in waste rooms) to provide brine volumes and a lookup table to provide actinide concentrations. The actinides that will be tracked in Salado and Culebra Brines by this table are thorium (Th), uranium (U), plutonium (Pu), neptunium (Np), and americium (Am). Other chemical factors originally believed to impact colloidal source terms were pH, pCO₂, major brine constituents, ionic strength, oxidation speciation and organic ligand concentrations. Fixing the brine compositions and the addition of MgO backfill has significantly reduced the number of variables in the lookup table.

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3.24.2. Review of Criteria

3.24.2.1. Information Used to Develop the Conceptual Model

The main sources of information used are journal articles, experimental programs, and classical thermodynamics. The conceptual model has made liberal use of research published in the journals. Items transferred to the Colloidal Actinide Source Term conceptual model from the journal articles are voluminous and are the basis of the experimental test program. Experimental work on actinide solubility was performed at a number of laboratories, including Sandia, Los Alamos, Lawrence Livermore, and Brookhaven National Laboratories, and Florida State University. The discipline of thermodynamics as a portion the chemical sciences is well founded. A major assumption of this science is one of equilibrium conditions.

No FEPs were included in the development of this conceptual model. In fact, colloids were not considered as a conceptual model until after the 1992 performance assessment was completed. The study of Ibaraki and Sudicky (1995) is very similar to the conceptual model developed here.

3.24.2.2. Validity of **Model** Assumptions

The majority of the assumptions used in the colloidal actinide source term are valid, in that they are either accurate scientific extrapolations or based on conservative measures. Four major assumptions made by DOE and discussed in the model description above are most probably valid in the context of this model. To assume that Dissolved and Colloidal Actinides Source Term models do not compete for actinides is certainly conservative and will overestimate the total actinide source term. The partitioning scheme used when the inventory is exceeded is reasonable and again conservative. The assumption that thermodynamic equilibrium is attained for intrinsic colloids and humic colloids is valid. The assumption that there is a steady state source of mineral fragments and microbes allows for conservatism, in that it provides an abundance of sorbing material.

Two other assumptions in the conceptual model concern the use of bounding calculations.

Concentrations of actinides in both intrinsic colloids (Pu^{+4}) and mineral fragments were below the detection limits of the experiments. Therefore, the actual detection limit was used as the bounding value for the intrinsic colloid, and an order of magnitude higher bounding value than the detection limit for mineral fragment.. These are probably adequate, possibly overly conservative estimates for concentrations in both cases and can be considered adequate.

3.24.2.3. Evaluation of Alternatives

The Colloidal Actinide Source Term conceptual model describes the quantity of actinides that would be mobilized as colloid species in WIPP brine, and would migrate with the brines away from the repository. At one time or another over the last four years, six alternative models were proposed for the Actinide Source term. The model names are as follows: (1) Expert Panel, (2) Inventory Limits, (3) Inventory Limits with realistically conservative Maximum Concentrations, (4) Fresh Water Estimates, (5) Chemical Model for Mobile Actinide Concentrations, and (6)

Inventory Limits with Sorption. Of the six models, numbers 1, 4, and 6 were not defensible. As of December 1994, the Expert Panel model was questioned as to its credibility and technical suitability, and the Fresh Water Estimate model was essentially undeveloped. Sorptive values for the Inventory with Sorption model were unavailable. Of the remaining three models presented, the Inventory model was complete and defensible but highly conservative. The model that, until recently, was used as the baseline was the Inventory Limits with Realistically Conservative Maximum Concentrations model. Essentially, this was a combination of the Inventory

Limits and Expert Panel models and was intended to be more judiciously conservative than the Inventory Limits model. The Chemical equilibrium model is based on thermodynamics and is robust but was only recently fully developed. The final model for the performance assessment (Chemical Equilibrium model) will contain submodels that investigate the source terms for both dissolved and colloidal actinide species.

