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LANL/ACRSP Parameter Recommendations for the CRA-2019 Deferred Performance Assessment

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History of Revisions

Revision Number	Effective Date	Pages Affected	Description of Revision
0	4/3/2019	All	Original Release
1		Minor edits on p. 14, 16, 22, 24, and 26	Minor editorial comments from the DOE-CBFO are incorporated – mainly qualifiers NA and ND used in tables are defined more explicitly. Table 3-4 was made consistent with Table 3-2. References were made consistent with Los Alamos style guide.

LANL/ACRSP PARAMETER RECOMMENDATIONS FOR THE CRA-2019 DEFFERRED PERFORMANCE ASSESSMENT

Executive Summary

The 50/50 oxidation state distribution of multivalent actinides, used since the CCA, continues to be recommended for CRA-2019. The colloid enhancement parameters (mineral = CONCMIN, intrinsic = CONCINT and microbial = CAPMIC/PROPMIC) that are recommended are shown in the Table below. A short summary of the basis and justification for each recommendation and parameter is given. These are provided as input to the deferred CRA-2019 performance assessment and fulfill a DOE-CBFO deliverable.

Colloid Enhancement Parameter Values Recommended for the CRA-2019 PA				
Actinide	**Actinide source Term Colloid Enhancement Parameters**			
	Intrinsic	**Mineral**	**Microbial**	
			CAPMIC	**PROPMIC**
Thorium	4.3×10^{-8} M	2.6×10^{-8} M	3.8×10^{-8}	0.21
Uranium	1.4×10^{-6} M	2.6×10^{-8} M	3.8×10^{-8}	0.21
Neptunium	4.3×10^{-8} M	2.6×10^{-8} M	3.8×10^{-8}	0.21
Plutonium	4.3×10^{-8} M	2.6×10^{-8} M	3.8×10^{-8}	0.21
Americium	9.5×10^{-9} M	2.6×10^{-8} M	2.3×10^{-9}	0.03

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LIST OF COMMONLY USED ACRONYMS

ACRSP	Actinide Chemistry and Repository Science Program (LANL-CO)
Am	Americium
An	Generic actinide
CAPMIC	PA parameter for the maximum concentration of bioassociated actinide colloids
CBFO	Carlsbad Field Office (DOE)
CCA	Compliance certification application (for WIPP)
Cm	Curium
CONCINT	PA parameter for the concentration of intrinsic actinide colloids
CONCMIN	PA parameter for the concentration of the mineral actinide colloids
CRA	Compliance recertification application (for WIPP)
DOE	Department of Energy
E_h	Redox potential
EPA	Environment Protection Agency
ERDA-6	Energy Research and Development Administration Well-6 (WIPP brine)
GWB	Generic Weep Brine (WIPP high Mg brine)
Hbt	*Halobacterium* – archaea (isolate) used in Los Alamos biosorption experiments
I	Ionic strength in M
LANL-CO	Los Alamos National Laboratory-Carlsbad Operations
MgO	Magnesium oxide – engineered barrier for the WIPP
Nd	Neodymium
Np	Neptunium
PA	Performance Assessment
pC_{H+}	pH in terms of concentration adjusted/corrected for high ionic strength
PROPMIC	PA parameter for the proportionality of dissolved and bioassociated actinides
Pu	Plutonium
SOTERM	Actinide Source Term (Appendix/Attachment for the WIPP CRA)
Th	Thorium
TRU	Transuranic
U	Uranium
WIPP	Waste Isolation Pilot Plant – Transuranic waste repository

LANL/ACRSP PARAMETER RECOMMENDATIONS FOR THE CRA-2019 DEFFERRED PERFORMANCE ASSESSMENT

1.0 INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) transuranic (TRU) repository continues to be the cornerstone of the US nuclear waste management effort. As a condition of operation, the Environmental Protection Agency (EPA) recertifies the WIPP every five years. In 2019, the recertification effort is moving forward on a dual track. The Compliance Recertification Application (CRA) was submitted in March 2019 as required by law. A deferred Performance Assessment (PA) activity, as well as additional CRA documentation, however, will not be completed until the end of 2019. This was done to provide the DOE with additional time to respond to issues raised by the EPA when they last recertified the WIPP in July 2017 [EPA 2017].

The purpose of this report is to recommend parameter values for use in the deferred PA calculation in the following two areas:

- Actinide redox: Oxidation state distribution
- Actinide colloid enhancement parameters: Intrinsic (CONCINT), mineral (CONCMIN) and microbial (CAPMIC and PROPMIC)

A restatement of parameter definitions, the recommended parameter values, along with a brief explanation/justification of the basis for their selection are provided in the following sections.

2.0   ACTINIDE OXIDATION STATE DISTRIBUTION

The WIPP project has had the same conceptual model for the oxidation state distribution of TRU actinides since the original compliance certification application (CCA) [DOE 1996]. The actinide model reflects the expected post closure conditions in the WIPP: Anoxic, the presence of excess zero-valent iron in TRU waste, and the potential saturation of the repository horizon with MgO (engineered barrier)-reacted high ionic-strength brine. Under these conditions, the oxidation state model consists of a range in E_h (based on expert opinion) that brackets the expected conditions and establishes a set of actinide oxidation states for the least reducing conditions and most reducing conditions expected. This is discussed in more detail in the CRA-2014 [DOE 2014] documentation [DOE Appendix SOTERM-2014; DOE Appendix PA-2014]. This modeling approach has been presented and discussed in the international community many times over the past several years and continues to be supported by WIPP-specific results obtained by the DOE [Reed 1994, 1998, 2006, 2010, 2012, 2013]. All of this, as well as the current status of our understanding, was recently summarized [Reed 2018].

