Sandia National Laboratories

Operated for the United States Department of Energy
by National Technology and Engineering Solutions
of Sandia, LLC.

Albuquerque, New Mexico 87185-0101
Livermore, California 94551-0969

date: July 9, 2025

to: Sandia National Laboratory WIPP Records Center

from: Paul E. Mariner (08844) PAUL MARINER (Affiliate)

Digitally signed by PAUL MARINER (Affiliate)
Date: 2025.07.09 14:28:10 -04'00'

subject: CRA-2026 IS updates to the WIPP humic colloids models for An(III) and An(IV)

Introduction

The Waste Isolation Pilot plant (WIPP) was initially certified as a 10-panel repository for long-term waste disposal for transuranic (TRU) waste, which served as the design layout and basis for the performance assessment (PA) calculations for the 2019 Compliance Recertification Application Deferred Performance Assessment (CRA-2019 DPA). Due to operational constraints, not all this volume is available for waste disposal. In March 2024 the DOE submitted the Replacement Panels Planned Change Request (RPPCR) seeking EPA approval of two replacement waste disposal panels. Although the RPPCR is expected to be approved prior to submittal of 2026 Compliance Recertification Application (CRA-2026), the replacement panels will not accommodate the entire allowable waste volume as specified in the WIPP Land Withdrawal Act (LWA), leading to the consideration of seven additional waste panels. Thus, the CRA-2026 performance assessment (PA) will consider two repository designs: 1) An interim state repository (CRA-2026 IS) with 12 panels; and 2) a final-state repository (CRA-2026 FS) with 19 panels, which provides sufficient storage for disposal of the entire WIPP LWA waste volume.

This memo documents an update to the PHUMSIM and PHUMCIM proportionality constants for An(III) and An(IV) humic colloids for CRA-2026 IS. These constants are recalculated to ensure consistency with the CRA-2026 IS baseline solubility calculations for GWB and ERDA-6 brines (Domski 2025). A separate memo documents the PHUMSIM and PHUMCIM updates for use in the PA calculations for the CRA-2026 FS (Mariner 2025).

Calculation of these constants follows the methodology developed in Mariner (2016), Mariner (2018), Mariner (2023), and Mariner (2025). The Interim State process model calculations differ enough from the Final State calculations that two of the four PHUMSIM and PHUMCIM values differ between IS and FS.

Humic Colloids Implementation in PA

The aqueous humic-bound concentration of actinide, symbolized as (AnHs), is implemented in PA using the following equation:

$$(\mathrm{AnHs}) = \mathrm{minimum}\{H * (\mathrm{An}), \mathrm{CAPHUM}\} \qquad \text{(Eq. 1)}$$

Exceptional Service in the National Interest

Information Only

(An) is the dissolved actinide solubility from the Dissolved Actinide Source Term model. This solubility includes the effects of organic ligands like EDTA estimated to be present in WIPP brines. *H* is the humic-bound actinide proportionality coefficient (either PHUMSIM or PHUMCIM), and CAPHUM is the total humic complexation site concentration (DOE 2014, SOTERM-5.2). PHUMSIM and PHUMCIM are the humic colloid proportionality coefficients for brines from the Salado and Castile formations, respectively. These coefficients are equilibrium ratios of (AnHs) to (An). As indicated by Eq. 1, (AnHs) is the product of *H* and (An) if the product is less than CAPHUM; otherwise, (AnHs) is set at the value of CAPHUM.

PHUMSIM and PHUMCIM are defined by oxidation state (DOE 2014, Table SOTERM-20). Each actinide and its oxidation state apply individually to Eq. 1 and use the PHUMSIM and PHUMCIM values defined for the oxidation state (DOE 2014, SOTERM-5.2). Humic-bound concentrations of each actinide and its oxidation state have the same CAPHUM limit. CAPHUM is constant at 1.1×10^{-5} molar (M) (DOE 2014, Table SOTERM-21), as established in the Compliance Certification Application (CCA) (DOE 1996, SOTERM.6.3.3). A simplifying conservative assumption of the humic colloids implementation in PA is that actinides do not compete with other oxidation states of the actinide or other actinides for humic complexation sites (DOE 2014, SOTERM-5.2).