The actinide inventory is originally determined by projections in the Baseline Inventory Report (BIR). A series of chemical reactions that will have a major impact on the colloidal actinide source terms are as follows:

- 1. Actinide dissolution reactions.*
- 2. Reactions between brines and organic waste.*
- 3. Reactions between brines and backfill materials.*
- 4. Reactions between actinides and dissolved ligands (organic and inorganic).*
- 5. Reactions that produce carrier colloids.*
- 6. Reactions among actinides to produce actinide-intrinsic colloids.*
- 7. Reactions between actinides and carrier colloids to produce radioactive mobile substrates.*
- 8. Actinide sorption onto immobile substrates.*

Of the eight reactions listed above, the first seven have been used in developing the current model. DOE has discarded reaction number 8. This decision is thought to be conservative and allows the possibility of more actinides being transported by colloids.

3.24.2.4. Uncertainties

The only uncertainty listed by DOE for this model involves the inventory limited concentration of the actinides. If the sum of the dissolved and colloidal actinides exceeds the inventory total, the actinide concentrations will then be proportioned between the two actinide groups (dissolved and colloidal). This philosophy appears reasonable.

Three lesser uncertainties that would add clarity to the model have not been resolved. First, it has been theorized that the Pu intrinsic colloid would act as a mineral fragment with time. Studies

have not proved this theory. The mechanistic operation of this intrinsic colloid has not been determined. A second uncertainty concerns site densities available on microbes for actinides. This parameter has not been determined. Third, it is assumed that humic colloids behave like dissolved actinides. This assumption has not been adequately supported.

3.24.2.5. Adequacy of the Conceptual Model

The present section addresses whether the conceptual model is adequate based on the four criteria above. The conservative bounding values for intrinsic and mineral fragment concentrations should (in a perfect world) be discarded and real measurements taken to obtain scientifically valid results. However, when one considers the magnitude and complexity of this conceptual model, and the fact that so many issues are well addressed, these items appear almost insignificant.

The outstanding issues that must be dealt with are the three unresolved uncertainties in Section 3.24.2.4. A further nagging problem exists in that two major appendices of the CCA are not available (MASS and PAR). If the discussions entailed in the appendices are reasonable and logical, and the uncertainties are qualified then the conceptual model would be wholly adequate and much more accurate from a scientific viewpoint.

3.24.2.6. Adequacy of Application

This section assesses whether the colloidal actinide source term conceptual model is applied into an acceptable overall performance modeling element. As discussed previously, this complex model has many variables concerning the four colloid types that are merged in. There is a well-documented data base for colloids both from the laboratory experiments specific to WIPP and journal articles. Such a series of articles has served well as a foundation for the model. As an input to the mathematical code NUTS, this conceptual model would present its results in a lookup table. The table takes into account brine compositions, proportionality constants, and oxidation state potentials, all of which allow a very robust model to be applied to the performance assessment modeling elements. The true unknowns are to be found in the assumptions that the chemistry rapidly approaches equilibrium, that the microbe culture is well known, and that the waste has uniform characteristics and inventory. These fundamental assumptions are a basis of the conceptual model and are most probably adequate and reasonable.

3.24.2.7. Accuracy of Results

Draft portions of the lookup tables were provided to the Panel by a Principal Investigator for the conceptual model. If one assumes that the dissolved actinide concentration values are accurate, that the brine stays buffered at a pH of 9-10 due to the addition of MgO, and that the other assumptions mentioned are valid, then the results of the colloidal actinide conceptual model are felt to be reasonably accurate. The only qualification to this opinion is that the results may be

too conservative. To assume concentrations no greater than detection limits of analytical equipment is deemed reasonable by regulatory agencies. However, this method may easily produce inflated values (as applied to intrinsic colloids and mineral fragments). To allow an order of magnitude increase greater than the experimental detection limit for mineral fragments is probably extreme and not truly representative of the chemical system involved.

The one remaining piece of information needed to thoroughly qualify the accuracy of the results would be a series of sensitivity analyses. These results are not currently available.

