579860

Notice: The current controlled version of this document is on the LCODocs website (https://lcodocs.lanl.gov/). A printed copy of the document may not be the current version.

LOS ALAMOS NATIONAL LABORATORY
CARLSBAD OPERATIONS

LCO-ACP-34, Revision 0

LANL ACRSP Parameter Recommendations for CRA-2024 Performance Assessment

Effective Date: 4-6-2023

Originators:

Jef Lucchini, LANL-CO ACRSP — 04/06/2023 — Date

Julie Swanson, LANL-CO ACRSP — 4-6-2023 — Date

Reviewed By:

Ceren Kutahyali Aslani, LANL-CO ACRSP — 04/06/2023 — Date

Approved by:

Jef Lucchini, LANL-CO ACRSP Team Leader — 04/06/2023 — Date

Priscilla Yanez, LANL-CO, Quality Assurance Manager — 4-6-2023 — Date

Douglas Weaver, WIPP/RSO Program Director — 4-6-2023 — Date

WIPP:4.4.1.1.1:PA:NQ:569293

Information Only

Revision Number	Effective Date	Description of Revision
0	4/6/2023	Initial Release

Information Only

Executive Summary

In this report, the Los Alamos National Laboratory (LANL) Actinide Chemistry and Repository Science Program (ACRSP) team provides detailed recommendations on the Waste Isolation Pilot Plant (WIPP) parameters regarding actinides, which will be used in the 2024 Compliance Recertification Application (CRA) Performance Assessment (PA) calculations. A summary of the values recommended for the WIPP parameters are included in the Table below. The shaded cells indicate a change of the values from the CRA-2019 values. A short summary of the basis and justification for each recommendation and parameter is given in this document.

Parameter values recommended for CRA-2024					
Actinide	OXCUTOFF	Colloids			
		Mineral	Intrinsic	Microbial	
		CONCMIN (M)	CONCINT (M)	CAPMIC (M)	PROPMIC
Th	1	2.6×10^{-8}	4.8×10^{-7}	6.95×10^{-4}	3.1
U	0.50	2.6×10^{-8}	1.4×10^{-6}	2.22×10^{-6}	0.0021
Np	0.50	2.6×10^{-8}	4.3×10^{-8}	2.33×10^{-6}	12
Pu	0.25	2.6×10^{-8}	4.3×10^{-8}	1.22×10^{-9}	0.3
Am	1	2.6×10^{-8}	6.7×10^{-7}	9.00×10^{-7}	3.52

Information Only

Table of Contents

	Executive Summary	3
	Acronyms	5
1.0	Introduction	7
2.0	Actinide Oxidation State Distribution	7
3.0	Colloid Enhancement Parameters	10
	3.1 Mineral Colloids	11
	3.2 Intrinsic Colloids	12
	3.3 Microbial Colloids	13
4.0	References	21

Information Only

Acronyms

ACRSP	Actinide Chemistry and Repository Science Program
Am	Americium
An	Generic actinide
arch	Archae
bac	Bacteria
°C	Celsius
CAPMIC	PA parameter for the maximum concentration of bioassociated actinide colloids
CBFO	Carlsbad Field Office (DOE)
CCA	Compliance certification application
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
DBR	Direct Brine Release
DOE	Department of Energy
EDTA	Ethylenediaminetetraacetic acid
E_h	Redox potential
EPA	Environment Protection Agency
ERDA-6	Energy Research and Development Administration Well-6
Fe	Iron
Fe(0)	Metallic iron
Fe_3O_4	Magnetite, an iron (II,III) oxide
$Fe(OH)_2(cr)$	Ferrous hydroxide, crystal
GWB	Generic Weep Brine
Hbt	*Halobacterium* – archaea (isolate) used in Los Alamos biosorption experiments
hrs	Hours
I	Ionic strength in M
LANL	Los Alamos National Laboratory
M	Mole per Liter
MgO	Magnesium oxide – engineered barrier for the WIPP
mo	Month
mL	Milliliter

Information Only

NaCl	Sodium chloride
Nd	Neodymium
nm	Nanometer
Np	Neptunium
ORP	Oxidation-reduction potential
OXCUTOFF	PA parameter indicating the fractional value for the lower oxidation state of an element
OXSTAT	PA indicator variable for elemental oxidation states
PA	Performance Assessment
pC_{H+}	pH in terms of concentration adjusted/corrected for high ionic strength
pH	Negative logarithm of proton activity
ppm	Parts per million
PROPMIC	PA parameter for the proportionality of dissolved and bioassociated actinides
Pu	Plutonium
$Pu(OH)_3$	Plutonium (III) hydroxide
$Pu(OH)_4$	Plutonium (IV) hydroxide
SNL	Sandia National Laboratories
SOTERM	Actinide Source Term
T	Temperature
Th	Thorium
TRU	Transuranic
U	Uranium
US	United States
WIPP	Waste Isolation Pilot Plant
wk	Week
XANES	X-ray absorption spectroscopy