For CRA-2019, we continue to recommend to the DOE-CBFO that the WIPP actinide oxidation state distribution model remain unchanged. This is captured by the actinide oxidation states and abundances listed in Table 2-1 (so-called 50/50 distribution). These are sampled in the following way in PA:

All PA vectors:	Am(III), Cm(III) and Th(IV)
Least-reduced PA vector (50% probability):	U(VI), Np(V) and Pu(IV)
Most-reduced PA vector (50% probability):	U(IV), Np(IV) and Pu(III)

In this context, the parameters that set the probability for the least and most reduced oxidation set in a PA vector should remain unchanged in the WIPP PA model.

Basis and Justification for the Parameter Recommendation

The oxidization state distribution of the TRU WIPP actinides has been and continues to be a somewhat contentious point of discussion with the EPA regulator, particularly in the case of plutonium. This is well justified given the increased amount of Pu in the CRA-2019 TRU waste inventory [PAIR 2018] and the many ongoing discussions of the possibility of additional plutonium in the WIPP beyond CRA-2019. Plutonium remains the most important TRU component in WIPP waste for a number of reasons. That being said, the following are the key points that justify leaving the oxidation state model for all the TRU actinides unchanged in CRA-2019:

1) There are no WIPP-relevant data that directly contradict the current model that has been now certified by the EPA four times (CCA, CRA-2005, CRA-2009, and CRA-2014). This

is particularly true for plutonium which continues to receive much attention in CRA-2019. As previously summarized [Reed 2018, Table 6] we see no evidence of Pu(V/VI) in the anoxic reducing conditions predicted, we see Pu(IV) under the most WIPP relevant conditions (Pu-239, $pC_{H+} \sim 9.4$, and iron II/III phases), and we see aqueous and sorbed Pu(III) when strongly reducing conditions are imposed under laboratory conditions.

2) The E_h range concept implemented in the CCA is a very sound concept that should not be readily abandoned (e.g. to disconnect Pu from the other multivalent actinides or use a redox indicator such as H_2 to define a system redox condition). We simply cannot reliably define the E_h in a defensible way as it relates to the oxidation states of the mobile actinide source term – this is beyond the state of the art. Measurements under laboratory conditions, using a Pt electrode, are also problematic and not defensibly reliable given the complexity of WIPP-relevant brine systems [ReCosy 2012].

3) The impacts of radiolysis, particularly as the plutonium content is increased, need to be more fully evaluated experimentally. Current geochemical and speciation models cannot explicitly model the impacts of radiolysis on the redox conditions although this can be done implicitly by expert opinion. Qualitatively, in a sodium chloride brine, these effects are known and lead to increased oxidation so it effectively leads to a positive shift in the system E_h. WIPP-specific data [Reed 2006; Reed 2018, Table 6] have shown that reduced iron will reduce Pu(V/VI) to Pu(III/IV). But there are no data that sufficiently address the combined impacts of iron and radiolysis on the long-term stability and prevalence of the Pu(III) oxidation state.

4) Lastly, there is much work that is ongoing in this field and significant progress was recently reported [Cho 2016; Altmaier 2017; Tasi 2018; NEA 2019] and should be reasonably expected in the next few years. These new data address both redox issues as well as the limitations in the WIPP actinide solubility model. In this context, it makes sense to understand these new results, establish consensus within the actinide repository science community and allow these data to lead us to the right conclusions and path forward should the safety case need to be modified.

In view of where things are today, and especially in the context of the increased importance of plutonium in the WIPP, we fully recognize that these CCA assumptions about oxidation state distribution need to be re-assessed and this is already underway. This needs to be done holistically, that is for all the multivalent actinides together, and in a way that follows and is confirmed by WIPP site-specific data and results.

Table 2-1. **Oxidation states of the actinides in the WIPP as used in the CRA-2014 PA [DOE Appendix SOTERM-2014, Table SOTERM–17]**

Actinide Element	Oxidation States, Abundance (%), and Analog Used (If Any)				
	Oxidation State[a,b]				EQ3/6 Speciation Data Used
	III	IV	V	VI	
Thorium	—	100 %	—	—	Thorium
Uranium	—	50 %	—	50 %	1 mM assumed for VI, Th for IV
Neptunium	—	50%	50 %	—	Np for V Th for IV
Plutonium	50 %	50 %	—	—	Am for III Th for IV
Americium	100 %	—	—	—	Americium
Curium	100 %	—	—	—	Americium

[a] Oxidation state distributions (percentages) refer to the percent of PA vectors that have 100% of the specified oxidation state.

[b] In PA calculations the distribution of oxidation states is correlated for U, Np, and Pu such that the states for all three elements are simultaneously either in the lower oxidation state (U(IV), Np(IV), and Pu(III)) or in the higher oxidation state (U(VI), Np(V), and Pu(IV)).

3.0   COLLOID ENHANCEMENT PARAMETERS

The WIPP colloid model, and associated parameters, did not change significantly from the CCA through CRA-2009. In this context, the enhancement parameters were found to meet/exceed compliance requirements for WIPP certification by the EPA in the CCA, CRA-2005 and CRA-2009 and significant comments/concerns specific to this model were not received.

As part of the CRA-2014 [Reed 2013], this model and the associated parameters were reviewed and found to be somewhat disconnected from the current understanding in the field. Additionally there were new WIPP-relevant data. This led to a decision to update the colloid enhancement parameters but the model itself was not changed. EPA comments on these changes were received as part of their CRA-2014 review [EPA 2017] but the updated parameters submitted were accepted.