3.24.2.8. Validity of Conclusions

This section judges whether the key conclusions that have been drawn on the results of the Colloidal Actinide Source Term conceptual model in the modeling framework are valid. Since this model is inexorably linked to the solubility concentrations of the dissolved actinide source term, one may conclude that this model is valid contingent on the validity of the other model (which was determined to be valid, with minor caveats). The overall decision of outcome validity is made slightly more difficult by the fact that the final complete table (6-10) and appendices (PAR and MASS) of the CCA have not been supplied as of this date. If those pieces of information not yet available are reasonable and adequate in their content, then it is sufficient to determine that the conclusions of this model as they apply to the full system, are valid.

3.24.2.9. Adequacy for Implementation

The Colloidal Actinide Source Term model is a reasonable, if somewhat overly conservative representation of how actinides would sorb onto colloids in the two major brines (Salado and Castile) available for the repository. This conceptual model is adequate to support performance assessment. However, this model is closely linked to the Chemical Conditions model (see discussion in Section 3.22 on MgO backfill).

For the sake of completeness and accuracy, the uncertainties listed in Section 3.24.2.4 that would benefit from more supporting evidence are:

Cl Pu intrinsic colloids are presumed to act like mineral fragments with time, but this assumption is not adequately supported. Cl Colloid site densities on microbes have not been thoroughly characterized. Humic acid colloids are presumed to behave like dissolved actinides, but this assumption is not adequately documented.

3.24.2.10. Dissenting Views

There were no dissenting views for this model.

Attachment 2

Explanation and Documentation of the Recommended Values for Mineral, Intrinsic, and Microbial Colloid Enhancement Parameters Based on New WIPP-Specific Data

Mineral Colloid Enhancement Parameters

There are no changes recommended for these enhancement parameters. The impacts of what is presented in this report are the following:

1. Literature data confirm the important role of iron and manganese oxides as the dominant mineral fragments noted in real-systems. This was also the observation made in the Pre-CCA WIPP experiments and is supported by the new WIPP-specific results summarized in Section 4.2.3 – see Table 4-4, mineral colloid column for pH 9-10 data.
2. There is no evidence in the actinide/analog solubility studies for significant Mg-derived mineral colloids. This is based on the lack of >10nm colloidal particles in the sequential filtration studies completed for Pu(III), Nd(III), Th(IV) and U(VI) that are summarized in Section 4. This addresses an EPA-raised concern that Mg-derived colloids were not considered in the CCA colloid model even though there is a substantial amount of MgO, and therefore Mg, in the WIPP.
3. Although there is an expectation that the sorption of actinides onto mineral colloids will be oxidation-state specific because it is linked to the aqueous chemistry, there are no new WIPP-specific data that address this issue. For this reason, there is no justification to change the extension of the Pu-derived mineral colloid enhancement factor (based on iron oxides) to all actinide species as is currently in the WIPP PA colloid model.

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Intrinsic Colloid Enhancement Parameters

Changes are recommended for the intrinsic colloid enhancement parameters based on the WIPP-specific sequential filtration results described in section 4 of this report. This parameter has been operationally defined as filterable species that are <10nm in size. It is calculated in the following way:

$$[\text{Actinide}/\text{analog intrinsic colloid}] = \\ [\text{Actinide}/\text{analog filterable by 10 nm}] - [\text{Actinide}/\text{analog filterable by 2.5 nm}]$$

The concentrations used in Table A2-1 are direct ICP-MS measurements from the sequential filtration studies and correspond to the data in the respective Figure identified for Section 4.

There are literature confirmations of the existence of intrinsic colloids for a number of actinides and structures for some of these nano-clusters (e.g. nano-colloids) are published. This literature and WIPP-specific observation deviates from the pre-CCA conclusions that only plutonium colloids are important. The WIPP colloid model recognized the formation of intrinsic colloids to be related to the oxidation-state-specific chemistry of the actinide although element-specific data are used in PA for convenience. Generally speaking, the presence of strong complexants (e.g., EDTA) causes a pronounced reduction in the concentration intrinsic colloids in favor of the formation of the aqueous complex. The reliance on non-EDTA data, in this context is conservative.