Information Only

1.0 Introduction

The Waste Isolation Pilot Plant (WIPP) transuranic (TRU) repository continues to be the cornerstone of the United States (US) nuclear waste management effort. As a condition of operation, the Environmental Protection Agency (EPA) recertifies the WIPP every five years. The last Compliance Recertification Application (CRA) was submitted to the EPA in March 2019 [DOE 2019]. For the CRA-2019 effort, the Los Alamos National Laboratory (LANL) Actinide Chemistry and Repository Science Program (ACRSP) team provided detailed recommendations in the LCO-ACP-24 report on the WIPP parameters regarding actinides, which were used in the Performance Assessment (PA) calculations [Reed 2019].

Similarly to the LCO-ACP-24 report, and addressing the needs expressed by the Sandia National Laboratories (SNL) [King 2022], the LANL/ACRSP team recommends, in this report, the parameter values for use in the CRA-2024 PA calculations in the following two areas:

- Actinide redox: Oxidation state distribution (OXCUTOFF)
- 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 the actinides since the original compliance certification application (CCA) [DOE 1996]. The actinide model reflects the expected post closure conditions in the WIPP: anoxic, presence of excess zero-valent iron in transuranic (TRU) waste, and 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 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 details in the CRA-2019 [DOE 2019] documentation [DOE Appendix SOTERM-2019; DOE Appendix PA-2019]. This modeling approach has been presented and discussed over the past several years, and has been supported by WIPP-specific results obtained by the Department of Energy (DOE) Carlsbad Field Office (CBFO) [Reed 1994, 1998, 2006, 2010, 2012, 2013, 2018].

Information Only

Since the CCA, the WIPP actinide oxidation state distribution model has been based on two sets of oxidation states that govern actinide solubility. The first set, which refers to the "low" oxidation states, includes Pu(III), Np(IV), and U(IV). The second set, which refers to the "high" oxidation states, includes Pu(IV), Np(V), and U(VI). Thorium, americium, and curium are not included in these two sets, as they are redox invariant under WIPP conditions, as Th(IV), Am(III) and Cm(III). In the PA parameterization, the release calculations use the OXCUTOFF and OXSTAT parameters to indicate the actinide oxidation state distribution. OXCUTOFF indicates the fractional value for the lower oxidation state of the actinide, and has a fixed value between 0 and 1. OXSTAT is a sampled value between 0 and 1 to determine the oxidation state of specific realizations. When the value of the OXSTAT parameter is sampled below OXCUTOFF, the lower oxidation state is dominant and controls the solubility of the element; if the OXSTAT value is above OXCUTOFF, the higher oxidation state is prevailing and controls the solubility of the element.

From the initial CCA to the last CRA (CRA-2019), the actinide oxidation state distributions have been parameterized in the following way in PA:

All PA vectors (100% probability):	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)

Recent WIPP-relevant experimental data and publications have challenged the 50/50 distribution for Pu, to the extent that for CRA-2024, we recommend to the DOE-CBFO a change in the oxidation state distribution for Pu. We propose that 75% of the PA vectors contain Pu(IV), and that 25% of the PA vectors contain Pu(III). No changes are suggested for the other actinides in the WIPP actinide oxidation state distribution model, since no new work has challenged the current assumptions for U, Np, Am, Cm and Th. The recommendations are summarized in Table 1, and the basis and justification for the change in the oxidation state distribution for Pu are following.

Table 1. Values for Pu, Np and U recommended for the OXCUTOFF parameter in CRA-2024.

Parameter values for OXCUTOFF recommended for CRA-2024	
Pu	0.25
Np	0.50
U	0.50

Information Only

Basis and Justification for the Parameter Recommendation for Pu

The oxidization state distribution of the actinides in the WIPP PA continues to be a point of discussion with the EPA regulator, particularly in the case of plutonium. In 2020, J. Schramke *et al.* published "a literature review to evaluate the effects of WIPP chemical and physical processes on dissolved (not colloidal) plutonium oxidation states that included reactions with reducing agents such as iron solids and aqueous species and radiolysis of solids and aqueous species" [Schramke 2020]. The main conclusion of their study is that "extremely reducing conditions, including the presence of metallic iron, $Fe(OH)_2$(cr), and/or magnetite will lead to plutonium solubility control by Pu(III) solid". This conclusion directly challenged the WIPP 50/50 distribution for Pu oxidation state. Most recently the EPA has concluded that the Pu oxidation state in the WIPP is 100% Pu(III) [EPA 2022].