The parameter changes implemented in CRA-2014, however, continue to be the subject of ongoing discussion with the EPA. This is particularly true for those that directly impact the mobile source term for plutonium. For the deferred CRA-2019 PA, the following are implemented or recommended:

1) The colloid model itself remains the same and will not be updated. This model remains unchanged since its implementation in the CCA but is flagged as a model that should be updated when there is an opportunity.

2) A fix to the PA calculation of the microbial colloid contribution was implemented [see Sarathi 2019 for a detailed description]. This change keeps PROPMIC essentially the same, but removes the zeroing out of the colloid contribution when [Actinide] = CAPMIC. In the current implementation, the colloidal contribution increases until CAPMIC is reached and then remains constant.

3) The colloid enhancement parameters CONCMIN, CONCINT, PROPMIC and CAPMIC were re-evaluated to include new data and/or address questions received from the EPA.

In this section, the recommended parameter values are discussed and the current justification for the values recommended are given.

3.1   Mineral Colloids

The mineral fragment colloidal contribution to the WIPP mobile actinide source term is defined by the CONCMIN parameter:

CONCMIN: Concentration limit of actinide associated with mobile mineral fragment colloids (units of mole of mineral-bound actinide / Liter). This is implemented in PA as an element-specific parameter.

Recommended value for CRA-2019:   CONCMIN = 2.6×10^{-8} M
(for all actinides and oxidation states)

Operationally, as of CRA-2014, this is defined as actinide colloidal species > 10 nm when mineral colloids are known to be present in the WIPP brine. This is discussed more completely in Reed 2013, section 4. A summary of the CONCMIN parameter values used by WIPP PA is shown in Table 3-1 (there is no change). In the CCA, although a wide range of colloids were considered, only the iron colloids were considered to be likely present in the WIPP. We have also evaluated the effects of magnesium hydroxide due to some MgO associated colloids reported [Altmaier 2004]. This type of colloid has not been observed for WIPP-relevant conditions.

Basis and Justification for the Parameter Recommendation

There are no new data since the CRA-2014 and this has not been an active area of research within the WIPP project. In CRA-2014, the basis of this parameter value was updated to reflect results from long-term solubility studies in the Pu-Fe system. For CRA-2019, the data presented in Reed 2013, Section 4.3 were re-evaluated over the full pH range of the data presented (see Table 4-4 in Reed 2013). All are captured by the 2.6×10^{-8} M recommended value for CONCMIN. In principle, these parameter values should be oxidation-state specific and dependent, to a much lesser extent, on the actinide. They, however, are phrased as element-specific parameters in WIPP PA. These parameter values are consistent with the CCA concept and approach.

Table 3-1 Summary of historical values of CONCMIN (moles/Liter) and those recommended for CRA-2019			
Actinide	**CCA through CRA-2009**	**CRA-2014**	**CRA-2019 (recommended)**
Thorium	2.6×10^{-8} M	2.6×10^{-8} M	2.6×10^{-8} M
Uranium	2.6×10^{-8} M	2.6×10^{-8} M	2.6×10^{-8} M
Neptunium	2.6×10^{-8} M	2.6×10^{-8} M	2.6×10^{-8} M
Plutonium	2.6×10^{-8} M	2.6×10^{-8} M	2.6×10^{-8} M
Americium	2.6×10^{-8} M	2.6×10^{-8} M	2.6×10^{-8} M

3.2 Intrinsic Colloids

The intrinsic colloidal contribution to the WIPP mobile actinide source term is defined by the CONCINT parameter:

CONCINT: Concentration limit of actinide associated with mobile intrinsic actinide colloids. This is implemented in PA as an element-specific parameter.

Operationally, as of CRA-2014, these were defined as nano-filterable species in our long-term multiyear site-specific solubility studies that are between 2.5 and 10 nm in size. "Classical" colloids are not observed in the high ionic-strength brines predicted for the WIPP.

For CRA-2019, the data in Reed 2013 (see Section 4.2 and 4.4) were re-examined over a broader pH range leading to increases in some of the recommended parameters. These recommended values, along with past values for the CONCINT parameter used by the WIPP, are summarized in Table 3-2 for each actinide and oxidation state. Although these types of intrinsic colloids are expected to be mostly dependent on oxidation state and, to a lesser extent, on the element, they are implemented in PA as element-specific values. When two different values exist for the same element, the higher value is used (a conservatism in the current approach). The element-specific values proposed are given in Table 3-3.

Table 3-2 Summary of oxidation-specific historical values of CONCINT (moles/Liter) and those estimated for CRA-2019			
[2]Actinide	[1]CCA through CRA-2009	CRA-2014	CRA-2019
Th(IV)	0	2×10^{-8} M	4.3×10^{-8} M
U(IV)	0	2×10^{-8} M	4.3×10^{-8} M
U(VI)	0	3×10^{-8} M	1.4×10^{-6} M
Np(IV)	0	2×10^{-8} M	4.3×10^{-8} M
Np(V)	0	ND	ND
Pu(III)	1×10^{-9} M	4×10^{-9} M	9.5×10^{-9} M
Pu(IV)	1×10^{-9} M	2×10^{-8} M	4.3×10^{-8} M
Am(III)	0	4×10^{-9} M	9.5×10^{-9} M
[1] For CCA through CRA-2009 only Pu intrinsic colloids are considered. [2] For element-specific parameters, the highest value is proposed. ND – not determined			

[2]Actinide	**[1]CCA through CRA-2009**	**CRA-2014**	**CRA-2019 (recommended)**
Thorium	0	2×10^{-8} M	4.3×10^{-8} M
Uranium	0	3×10^{-8} M	1.4×10^{-6} M
Neptunium	0	2×10^{-8} M	4.3×10^{-8} M
Plutonium	1×10^{-9} M	2×10^{-8} M	4.3×10^{-8} M
Americium	0	4×10^{-9} M	9.5×10^{-9} M

Table 3-3   Summary of element-specific historical values of CONCINT(moles/Liter) and those recommended for CRA-2019

[1] For CCA through CRA-2009 only Pu intrinsic colloids are considered.
[2] For element-specific parameters, the highest oxidation-specific value is used.