The general approach used to determine the intrinsic colloid parameters from the WIPP specific data was:

1. Select data from each actinide/analog brine system that is at or near the WIPP-model predicted pC_{H^+} of $\sim 9.5 \pm 0.5$. (i.e., 9 to 10). The colloidal fractionation and actinide/analog concentration is dependent on pC_{H^+} - both of which contribute to the calculation of the intrinsic colloid concentration.
2. Calculate the concentration of intrinsic colloids in this pC_{H^+} range as the colloidal fraction x total actinide/analog concentration.
3. Select the highest concentration for each actinide/analog species as the recommended value for the intrinsic colloid enhancement factor

The result of the application of this approach to the data presented in Section 4 is in Table A2-1. The concentration data used for these calculations are the 10 nm and 2.5 nm concentration data for the experiment identified and shown in the respective Figure. These data are direct ICP-MS concentration measurements that are in the supporting QA documentation for this report.

Table A2-1 Actinide-Analog-Specific Data Used to Determine the WIPP-relevant ($pC_{H^+} = 9.5 \pm 0.5$) Intrinsic Colloidal Contribution (Source Data Reference: Los Alamos Summary Data Package: LCO-ACP-18)				
Experiment (see Figures in Section 4)	^a 10 nm – Filtered concentration (M)	^b 2.5 nm Filtered Concentration (M)	^c Concentration of Intrinsic Colloids (%Colloidal Fraction) (M)	Selected Value for Table 6.1
Actinide/Analog: Nd (III)				
UE10CO-1 at $pC_{H^+} = 9.1$; Figure 4-2	9.5 E-9 M	7.4 E-9 M	2 E-9 M (22%)	¹ 2 E-9 M
Actinide/Analog: Pu (III)				
ERDA-6 at $pC_{H^+} = 9.1$; Figure 4-4	8.4 E-9 M	1.1 E-9 M	7.4 E-9 M (87%)	² 4 E-9 M
ERDA-6 at $pC_{H^+} = 9.1$; Magnetite data (no Figure)	5.2 E-9 M	7.3 E-10 M	4.5 E-9 M (86%)	
ERDA-6 at $pC_{H^+} = 9.5$; Figure 4-4	1.5 E-9 M	5.7 E-10 M	9.3 E-10 M (62%)	
Actinide/Analog: Th(IV)				
UG9C2-2 at $pC_{H^+} = 9.1$; Figure 4-7	4.6 E-8 M	3.6 E-8 M	1.0 E-8 M (22%)	³ 2 E-8 M
UG9C2-2 at $pC_{H^+} = 9.1$; Figure 4-7	4.9 E-8 M	2.7 E-8 M	2.2 E-8 M (45%)	
Actinide/Analog: U(VI)				
ERDA-6 at $pC_{H^+} = 9.3$ oversaturation Figure 4-8	6.64 E-7 M	6.01 E-7M	6.3 E-8 M (9%)	⁴ 3 E-8 M
ERDA-6 at $pC_{H^+} = 9.8$ undersaturation Figure 4-8	1.2 E-7 M	1.2 E-7 M	~ 0	
a – Concentration of the actinide/analog that is filterable through a 10 nm-size filter (so truly dissolved + intrinsic colloidal species) b – Percent of the “10 nm” concentration that is a colloidal actinide/analog species c- Concentration of actinide/analog species that is characterized as intrinsic (2.5 to 10 nm) 1 – value taken without adjustment 2 – average of the three values taken, rounded to one significant figure 3 – average of the two values taken, rounded to one significant figure 4 – average of the two values taken, rounded to one significant figure				

Information Only

Microbial Colloid Enhancement Parameters

Microbial colloid enhancement parameters were determined for the An(III) and An(IV) actinides. Specifically Nd(III) and Th(IV) were used as the oxidation-state analogs. Additionally, the sorption of Np(V) onto *Chromohalobacter sp.* at $I = 4$ M brine has been published [Ams, 2013].