In this context, the LANL ACRSP has been conducting Pu solubility experiments in 90% strength Generic Weep Brines (GWB) at pC_{H+} 9 and 10, in the presence of WIPP-relevant organic complexants (EDTA, oxalate, citrate, acetate), using Pu-239 isotope (to maximize radiolytic effects) in the $Pu(OH)_3$ and $Pu(OH)_4$ forms, and magnetite Fe_3O_4 (estimated to be the most stable oxidized iron phase under WIPP conditions) and metallic Fe, from an undersaturation approach in a nitrogen-controlled atmosphere [Beam 2023]. Results after 205 days in the experiments, using X-ray absorption spectroscopy (XANES), show that Pu(IV) is the dominant oxidation state under the investigated WIPP-relevant conditions [Beam 2023].

The results of these two investigations [Schramke 2020, Beam 2023] are mainly the basis for the recommended change in the oxidation state distribution of Pu. The following are the key points of discussion of these two studies, in order to establish a sound justification for the recommended change in the oxidation state model values for Pu in the WIPP PA calculations for CRA-2024:

1) Beam's data are the first experimental data obtained in WIPP-relevant conditions to provide a basis for a more realistic, data-driven oxidation state ratio for Pu in the WIPP PA model. In Beam's Pu-239 solubility experiments, strongly reducing conditions were maintained though the addition of iron. However, these reducing conditions were not strong enough to maintain Pu(III) stability during the duration of the experiments. Even in the experimental solutions containing initially 100% Pu(III) (as a $Pu(OH)_3$ phase), Pu(IV) solids were confirmed to be the dominant oxidation state [Beam 2023], by over 75% (Table 6). This demonstrates that those systems, which started with Pu(III), reached a redox balance that includes in a large majority Pu(IV). However, in all Beam's 16 experimental solutions closely representing the WIPP conditions, Pu(III) solid phases were still measured after 205 days, but in amount less than 25% [Beam 2023] (Table 6).
2) The E_h range is a very sound concept for the WIPP PA, but the limits of this range (i.e., the upper and lower values) have not been reliably defined as it relates to the oxidation states

Information Only

of the mobile actinide source term, given the complexity of the WIPP brine systems. The factors affecting the WIPP E_h range and the actinide oxidation states are known: high pH, high ionic strength, radiolysis, presence of organic complexants, anoxic and strong reducing conditions. Those combined effects have been taken into consideration in Beam's study [Beam 2023]. However, this work needs to be extended to other actinides of interest for the WIPP (Np, U) in order to better define the E_h range applicable to the WIPP conditions, and consequently, support the updated E_h approach [Beam 2022].

3) The impact of radiolysis, particularly as the Pu-239 inventory increases in the repository [PAIR 2022], has to be more fully evaluated experimentally, since radiolysis can influence the potential redox of any chemical systems. Current geochemical and speciation models cannot explicitly model the impacts of radiolysis on the redox conditions. Qualitatively, in simple brine systems (e.g., NaCl), radiolytic effects are known, and were proven to lead to increased oxidation, so the E_h values effectively increase. The preliminary experimental data presented in [Beam 2023] is a first attempt to point out the role of radiolysis in WIPP-specific reducing conditions, by using Pu-239, which is expected to account for 87% of the Pu activity in the WIPP after 10,000 years [PAIR 2022]. However, because of the relatively short duration of the experiments for the reported first data (205 days), the measured oxidation-reduction potentials (ORP) may not be fully representative of the long-term redox stability of the WIPP. Future samplings and ORP measurements of these experiments will provide more insights on the redox trend of these solutions. Presently, however, there are no experimental data that sufficiently address the combined impacts of iron (expected to maintain strongly reducing conditions) and radiolysis (suspected to lead the systems to more oxidizing conditions) on the long-term stability and prevalence of the Pu(III) oxidation state predicted in [Schramke 2020].

The recommended change in the OXCUTOFF parameter regarding Pu redox potential distribution is driven by the most recent site-specific experimental data from [Beam 2023], which leaves some room for the coexistence of Pu(IV) and Pu(III). In the current state of the knowledge, the most adequate values for Pu redox in the WIPP PA model are 0.75 for the least reduced PA vector (i.e., Pu(IV)), and 0.25 for the most reduced PA vector (i.e., Pu(III)).