Basis and Justification for the Parameter Recommendation

Since the CRA-2014, there are no new data for the CONCINT parameter and this is not an active area of research within the WIPP project. In response to EPA comments received, the filtration data presented in CRA-2014 were re-evaluated over a broader pC_{H+} range. The specifics of this evaluation are summarized in Table 3-4 and discussed in more detail in Appendix A.

In the CCA, there was an understanding that only plutonium forms colloids and that Pu(III) and Pu(IV) had the same colloidal tendencies. The parameter value recommended for CONCINT was based on a null result and the sensitivity of the analytical technique used. The approach used in CRA-2014 and also recommended for CRA-2019 achieves the following:

- It corrects the assertion that only plutonium forms WIPP-relevant colloids and that Pu(III) and Pu(IV) have the same colloidal tendencies. In fact all actinides seem to have a very small fraction of nano-filterable species and this seems to follow oxidation-state specific trends.
- It shifts the basis of the parameter values to data from the long-term multiyear solubility studies in WIPP-relevant brines, rather than a null result in a short term experiment (~ 1 week). This significantly strengthens the basis for the CONCINT values selected.

Actinide	CRA-2014 CONCINT Value	pC_{H+} Range Evaluated	CRA-2019 CONCINT Value	Broader pC_{H+} Range Evaluated
Th(IV)	2×10^{-8} M	~ 9.1	4.3×10^{-8} M	8.1, 8.5 and 9.2
U(IV)	2×10^{-8} M	Same as Th(IV)	4.3×10^{-8} M	Same as Th(IV)
U(VI)	3×10^{-8} M	9.3 and 9.8	1.4×10^{-6} M	8.6, 8.9, 9.3 and 9.8
Np(IV)	2×10^{-8} M	Same as Th(IV)	4.3×10^{-8} M	Same as Th(IV)
Np(V)	ND	NA	ND	NA
Pu(III)	4×10^{-9} M	9.1 and 9.5	9.5×10^{-9} M	7 , 8.3, 9.1, and 9.5
Pu(IV)	2×10^{-8} M	Same as Th(IV)	4.3×10^{-8} M	Same as Th(IV)
Am(III)	4×10^{-9} M	Same as Pu(III)	9.5×10^{-9} M	Same as Pu(III)

Table 3-4   Comparison of CRA-2014 and CRA-2019 CONCINT values along with the pC_{H+} range used in their evaluation

*pC_{H+} 8.6 data not used as this seems to be a significant outlier. Average % colloidal across this pH range was 55%. This translates into an effective concentration of 8×10^{-9} M when long-term solubility data are used to adjust for metastability.

ND – not determined   NA – not applicable

There remain a number of conservatisms that exaggerate the intrinsic colloid contribution in the approach currently being used. Thorium, in particular, has a high tendency towards the formation of metastable colloids and there is wide scatter in the data when a wider pH range is considered. In this context it is not a good analog for the other An(IV) actinides and overestimates the colloidal contribution. Additionally, these data are from experiments without organic complexants, most importantly EDTA and Citrate. These complexants, in effect, will greatly reduce these types of intrinsic colloids and we rarely see nano-filterable species in these more repository-relevant systems.

3.3   Microbial Colloids

Two parameters are used in PA to represent the microbial colloid contribution to the mobile actinide concentration - PROPMIC and CAPMIC:

PROPMIC: Proportionality constant for the concentration of actinides associated with mobile microbes (moles of microbe-bound actinide/moles of dissolved actinide)

CAPMIC: Maximum (cap) concentration of actinide associated with mobile microbes (moles of microbe-bound actinide/L)

The parameter values recommended for CRA-2019 are given in Table 3-5. The historical values used since the CCA, are given in Table 3-6. The CRA-2019 recommendations are based on the following assumptions, results or changes:

1) The biomass approach to determine CAPMIC [see discussions in Swanson 2018b], which was introduced in CRA-2014, is re-affirmed and has been retained. This is defensibly conservative although it considerably lowers the values used prior to CRA-2014.

2) The values for PROPMIC recommended are the archaeal, rather than bacterial, values used in CRA-2014. Additionally, when available, data with EDTA present are used. Both of these changes bring the parameters more in line with the expected long-term conditions in the WIPP.

3) The PROPMIC values are potentially specific to the element and oxidation state. However these are converted to element-specific values to match the current WIPP PA modeling approach although we continue to note that this should be changed to be more consistent with the overall WIPP actinide chemistry model. When there are different values for each oxidation state of a particular element, the higher of the two was selected.

4) Longer-term data (weeks rather than hours) obtained in WIPP-relevant brines are used when available to address the potential for bio-uptake and long-term interactions [Swanson 2019; Appendix B].