The effect of pH on biosorption, when only surface complexation predominates and there is no precipitation, is fairly well understood. For the Np(V) case, which is the simplest and most straightforward example, biosorption increased with pH until almost $\text{pH} \sim 10$ because NpO_2^+ remains positively charged (it does not hydrolyze until $\text{pH} > 10$) and the increasing pH leads to an increasingly negative charge on the surface of the microorganism (so there is a stronger attraction between the neptunyl species and the microorganism). Above pH 10, hydrolysis and carbonate complexation lead to the formation of negatively-charged complexes that are repulsive leading to a net decrease in the extent of biosorption. For Np(V), the biosorption decreases from $\sim 75\%$ to $\sim 65\%$ (so approximately 10%) between pC_{H^+} 8.5 and 9.5. All of this can be readily modeled using surface complexation models and there is clearly demonstrated equilibration between the aqueous speciation and the adsorbed surface complex. This is shown in the following Figure (this is Figure 3-2 from Ams, 2013):

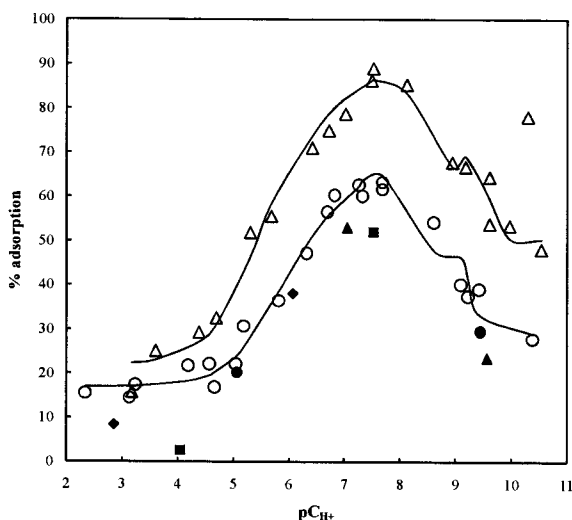


Figure 3-2

Experimental data for neptunium (V) adsorption onto *Chromohalobacter sp.* as a function of pH in 2 (open circles) and 4 (open triangles) M NaClO_4 . Adsorption experiments were performed with 5×10^{-6} M total neptunium (V) and 5 g/L (wet weight) bacteria [Ams, 2013]. Solid curves represent best-fit calculated surface complexation models. Solid diamonds, squares, triangles, and circles represent the results of desorption experiments performed with 5×10^{-6} M total neptunium (V) and 5 g/L (wet weight) bacteria in 2 M NaClO_4 .

This pH profile is relatively unique to the neptunyl case – but it is reviewed here to give perspective to the arguments that are made for the An(III) and An(IV) cases investigated that are of most interest to the WIPP. Unlike the An(V) species, An(III) and An(IV) – also An(VI) – are strongly hydrolyzed or complexed at well below $\text{pH} = 7$ and exist primarily as anionic species in the pC_{H^+} 8-10 range that is usually considered in WIPP-related experiments (see Table 5-8 and 5-9 for americium and thorium respectively). Current modeling does however predict some cationic species for the An(III) case whereas all the An(IV) is either neutral or anionic. There is

also a significant drop in solubility between $pC_{H^+} = 8.5$ to 10. For these reasons, a mostly flat or decreasing (not increasing) biosorption trend is expected. Experimentally, precipitated and bioassociated actinide species both show up as part of the filtrate and cannot be distinguished – this can lead to an apparent increase in biosorption, when in fact there is probably a decrease. In particular, large changes in apparent biosorption associated with small increases in pH are usually due to precipitation, not sorption, since sorption does not change dramatically with pH (Figure 3-2 above). This is sorted out experimentally by performing experiments at or below the solubility limit throughout the pH range of interest to suppress precipitation and establishing the biomass dependency since a change in biomass, if sorption is the predominant interaction, should lead to a linear increase in adsorbed species (and ideally have a zero intercept) – so this also supports a biosorption rather than precipitation pathway.