3.0 Colloid Enhancement Parameters

In the following three sub-sections, the recommended parameter values for mineral, intrinsic and microbial colloids are presented and discussed.

Information Only

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.

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 in details in [Reed 2013], section 4.

Since the CRA-2019, only one experimental study in WIPP-relevant systems has been reported regarding mineral colloids of actinides. The LANL ACRSP team investigated the effect of dissolved silica on the solubility of An(III) and An(IV) solids, as well as the possibility of actinide-silica colloids, in 5 M NaCl solutions [Beam 2022b]. At pH values relevant to WIPP, no significant colloid fraction was observed by sequential filtration. Additionally, no increase in solubility was observed in the presence of sodium metasilicate. This indicates that actinide-silica colloids do not form under conditions that simulate a Direct Brine Release (DBR) into the repository.

Therefore, there are no changes recommended for the CONCMIN parameter values used by WIPP PA. The recommended values for the CONCMIN parameter for all actinides and oxidation states are identical to those used in the CRA-2019. They are summarized in Table 2.

Table 2. Values for the actinides recommended for the CONCMIN parameter in CRA-2024.

Parameter values for CONCMIN recommended for CRA-2024	
Actinide	CONCMIN (M)
Th	2.6×10^{-8}
U	2.6×10^{-8}
Np	2.6×10^{-8}
Pu	2.6×10^{-8}
Am	2.6×10^{-8}

Information Only

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.

Although these types of intrinsic colloids are mostly dependent on oxidation state and, to a lesser extent, on the element, they are implemented in PA as element-specific values [Reed 2019]. Operationally, as of CRA-2014, these were defined as nano-filterable species in the ACRSP long-term multiyear WIPP-specific solubility studies that are between 2.5 and 10 nm in size. For CRA-2019, the data in [Reed 2013] (Section 4.2 and 4.4) were re-examined over a broader pH range, and updated values for the CONCINT parameter were recommended and used in the WIPP PA.

There have been no new WIPP-relevant data since the CRA-2019 on this topic. However, the EPA has recently proposed a couple of changes to the CONCINT parameter for Am and Th [EPA 2022]. They recommended to increase the Am intrinsic colloid concentration from 9.5×10^{-9} M used in the CRA-2019 PA calculations [Reed 2019] to 6.7×10^{-7} M [EPA 2022] (Section 8.1.4), an upper bound concentration for the long-term Nd(III) solubility experiments carried out by [Borkowski 2010] and revisited by [Reed 2013]. The EPA also recommended to increase the Th intrinsic colloid concentration from 4.3×10^{-8} M [Reed 2019] to a value of 4.8×10^{-7} M [EPA 2022] (Section 8.1.5), which appears to be more consistent with the Th(IV) experimental data considered in the WIPP PA [Altmaier 2004, Borkowski 2012]. Even though those proposed two changes are an increase of about one to two orders of magnitude, they would ultimately not have a significant impact on the WIPP PA calculations, particularly because none of the Th and Am inventories [PAIR 2022] significantly contribute to the overall release of radioactivity from the WIPP during the 10,000 year regulatory period. Therefore, the two changes proposed by the EPA are considered acceptable.

The values for the CONCINT parameter recommended for CRA-2024 are included in Table 3.

Information Only

Table 3. Values for the actinides recommended for the CONCINT parameter in CRA-2024.

Parameter values for CONCINT recommended for CRA-2024	
Actinide	CONCINT (M)
Th	4.8×10^{-7}
U	1.4×10^{-6}
Np	4.3×10^{-8}
Pu	4.3×10^{-8}
Am	6.7×10^{-7}

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 concentration of actinide associated with mobile microbes (moles of microbe-bound actinide/L).

The parameter values recommended for CRA-2024 are given in Tables 4 and 5 and are discussed in more detail below.

Information Only

Table 4. Element-specific values for CAPMIC and PROPMIC recommended for CRA-2024.

Parameter values for CAPMIC and PROPMIC recommended for CRA-2024		
Actinide	CAPMIC (M)	PROPMIC
Th	6.95×10^{-4}	3.1
U	2.22×10^{-6}	0.0021
Np	2.33×10^{-6}	12
Pu	1.22×10^{-9}	0.3
Am	9.00×10^{-7}	3.52

Table 5. Oxidation state-specific values for CAPMIC and PROPMIC recommended for CRA-2024.