Basis and Justification for the Parameter Recommendation

Significant progress was made in understanding key microbial effects on the mobile actinide source term [Swanson 2018 a, b and c; Swanson 2019]. Ideally, the CAPMIC and PROPMIC parameters should be measured in actively growing cultures under WIPP-relevant conditions (anoxic, $pC_{H+} \sim 9.4$, presence of organic chelators, and I>5 complex brines). This is, however, problematic as we cannot grow near-field isolates under these conditions [Swanson, 2018c]. Additionally, many experiments must be set up under simpler and more controlled conditions, in order to better understand the bio-association mechanisms and the linkages with the actinide chemistry and speciation. Given these limitations, the most realistic experiments would use

Table 3-5 Parameter values for CAPMIC and PROPMIC recommended for CRA-2019

Actinide and Oxidation State	Oxidation-State Specific Parameters		Element-Specific Parameters		Actinide Element
	CAPMIC (M)	PROPMIC	CAPMIC (M)	PROPMIC	
Th(IV)	3.8×10^{-8}	0.21	3.8×10^{-8}	0.21	Thorium
U(IV)	3.8×10^{-8}	0.21	3.8×10^{-8}	0.21	Uranium
U(VI)	3.8×10^{-8}	ND			
Np(IV)	3.8×10^{-8}	0.21	3.8×10^{-8}	0.21	Neptunium
Np(V)	3.8×10^{-8}	ND			
Pu(III)	3.8×10^{-8}	0.03	3.8×10^{-8}	0.21	Plutonium
Pu(IV)	3.8×10^{-8}	0.21			
Am(III)	3.9×10^{-10}	0.03	2.3×10^{-9}	0.03	Americium
ND – not determined.					

Table 3-6 Historical values of PROPMIC and CAPMIC used in WIPP PA

[1]Element	CCA through CRA 2004		CRA 2009		[2]CRA-2014	
	PROPMIC	CAPMIC (M)	PROPMIC	CAPMIC (M)	PROPMIC	CAPMIC (M)
Th	3.1	0.0019	3.1	0.0019	1.76	2.3E-06
U	0.0021	0.0021	0.0021	0.0021	1.76	2.3E-06
Np	12.0	0.0027	12.0	0.0027	1.76	2.3E-06
Pu	0.3	6.8E-05	0.3	6.8E-05	1.76	2.3E-06
Am	3.6	NA	3.6	1.0	0.32	3.1E-08

[1]For U, Np and Pu, the parameter values are dominated by the An(IV) component which has the largest values for PROPMIC
[2]Up through CRA-2014, parameters recommended were based on bacterial, not archaeal, data.
NA - not available – this was changed to 1.0 M during the CRA-2004 process

haloarchaea grown under oxic conditions in WIPP brines at WIPP-relevant pHs and in the presence of ligands.

For the CCA through CRA-2009, these values were derived from a limited series of experiments [Papenguth 1996] that estimated the association of complexed actinides with halophilic organisms under growth conditions. The apparent toxicity of those same complexes were also evaluated under the same conditions. For CRA 2014, new values were proposed that were based on the association of actinides with a fixed concentration of resting cells of halophilic organisms [Reed 2013]. For the upcoming CRA 2019, more values have been generated, based on the same fixed biomass concept but with longer term data [Swanson 2019].

Haloarchaeal longevity in subterranean halite is well documented. These organisms are not necessarily active, but they will be present throughout the repository's lifetime. Halophilic bacteria can survive if they are able to balance energy production from emplaced waste (as electron donors/carbon sources) with that needed to maintain osmotic equilibrium, but their long-term survival will be limited by the fact that WIPP is a closed system [Swanson 2016]. Since there have been no anaerobic, extreme halophiles isolated from WIPP halite or any other subterranean halites to date, the use of archaeal data over bacterial is more realistic.

The use of WIPP brines at higher pH is also more realistic (again, initial experiments must sometimes be carried out in simplified brines). Other constituents of these brines may be involved in actinide complexation (e.g., borate) or may significantly affect microorganisms (e.g., magnesium). While values can be derived under these conditions, these additional effects require further investigation to better understand the mechanisms controlling an actinide's final disposition.

Since EDTA is the strongest complexant present in WIPP waste, the assumption is made that actinides will be preferentially bound as an EDTA complex. Thus, association data derived in the presence of EDTA may be more realistic. However, these values are often much lower than those in the absence of ligands, and this realism has raised concerns with EPA.

Arguments for the biomass approach

The biomass-based concept for parameter derivation is founded on the assertion that the conditions projected for the WIPP after closure will constrain microbial growth, activity, and survival. These conditions include:

- High salt concentrations
- Low water activity
- Anoxia
- The presence of chaotropic solutes
- Alkaline pH
- Radioactivity
- A lack of ideal substrates

Under ideal conditions in a generic halophile medium (i.e., aerobic, optimum pH, suitable growth substrates), haloarchaeal numbers in our experiments have never exceeded 5×10^9 cells/ml. In aerobic incubations containing 95% formulations of GWB and ERDA-6 amended with WIPP-relevant organics (acetate, citrate, oxalate, EDTA), cell numbers never exceeded 1×10^9 cells/ml [Swanson 2013]. None of the haloarchaea isolated from WIPP halite are capable of anaerobic growth, and to reiterate, no obligately anaerobic extreme halophiles have been isolated from subterranean halite.

The only anaerobic incubations of WIPP-related samples yielded up to 2.24×10^8 cells/ml in the presence of excess nitrate and inoculated with a mix comprising not only WIPP halite, but brine lake sediments and brines and muck pile salt [Francis 1993; Francis 1997; Gillow 2006]. Because of this rich inoculum, we believe that these are also optimistic numbers.