For Nd(III), the An(III) analog that was investigated, our experiments were performed below the solubility limit of Nd [Borkowski, 2008] and pre-filtration effectively eliminated significant colloidal contribution. This led to a relatively well-behaved system as is evidenced by the linear biomass dependency (see Figures 5-4, 5-5, 5-6) – especially at $pC_{H^+} \sim 8.9$. At higher pH, however, a non-zero intercept is observed that suggest some contribution from precipitation that is probably catalyzed by the addition of the microbe to these systems. For these reasons, the lower pH data are favored and this is believed to introduce an error of ~ 10 -20% (so relying on $pC_{H^+} \sim 8.5$ to 9, vs. the more repository-relevant $pC_{H^+} > 9.2$).

In the case of Th(IV), as the An(IV) analog, the system investigated is more complex. This complexity is well documented in our long-term studies [Borkowski, 2012]. In this system, metastable colloidal species are readily formed as an unavoidable complexity and there was strong coupling between precipitation and bioassociation in all the higher pH systems investigated. This is evidenced by the highly non-linear biomass dependencies noted for both archaea (Figure 5-10 – lower) and inverse relationship to biomass for the bacteria (Figure 5-10 – top). This contrasts with the relatively linear behavior and near-zero intercepts observed at $pC_{H^+} \sim 8.6$. These lower pH data provide the best measurement of biosorption and are most reliably used in the derivations of the PROPMIC values. Again, a somewhat lower pH, leads to an estimated added uncertainty of 10-20%.

For the reasons stated above, the following path was chosen for the recommended biosorption values:

Np(V):

This was not determined under the QL1 WIPP program. Data from the literature publication (see Figure 3-2) are used as an estimate for the bacterial contribution since this was done at $I = 4$ M using the same organism used in the WIPP studies (*Chromohalobacter sp.*)

Thorium (IV) for An(IV):

- Non-EDTA system is recommended. At $pC_{H^+} \sim 9.5$ or greater, hydrolysis predominates and the results are independent of the presence of EDTA. A lower pH, the EDTA complex was metastable over the 2-hour timeframe of the experiments.
- Lower pH data ($pC_{H^+} = 8.5$ and ~ 9) were used preferentially. There was a better correlation with biomass – so sorptive processes predominated over precipitation.
- Higher-pH data was not well-behaved due to the significant coupling with precipitation and should not be considered.

Neodymium (III) for An(III):

- EDTA system is recommended since this is the repository relevant condition and current WIPP modeling predicts that the An(III) actinides will predominantly speciate as an EDTA complex (also note calculation discussed in Section 5.5). The complexation of neodymium with EDTA was stable and is the dominant species in solution. This complexation also lowers the extent of sorption observed since it competes with the microbial surface complexants.
- Lower pH data are probably better isolated from precipitation and the relatively small shift in pH should not introduce significant error in the sorption measured (expected to be $<15\%$).

Microorganism:

- Data for both bacteria (*Chromohalobacter sp.*) and archaea (*Halobacterium noricense*) were obtained. These are both presented. Sorption towards archaea was significantly lower for the Nd(III) and Th(IV) systems investigated. This was attributed to differences in the surface complexation properties of the bacterial vs. the archaeal microorganism.
- Bacteria are expected to be more prevalent in the far field at WIPP [Swanson, 2012a and 2013b] and their sorptive properties are the most representative for transport in the Culebra.
- Archaea are expected to predominate in the WIPP (Salado) [Swanson, 2012a and 2013b]. The archaeal data are, for this reason, the most representative to define the effect of biosorption on the actinide source term.

Two microbial enhancement parameters are needed: PROPMIC and CAPMIC.

PROPMIC

PROPMIC is calculated from the ratio of the sorbed and dissolved actinide/analog:

$$PROPMIC = \frac{[Actinide\ or\ Analog\ Sorbed]}{[Actinide\ or\ analog\ remaining\ in\ solution]}$$

This is calculated from the biosorption data (see Section 5.4) which is usually plotted as the % sorbed which is somewhat different than the PROPMIC value. The % sorbed data is slightly different and given by the following equation:

$$\% Sorbed = \frac{[initial\ actinide\ or\ analog] - [Filtered\ actinide\ or\ analog]}{[initial\ actinide\ or\ analog]} \times 100$$