Parameter values for CAPMIC and PROPMIC recommended for CRA-2024		
Actinide and Oxidation State	CAPMIC (M)	PROPMIC
Th(IV)	See element-specific Table 4	See element-specific Table 4
U(IV)		
U(VI)		
Np(IV)		
Np(V)		
Pu(III)	9.00×10^{-7}	3.52
Pu(IV)	See element-specific Table 3	See element-specific Table 3
Am(III)	9.00×10^{-7}	3.52

For the CCA through CRA-2009, these values were derived from a series of experiments that measured the association of complexed actinides with halophilic organisms under growth conditions and the toxicity of those same complexes under the same growth conditions [Papenguth 1996]. 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 CRA-2019, new values were generated for the +3 state, based on longer term experimental data [Swanson 2019].

Information Only

New Data and Recommendations

A series of experiments has focused on the +3 analog, neodymium, and its interaction with several WIPP microbial isolates in simple sodium chloride solutions and in WIPP brines. These data have resulted in yet new values for the An(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 absence of ligands. It should be noted that these differences do not apply to the EDTA case, where there was negligible loss of Nd from solution at any time point. Regarding the case of internal uptake, it should be noted that the organisms in all of these new experiments settled out of suspension over time and are therefore not considered mobile, according to the CCA definition. Again, this results in an overestimation of PROPMIC and CAPMIC values.

As a result of continued discussions with the EPA, the DOE has reassessed the 2014 and 2019 parameter values. From the CCA through CRA-2009, these values were provided based on element. For CRA-2014, two sets of values were presented: element-specific and oxidation state-specific. However, only the element-specific values were used in PA during that CRA and for CRA-2019. The goal of experimental work is to address each relevant oxidation state of each element. Because there are no new data for oxidation states other than +3, the recommended parameters will continue to be element-specific.

A summary of past, current and 2024-recommended parameters is provided in Tables 6 and 7.

Table 6. Element-specific PROPMIC values; historical and proposed new values.

Element	CCA through CRA-2009	CRA-2014*	CRA-2019**	EPA suggested values†	CRA-2024 proposed values
Am	3.6	0.32	0.03	3.6	3.52
Pu	0.3	1.76	0.21	2.18	0.3
Th	3.1	1.76	0.21	3.1	3.1
Np	12.0	1.76	0.21	12	12.0
U	0.0021	1.76	0.21	0.0021	0.0021

*bacterial values
**archaeal values originally presented in [Reed 2013]
† [EPA 2022]

Information Only

Table 7. Element-specific CAPMIC values (given in M); historical and proposed new values.

Element	CCA through CRA-2009	CRA-2014*	CRA-2019**	EPA suggested values†	CRA-2024 proposed values
Am	1	3.1×10^{-8}	2.3×10^{-9}	6.28×10^{-6}	9.00×10^{-7}
Pu	6.5×10^{-5}	2.6×10^{-6}	3.8×10^{-8}	2.18×10^{-5}	1.22×10^{-9}
Th	0.0019	2.6×10^{-6}	3.8×10^{-8}	2.12×10^{-2}	6.95×10^{-4}
Np	0.0027	2.6×10^{-6}	3.8×10^{-8}	1.01×10^{-3}	2.33×10^{-6}
U	0.0021	2.6×10^{-6}	3.8×10^{-8}	8.14	2.22×10^{-6}

*bacterial
**archaeal originally presented in [Reed 2013]
† [EPA 2022]

Justifications for the Recommended Values

PROPMIC parameters values will change based on the EPA's request to keep CCA values, with the exception of An(III) [EPA 2022]. The recommended value for Am(III) and Pu(III) is based on the highest value obtained in recent experiments (Figure 1): 3.52. This value was obtained from experiments with *Halobacterium* sp. in ERDA-6 brine after approximately 5 weeks duration. While we hypothesize that this higher value is due to induced precipitation, we currently do not have data to support this. Therefore, we recommend this calculated value.