Experiments to evaluate long-term bioassociation trends

In CRA-2014, the experimental focus was on the surface complexation of various actinides/analogs with representative archaea and halophilic bacteria. This was a relatively fast process (typically less than 2 hours). In response to these data the EPA requested a longer-term evaluation to address the potential for internal biouptake that would contribute to the overall bioassociation (PROPMIC) parameter. For this reason, a series of new experiments that focused solely on the +3 analog, neodymium, and its interaction with the haloarchaeon, *Halobacterium* sp. were performed. Additionally, the longer-term data in prior studies were examined. These data have resulted in new values for the Am(III) PROPMIC and CAPMIC parameters and are more extensively presented in appendix B and further presented and discussed in Swanson 2019.

Under the most WIPP-relevant conditions (presence of EDTA, archaea, and simulated WIPP brine at $pC_{H+} \sim 9$) there was no measurable biosorption observed for GWB brine and only 3% bioassociation in ERDA-6 brine evaluated over a period of $\sim$ one month. At $pC_{H+} \sim 6$ with simplified brines a fast association followed by a slow loss of neodymium from solution was observed. Our best interpretation of these data is that there is bio-catalyzed extracellular precipitation but additional work is needed to confirm this hypothesis. This is however consistent with the higher pH thorium data reported for CRA-2014 where inverted biomass dependency curves were noted indicating that bio-induced precipitation was occurring. Overall, there does not seem to be a significant amount of bio-uptake when WIPP-relevant conditions are present.

4.0 REFERENCES

Borkowski 2010	M. Borkowski, J-F. Lucchini, M.K. Richmann, and D.T. Reed, "Actinide (III) Solubility in WIPP Brine: Data Summary and Recommendations," Los Alamos National Laboratory report LA-UR 14360 (2010).
Altmaier, 2004	M. Altmaier, V. Neck, and Th. Fanghänel, "Solubility and Colloid formation of Th(IV) in concentrated NaCl and MgCl$_2$ Solutions," *Radiochimica Acta*, vol. 92: 537–43 (2004).
Altmaier, 2017	M. Altmaier, D. Fellhauer, X. Gaona, and E. Yalcintas, "Assessment of Np(IV) and U(IV) as Improved Analogs for Pu(IV) in High Ionic. Strength Brine Systems," Karlsruhe Institute of Technology report (2017).
Cho 2016	H. R. Cho, Y-S Youn, E. C. Chang and W. Cha., "Hydrolysis of Trivalent Plutonium and Solubility of Pu(OH)$_3$ (am) Under Electrolytic Reducing Conditions," *Dalton Trans.*, **45**, 19449 (2016).
DOE 1996	U.S. Department of Energy (DOE). Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant (October). 21 vols. DOE/CAO-1996-2184. Carlsbad, NM: Carlsbad Field Office (1996).
DOE 2014	U.S. Department of Energy (DOE). Title 40 CFR Part 191 Compliance Recertification Application for the Waste Isolation Pilot Plant (March). 10 vols. DOE/WIPP 2004-3231. Carlsbad, NM: Carlsbad Field Office (2014)
DOE Appendix PA-2014	U. S. Department of Energy, 2014 Recertification Application, Appendix PA, (2014).
DOE Appendix SOTERM-2014	U. S. Department of Energy, 2014 Recertification Application, Appendix SOTERM, (2014).
EPA 2017	U.S. Environmental Protection Agency, Technical Support Document for Section 194.24: Evaluation of the Compliance Recertification Actinide Source Term, Gas Generation, Backfill Efficacy, Water Balance, and Culebra Dolomite Distribution Coefficient Values (July 2017).
Francis 1993	A.J. Francis and J.B. Gillow, "Effects of microbial processes on gas generation under expected Waste Isolation Pilot Plant repository conditions," Sandia National Laboratories report SAND93-7036 (1993).
Francis 1997	A.J. Francis, J.B. Gillow, and M.R. Giles, "Microbial gas generation under expected Waste Isolation Pilot Plant repository conditions," Sandia National Laboratories report SAND96-2582 (1997).
Gillow 2006	J.B. Gillow and A.J. Francis, "Microbial gas generation under expected Waste Isolation Pilot Plant repository conditions: final report," Brookhaven national laboratory report BNL-96148-2011-IR (2006).
NEA 2019	Actinide Update Blue Book, Nuclear Energy Agency, Thermodynamic Database Project, pending, 2019.

PAIR 2018   G. D. Van Soest, "Performance Assessment Inventory Report – 2018," Los Alamos National Laboratory report INV-PA-18 (2018).

Papenguth 1996   H.W. Papenguth, "H.W. Papenguth to Christine T. Stockman: Parameter Record Package for Colloidal Actinide Source Term Parameters: Attachment A: Rationale for Definition of Parameter Values for Microbes," Sandia National Laboratories record WPO 35856 (May 7, 1996).

ReCosy 2012   M. Altmaier, B. Kienzler, L. Duro, M. Grive and V. Montoya (eds.), "4th Annual workshop Proceedings of the Collaborative Project Redox Phenomena Controlling Systems (7th EC FP CP RECOSY)," (2012).

Reed 1994   D.T. Reed, and S. Okajima, "Stability and Speciation of Plutonium(VI) in WIPP Brine," *Radiochim. Acta* 66/67: 95-101 (1994).

Reed 1998   D.T. Reed, S. B. Aase, D. Wygmans and J. E. Banaszak, "The Reduction of Np(VI) and Pu(VI) by Organic Chelating Agents," *Radiochim. Acta* 82: 109-114 (1998).

Reed 2006   D.T. Reed, J-F. Lucchini, S.B. Aase and A.J. Kropf, "Reduction of Plutonium (VI) in Brine under Subsurface Conditions," *Radiochim. Acta.*, 94: 591-597 (2006).