PROPMIC Values based on "low pH" pCH+ ~ 8.6-8.9 data (Source Data Reference: Los Alamos Summary Data Package: LCO-ACP-18)						
Biosorption Experiment	[actinide or analog] Sorbed (M)	[Actinide or analog] in solution (M)	PROPMIC	#PROPMIC 50% contingency	# cells/Liter (from experiment)	*Moles An/ Cell
Th(IV) Biosorption						
Th(IV) hydroxide at pCH+ = 8.6 with archaea	4.67 E-8	3.38 E-7	0.14	0.21	1.23 E13	3.8 E-21
Th(IV) hydroxide at pCH+ = 8.6 with Bacteria	1.96E-7	1.68 E-7	1.17	1.76	8.7 E11	2.3 E-19
Nd (III) Biosorption						
Nd(III)-EDTA at pCH+ ~ 8.5 with archaea	8.00 E-10	2.42 E-8	0.033	0.050	2.05 E 13	3.9 E-23
Nd(III)-EDTA at pCH+ ~ 8.7 with bacteria	4.50 E-9	2.15 E-8	0.21	0.32	1.45 E12	3.1 E-21
Np(V) Biosorption [Ams, 2013], also see Figure 3-2						
Np(V) in carbonate media, I = 4 M sodium perchlorate with bacteria	2.9 E-6	2.1 E-6	1.4	Not Applicable	7.25 E12	4.0 E-19
#this accounts for the uncertainty due to lower pH data *this is [actinide or analog sorbed] / # of cells/Liter						

CAPMIC

A biomass-derived CAPMIC, as opposed to a toxicity-based CAPMIC, is recommended. This takes the moles of actinides/microbe measured in the biosorption experiments and multiplies this by the highest cell density (cells/L) expected. In this way, an upper limit to the mobile biosorbed actinide concentration is established. In this context, CAPMIC is given by:

$$\text{CAPMIC} = \frac{[\text{actinide or analog sorbed in M}]}{(\# \text{cells per Liter})} \times (\text{maximum \# cells per Liter expected})$$

The maximum # of cells/L expected (see discussion in Section 5.2, review of assumption #1) is 10^{12} /L. This contrasts with the typically 10^7 , but as high as 10^{10} cells/L that are seen in nature so a 10^{12} number is viewed as extremely conservative. For Np (V), see Ams 2013 and Figure 3-2, this value is given by the following:

$$\text{CAPMIC} = (4 \times 10^{-19} \text{ mole/cell}) (1 \times 10^{12} \text{ cells/Liter}) = 4 \times 10^{-7} \text{ M}$$

CAPMIC Values based on “low pH” pC_{H+} ~ 8.6-8.9 data				
(Source Data Reference: Los Alamos Summary Data Package: LCO-ACP-18)				
Biosorption Experiment	Moles An/Cell (Table above)	*CAPMIC	CAPMIC (10X Contingency)	#CAPMIC Average of all Experiments
Th(IV) Biosorption				
Th(IV) hydroxide at pC _{H+} = 8.6 with archaea	3.8 E-21	3.8 E-9 M	3.8 E-8	1.9 E-8 M
Th(IV) hydroxide at pC _{H+} = 8.6 with Bacteria	2.3 E-19	2.3 E-7 M	2.3 E-6 M	1.7E-6 M
Nd (III) Biosorption				
Nd(III)-EDTA at pC _{H+} ~ 8.5 with archaea	3.9 E-23	3.9 E-11 M	3.9 E-10 M	6.7 E-10 M
Nd(III)-EDTA at pC _{H+} ~ 8.7 with bacteria	3.1 E-21	3.1 E-9 M	3.1 E-8 M	7.6 E-9 M
Np(V) Biosorption [Ams, 2013], also see Figure 3-2				
Np(V) in carbonate media, I = 4 M sodium perchlorate with bacteria	4.0 E-19	4.0 E-7 M	4.0 E-6 M	NA
*CAPMIC is moles An/Cell x 1E12 cells/L – these are based on “low pH” data in PROPMIC table # this is provided for comparison so show that conservatism captures all our data				