Information Only

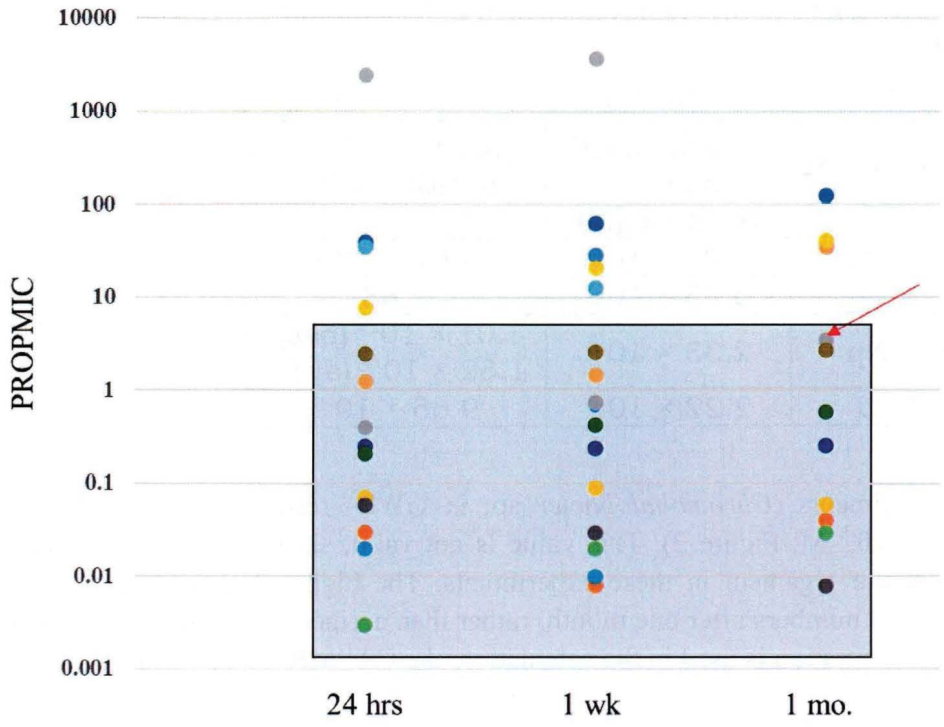


Figure 1. PROPMIC values calculated from experiments with Nd and WIPP-relevant isolates [Swanson 2022]. All experiments conducted in WIPP brines fall within the shaded box. Red arrow denotes highest calculated value.

CAPMIC values will also change from the CRA-2019 values in response to the EPA's request. The EPA had recommended that DOE use CAPMIC values generated from the original [Papenguth 1996] data but recalculated to conform with the biomass-based approach [Peake 2020]. However, the CCA experiments were toxicity-based and were not designed to target a high, fixed biomass concentration (10^9 cells/ml). To be self-consistent with methodology, DOE has chosen to use the data from the CCA filtration studies as presented in [Francis 1998], as this approach adheres more closely to the definition of CAPMIC. Even so, the biomass concentrations in those experiments were often very low, such that using the high, fixed multiplier unreasonably overestimates the CAPMIC values to concentrations that exceed inventory (Table 8).

Information Only

Table 8. Comparison between CAPMIC values calculated with and without the high biomass concentration multiplier.

Element	CAPMIC values based on actual biomass (M)	CAPMIC values based on fixed multiplier (M)
Pu	1.22×10^{-9}	4.07×10^{-9}
Th	6.95×10^{-4}	1.88
Np	2.33×10^{-6}	1.01×10^{-3} (bac), 1.52×10^{-7} (arch)
U	2.22×10^{-6}	9.65×10^{-6}

One set of recent experiments (*Chromohalobacter* sp. in GWB) resulted a high calculated CAPMIC value (9.86×10^{-5} M; Figure 2). This value is not valid, since there was little to no association of Nd with the organism in these experiments. The high value is a result of the significant decrease in cell numbers after one month, rather than an increase in bioassociation (if the original biomass concentration is used in the calculation, the CAPMIC is 1.5×10^{-7} M).