Reed 2010   D.T. Reed, M.K. Richmann, J-F. Lucchini and M. Borkowski, "Reduction of Higher-Valent Plutonium by Iron Under Waste Isolation Pilot Plant (WIPP)-Relevant Conditions; Data Summary and Recommendations," Los Alamos National Laboratory report LA-UR-10-01254, designated LCO-ACP-09 (2010).

Reed 2012   D.T. Reed, M. Borkowski, J. Swanson, M. Richmann, H. Khaing, J-F. Lucchini, and D. Ams, "Redox-Controlling Processes for Multivalent Metals and Actinides in the WIPP." 3rd Annual Workshop Proceedings of the Collaborative Project Redox Phenomena Controlling Systems, 251-263 (2012).

Reed 2013   D.T. Reed, J.S. Swanson, J-F. Lucchini, and M.K. Richmann, "Intrinsic, Mineral and Microbial Colloid Enhancement Parameters for the WIPP Actinide Source Term," Los Alamos National Laboratory report LA-UR 13-20858, designated LCO-ACP-18 (2013).

Reed 2018   D.T. Reed, "Plutonium Oxidation State Distribution in the WIPP: Conceptual Model, Current Issues, and a Summary of Project-Specific Data," Los Alamos National Laboratory report LA-UR 18-25748 (2018).

Sarathi 2019   R. Sarathi, "Explanations of CAPMIC definition and usage in PA calculations, Memo to R. Camphouse," Sandia National Laboratories, record 557731 (1/14/2019).

Swanson 2013   J.S. Swanson, D.M. Norden, H.M. Khaing, and D.T. Reed, "Degradation of Organic Complexing Agents by Halophilic Microorganisms in Brines," *Geomicrobiology Journal* 30: 189-198 (2013).

Swanson 2016   J.S. Swanson, A. Cherkouk, T. Arnold, A. Meleshyn, and D.T. Reed , "The microbiology of subsurface, salt-based nuclear waste repositories: using microbial ecology, bioenergetics, and projected conditions to help predict microbial effects on repository performance," Los Alamos National Laboratory report LA-UR-16-28895 (2016).

Swanson 2018a   J.S. Swanson, D.T. Reed, A. Cherkouk, T. Arnold and A Meleshyn, "Microbial Influence on the Performance of Subsurface, Salt-Based Radioactive Waste Repositories: An Evaluation Based on Microbial Ecology, Bioenergetics and Projected Repository Conditions," NEA report No. 7387, (2018).

Swanson 2018b   J.S. Swanson and D.T. Reed, "Biomass-Based Approach to Determine the CAPMIC Bio-colloid Parameter for the WIPP Mobile Actinide Source Term," Los Alamos National Laboratory report LA-UR 18-22808, designated LCO-ACP-023 (2018).

Swanson 2018c   J.S. Swanson and D.T. Reed, "Update on Microbiology Research for the Waste Isolation Pilot Plant," Los Alamos National Laboratory report LAUR 18-31313 (2018).

Swanson 2019   J.S. Swanson, C. Hazelton, F.E. Stanley, E. Yalcintas, and D.T. Reed, "Review of the Microbial Colloid Contribution to the WIPP Actinide Source Term," Los Alamos National Laboratory report LA-UR 19-22310 (2019).

Tasi 2018   A. Tasi, X. Gaona, D. Fellhauer, M. Bottle, J. Rothe, K. Dardenne, D. Schild, M. Grive, E. Colas, J. Bruno, K. Kallstrom, M. Altmaier and J. Geckeis, "Redox behavior and solubility of plutonium under alkaline, reducing conditions," *Radiochim. Acta*, https://doi.org/10.1515/ract-2017-2870 (2018).

APPENDIX A

Process for the Selection of Expanded pC_{H+} range CONCINT Values

The data and results that support the recommended CONCINT values were previously reported [Reed 2013] and supported by the data summary packages SDP LCO-ACP-18 and C4 which document the traceability of these QL1 data. Table A-1 summarizes the results of long-term solubility studies were not included in CRA-2014 (so extend the breadth and pC_{H+} range of the analysis). This was done per the request of the EPA. The basis of the recommendation made in 2014 are also shown in Table A-2 for comparison (Table A2-1 in Reed 2013). The specific data and rationale for the parameters selected for CRA-2019 are summarized in this Appendix.

Table A-1 Summary of Wider pC_{H+} Range Analysis of Long-term Actinide Solubility Data [Data packages SDP LCO-ACP-18 and C4]						
Actinide	**Experiment**	**pC_{H+}**	**[An] at 10 nm filtration**	**[An] at 2.5 nm filtration**	**[An] Colloidal (M)**	**% Colloidal**
Plutonium (III)	GWB	7	9.94E-09	4.08E-10	9.53E-09	96%
	ERDA-6	8.3	1.60E-08	1.14E-09	1.49E-08	93%
Thorium (IV)	UG8CO-2 (1)	8.13	3.66E-08	1.41E-08	2.25E-08	61%
	UG8CO-2 (2)	8.13	3.93E-08	1.27E-08	2.66E-08	68%
	G8C2-1 (1)	8.54	3.11E-07	6.17E-08	2.49E-07	80%
	G8C2-1 (2)	8.54	3.68E-07	5.43E-08	3.14E-07	85%
	E10C3-1 (1)	9.18	1.51E-06	5.02E-07	1.01E-06	67%
	E10C3-1 (2)	9.18	1.33E-06	8.14E-07	5.16E-07	39%
Uranium (VI)	TI-GW-9.1	8.9	1.80E-06	3.97E-07	1.40E-06	78%
	T3-GW-C3-9.1	8.9	3.60E-05	2.45E-05	1.15E-05	32%
	T3-ER-C3-9.1	8.6	6.64E-07	2.36E-07	4.28E-07	64%
	T8-GWE-9.1	8.6	5.51E-07	2.51E-07	3.00E-07	54%

Comments:
Pu: These data are encompassed by the data used in CRA-2014
Th: Wide scatter in the data due to Th metastability. Apply percentage rather than concentrations measured
U: T3-GW-C3-9.1 is an outlier. Otherwise these data are encompassed by those used in CRA-2014

CRA-2019 Recommendations

An(III):   Pu(III) data are used. All colloidal concentrations observed were: 9.5×10^{-9} M, 1.5×10^{-9} M, 7.4×10^{-9} M, 4.5×10^{-9} M, and 9.3×10^{-10} M. Average is 4.8×10^{-9} M and highest observed was 9.5×10^{-9} M. Highest value observed is recommended.