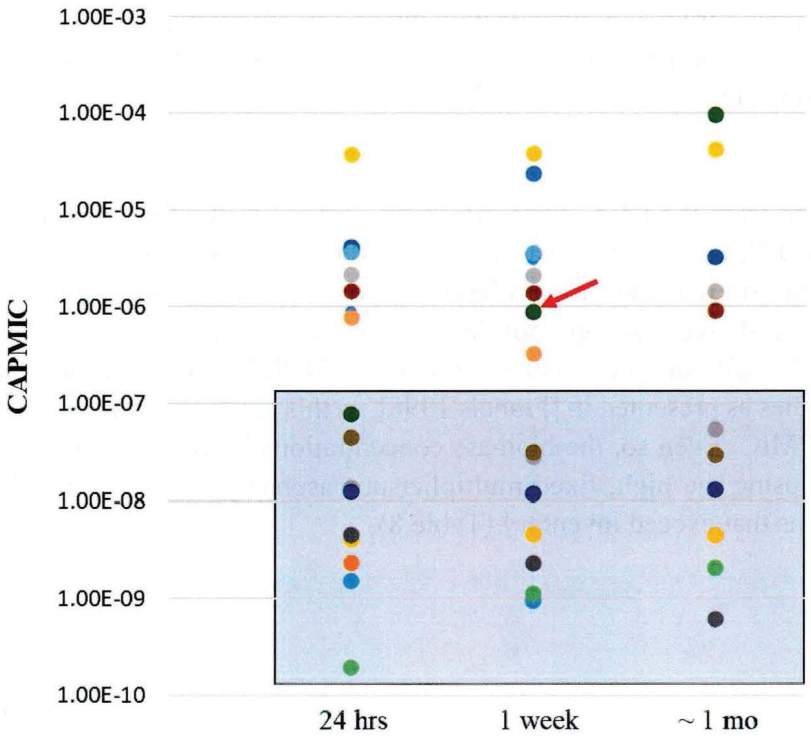


Figure 2. CAPMIC values calculated from experiments with Nd and WIPP-relevant isolates [Swanson 2022]. All data points within the shaded box are from experiments conducted in WIPP

Information Only

brines. Red arrow denotes highest calculated value from experiments in WIPP brine that does not exceed actual inventory concentration.

Additional Comments

DOE has stated previously that biosorption results can vary depending upon many factors, including the organism and test matrix [Swanson 2018b; Swanson 2019]. The literature survey conducted by the EPA has also shown that biosorption data can be highly variable [EPA 2022]. Because of this variability, the DOE has emphasized that data should be generated using WIPP-relevant organisms under WIPP-relevant conditions. This approach may have narrowed the extent of the variability, but it is still present, as evident in Figures 1 and 2. Even so, the new data show some trends:

- More biological influence is observed in ERDA brine than in GWB
- Behavior is more similar between NaCl-based matrices (e.g., ERDA and simplified NaCl) than between ERDA and GWB
- There is a likely effect of magnesium on the extent of biological influence
- The release of ligands, such as dipicolinate, from test organisms negates the colloid effect
- For PROPMIC:
    - Values tend to increase with time until they can no longer be defined (consequence of the method used to calculate PROPMIC)
    - Values are lower when the tested biomass concentration is lower
    - Values are lower in WIPP brines than in simplified NaCl solutions
- For CAPMIC:
    - Values do not vary significantly with time as PROPMIC values do
    - Values are higher when the tested biomass is lower (due to normalization to the high target concentration)
    - Values are lower in WIPP brines than in simplified NaCl solutions

The DOE can continue to conduct experiments on other oxidation states, especially An(IV). This may result in further changes to parameter values for future CRAs. Finally, it should be noted that many conservatisms are already built into PA.

- Each actinide is considered individually, such that each could theoretically associate to maximum capacity with each organism. This is impossible in reality, as there are a finite number of surface binding sites, and only one actinide can bind to a site at a time.
- Although PA refers to the mobile microbe population, current experiments are carried out using all microbes in suspension, not just those that might be considered mobile (i.e., suspended only).
- Results from current (and former) studies do not differentiate between actinide that has precipitated and that which is associated. This results in an overestimation of association. However, since this distinction is not made, the overestimation is accepted.

Information Only

- New values are derived from experiments using uncomplexed actinides. Nd-EDTA studies resulted in little to no association of Nd [Swanson 2019]; experiments in which the ligand dipicolinate was produced resulted in little to no association of Nd [Swanson 2021].

Summary: Sources of 2024 Proposed CAPMIC Values

- Am: highest calculated value from new experiments in WIPP brines (see Figure 2 above and [Swanson 2022])
- Pu: from measurements of associated actinide in [Francis 1998]; both archaeal and bacterial data are available; value chosen is the greater of the two = 1.22×10^{-9} M
- Th: from measurements of associated actinide in [Francis 1998]; no archaeal data available; therefore, used bacterial value = 6.95×10^{-4} M
- Np: from measurements of associated actinide in [Francis 1998]; both archaeal and bacterial data available; value chosen is the greater of the two = 2.33×10^{-6} M
- U: from measurements of associated actinide in [Francis 1998], data taken from U-nitrate experiments, since those were also used for PROPMIC; both archaeal and bacterial data available; value for archaea chosen = 2.22×10^{-6} M

Information Only

4.0 References

Beam 2022a — J. Beam, "Memo to Anderson Ward: Justification for Updating OXSTAT Parameter in Performance Assessment Calculations." May 31, 2022. Los Alamos National Laboratory, Los Alamos, NM. LA-UR-22-30617.

Beam 2022b — J.C. Beam, "Actinide (III/IV) – Silica Colloids in the WIPP." Los Alamos National Laboratory report LCO-ACP-27, Revision 0. (2022).

Beam 2023 — J. Beam, "Plutonium Oxidation State Distribution under WIPP Relevant Conditions." Los Alamos National Laboratory report LCO-ACP-31, Revision 1. LA-UR-23-20189 (2023).

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 LCO-ACP-08, Revision 0, LA-UR 14360 (2010).

Borkowski 2012 — M. Borkowski, " Numerical Values for Graphs Presented in Report LCO-ACP_08, Rev. 0, Entitled Solubility of An(IV) in WIPP Brine: Thorium Analog Studies in WIPP Simulated Brine, and for Graphs Published in Borkowski, M. *et al.* Radiochimica Acta 98 (9-11), 577-582 (2010)." Los Alamos National Laboratory report LANL-CO ACRSP ACP-01/2012, Revision 0, LA-UR-12-26640 (2012).

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*, 92: 537–43 (2004).

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 2019 — U.S. Department of Energy (DOE). Title 40 CFR Part 191 Compliance Recertification Application for the Waste Isolation Pilot Plant (March). Carlsbad, NM: Carlsbad Field Office (2019).

DOE Appendix PA-2019 — U. S. Department of Energy, 2019 Recertification Application, Appendix PA, (2019).

DOE Appendix SOTERM-2019 — U. S. Department of Energy, 2019 Recertification Application, Appendix SOTERM, (2019).

EPA 2022 — U.S. Environmental Protection Agency (EPA), Technical Support Document for Section 194.24: Evaluation of the Compliance Recertification Application (CRA-2019) Actinide Source Term, Gas Generation, Backfill Efficacy, Water Balance, and Culebra Dolomite Distribution Coefficient Values. Washington, DC: Office of Radiation and Indoor Air, EPA-HQ-OAR-2019-0534 (March 2022).

Information Only

Francis 1998 A.J. Francis, J.B. Gillow, C.J. Dodge, M. Dunn, K. Mantione, B.A. Strietelmeier, M.E. Pansoy-Hjelvik, H.W. Papenguth, "Role of Bacteria as Biocolloids in the Transport of Actinides from a Deep Underground Radioactive Waste Repository," *Radiochimica Acta*, 82: 347-354 (1998).

King 2022 S. King, "Letter to Jeremy Beam: Sandia's needs for WIPP parameter recommendations for Compliance Recertification Application 2024 Performance Assessment," December 12, 2022; Sandia National Laboratories, Carlsbad, NM.

PAIR 2022 G. D. Van Soest, "Performance Assessment Inventory Report – 2022," Los Alamos National Laboratory report INV-PA-22 (2022).

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).

Peake 2020 Fourth Set of EPA Completeness Comments and Questions for Compliance Recertification Application 2019 (CRA-2019). U.S. Environmental Protection Agency, Center for Waste Management and Regulation, Washington, D.C. Letter to M. Brown, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico (July 17, 2020).

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, 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, Revision 0 (2013).

Information Only

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, designated LA-UR 18-25748 (2018).

Reed 2019 D.T. Reed, J. Swanson, and F. Stanley. "LANL/ACRSP Parameter Recommendations for the CRA-2019 Deferred Performance Assessment," Los Alamos National Laboratory report, designated LCO-ACP-24, Revision 1. LA-UR-19-22787 (2019).

Schramke 2020 J.A. Schramke, E.F.U. Santillan, R.T. Peake, "Plutonium oxidation states in the Waste Isolation Pilot Plant repository". *Applied Geochemistry* 116, 104561 (2020).

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 2019 J.S. Swanson, "Review of the Microbial Colloid Contribution to the WIPP Actinide Source Term," Los Alamos National Laboratory report LCO-ACP-23, Revision 0, LA-UR 19-22310 (2019).

Swanson 2021 J. Swanson, A. Navarrette, C. Hazelton, M. Richmann, F. Stanley, "Biomass and Salt-Dependent Effects of Bacillus Spores on Radionuclide Migration from the Waste Isolation Pilot Plant," *Chemosphere* 280: 130680 (2021).

Swanson 2022 J.S. Swanson, "Biologically Influenced Transport of the +3 Actinide Oxidation State from the WIPP Environment, Using Neodymium as an Analog," Los Alamos National Laboratory report LCO-ACP-32, Revision 0, LA-UR-22-32936 (2022).

Information Only