Recommended value for An(III) CONCINT is 9.5×10^{-9} M.

An(IV):   Thorium(IV) data is the only option and these are not a good analog. Since wide scatter is observed and metastability predominated, percentages are used rather than absolute concentrations for Pu(IV). Highest % observed was 85%, this is multiplied by the observed total Th concentration of 5×10^{-8} M (pC_{H+} 9.1 10 nm filtration data), this gives a value of 4.3×10^{-8} M. This value is recommended.

Recommended value for An(IV) CONCINT is 4.3×10^{-8} M.

An(V):   An(V) was not evaluated. There are no data for this oxidation state.

An(VI):   Uranium(VI) data is the only option for An(VI). All the colloidal concentrations observed were: 0 M, 6.3×10^{-8} M, 1.4×10^{-6} M, 4.3×10^{-7} M and 3.0×10^{-7} M. The average value obtained, in this broader consideration, increases from 3×10^{-8} M to 4.4×10^{-7} M. The highest observed value was 1.4×10^{-6} M. The highest value is recommended for CRA-2019.

Recommended value for An(VI) CONCINT is 1.4×10^{-6} M.

Table A-2 Actinide-Analog-Specific Data Used to Determine the WIPP-relevant (pC_{H+} = 9.5 + 0.5) Intrinsic Colloidal Contribution (Table A2-1 in Reed 2013 – somewhat updated)

(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	2.1 E-9 M (22%)	[1]2.1 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]4.3 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]1.6 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	6.6 E-7 M	6.0 E-7M	6.3 E-8 M (9%)	[4]3.2 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

APPENDIX B

Experiments to evaluate long-term bioassociation trends

A series of new experiments has focused solely on the +3 analog, neodymium, and its interaction with the haloarchaeon, *Halobacterium* sp. These data have resulted in new values for the Am(III) PROPMIC and CAPMIC parameters. It is apparent that there are more mechanisms involved in the loss of Nd from solution than simple surface complexation. Biosorption likely accounts for the Nd loss measured at the earliest time points of the experiments. However, the continued loss of Nd from solution over time is more likely to be due to precipitation or internal uptake. Although we hypothesize that biologically-induced precipitation (either at the cells' surfaces or precipitation from solution) is the major cause of loss, rather than internalization, we currently do not have sufficient evidence to support this with certainty, and this is still under investigation. These mechanisms will lead to overestimations of both PROPMIC and CAPMIC values in the non-EDTA case. It should be noted that these differences do not apply to the EDTA case, where there is negligible loss of Nd from solution at any time point.

These parameters were derived as follows. Actual calculations are presented in data package "3-27-2019 Calculations of PROPMIC and CAPMIC for Parameter Recommendation Report". The results are summarized in Table B-1.

Experimental conditions:

- o Brines with 90% GWB formulation, 90% ERDA-6 formulation, 90% pC$_{H+}$ 9.5-specific formulation
- o Anoxic preparation of brines and anoxic experimental conditions
- o pC$_{H+}$:
  - ▪ GWB: 8.4
  - ▪ ERDA-6: 8.8
- o Target [biomass] of 10^9 cells/ml
- o Target [Nd] of 0.2 μM
- o When added, target [EDTA] of 0.1 mM

Derivation of parameter values:

$$\text{PROPMIC} = \frac{\text{(moles "microbe-bound" An/L)}}{\text{(moles dissolved An/L)}}$$

where "microbe-bound" An = {[Nd] in abiotic filtrate} − {[Nd] in biotic filtrate} and "dissolved An" is the [Nd] in biotic filtrate

$$\text{Moles Nd/cell} = \frac{\text{(moles "microbe-bound" An/L)}}{\text{(cells/L)}}$$

where "cells/L" are based on both live and dead cell counts

$$\text{CAPMIC} = \text{(moles An/cell)} * (1E+12 \text{ cells/L}),$$

where 1E+12 cells/L is fixed biomass concentration

EXPERIMENTAL CONDITION	PROPMIC	CAPMIC, M
Table B-1 Summary of Nd³⁺ Bio-association Results in WIPP-Relevant Brines		
GWB		
NON-EDTA case, 2 weeks	0.01	4.58E-10
NON-EDTA case, 5 weeks	0.04	4.38E-09
EDTA case, 12 days	0.01	1.21E-09
EDTA case, 1 month	0.00	~0[1]
ERDA		
NON-EDTA case, 2 weeks	1.79	4.03E-08
NON-EDTA case, 5 weeks	3.51	2.23E-07
EDTA case, 12 days	0.02	1.29E-09
EDTA case, 1 month	0.03	2.31E-09
[1]This value is negative when calculated using the approach summarized in this section – which has no physical meaning – so reset to ~ 0		

Table B-1 Summary of Nd^{3+} Bio-association Results in WIPP-Relevant Brines