Humic Colloid Parameter Values for CRA-2026 IS

The An(III) and An(IV) humic colloid parameter values determined for CRA-2026 IS are shown in Table 1. The values are for parameters PHUMSIM and PHUMCIM of PHUMOX3 and PHUMOX4, i.e., actinides with oxidation states of III and IV, respectively. The PHUMSIM and PHUMCIM values for Np(V) and U(VI) (i.e., PHUMOX5 and PHUMOX6) are unchanged from DOE (2014, Table SOTERM-21), as are the values for CAPHUM.

Table 1: Updated An(III) and An(IV) humic colloid parameter values for CRA-2026 IS.

Actinide	PHUMSIM[a]	PHUMCIM[a]
PHUMOX3	0.3	0.3
PHUMOX4	0.02	0.01

[a] In units of moles colloidal actinide per mole dissolved actinide (An)

These values are derived using the methods documented in Mariner (2018), Mariner (2016), Mariner (2023), and Mariner (2025).

PHUMSIM and PHUMCIM for An(III)

The An(III) PHUMSIM and PHUMCIM value of 0.3 for the CRA-2026 IS is a result of updating the CRA-2026 FS calculations of Mariner (2025) with the CRA-2026 IS baseline solubility calculations of Domski (2025). An(III) complexes strongly with EDTA in the pH range of the equilibrated brines (8.7 – 8.9). A smaller direct brine release volume for CRA-2026 IS, in comparison with CRA-2026 FS, causes an increase in the organic ligand concentrations, including EDTA, which causes increases in the An(III) dissolved source term (Domski 2025).

New PHUMSIM and PHUMCIM values were derived for An(III) by taking the following steps:

1. An(III)-humic complexation log K values (and their corresponding stability constants) were not recalculated for the process model because the thermodynamic database (DATA0.FM6)

Information Only

did not change from Mariner (2023) and the pH dependence of the humic complexation stability constant was already established.

2. New process model ratios of humic-bound An(III) to An(III) baseline solubility were calculated following the process in Section 5 of Mariner (2018). An example of this calculation is shown in Appendix 1. Aqueous speciation from the Domski (2025) baseline solubility calculations were used to calculate conservative equilibrium ratios of humic-bound An(III) concentration to An(III) baseline solubility. Following the previously established methodology, PHUMSIM and PHUMCIM values for An(III) of 0.3 were determined for each.

The updated calculations are located at /nfs/data/CVSLIB/WIPP_EXTERNAL/ap167/CRA-2026-IS. The updated calculations for An(III) are the Mathcad calculations (files *.mcdx). The 1× minimum brine volume Mathcad calculation is shown in Appendix 1.

The An(III) PHUMSIM and PHUMCIM value of 0.3 is expected to be conservative due to four conservative assumptions built into the Am(III)-humic complexation process model. First, the process model conservatively assumes that the entire concentration of humic colloids is composed of humic acid. Humic acid has a significantly greater affinity for complexing actinides than fulvic acid (e.g., Sonke and Salters 2006; Stern et al. 2007; Mariner and Sassani 2014, Sections 4.2.3 and 5.3.4.2). Humic colloids in natural groundwater are a combination of humic and fulvic acids (Buffle 1988). Second, the values used for the stability constant for actinide-humic complexation are derived at one molar ionic strength and are not adjusted to the ~6 molar ionic strength of WIPP brines (Mariner 2016, Section 5.1). High ionic strength tends to reduce humic complexation (Laszak and Choppin 2001, Fig. 4; Sonke and Salters 2006, Eq. 9). Third, to guard against overestimation of competition by calcium and magnesium for the available humic complexation sites, the values used for the stability constants for Ca-humic and Mg-humic complexation are set significantly lower than observed at the expected high ionic strength and pH of the MgO-equilibrated brines (Laszak and Choppin 2001; Mariner 2016, Section 5.2). Fourth, the (AnHs):(An) ratios calculated by the process model based on the above conservative assumptions for 1×, 3×, and 5× minimum brine volumes are 0.047, 0.129, and 0.206 (PHUMSIM) and 0.056, 0.146, and 0.232 (PHUMCIM), respectively; final PHUMSIM and PHUMCIM values were determined by rounding up the maximum value among brine volume calculations to the nearest single significant figure. As for the value of the total concentration of humic complexation sites (equivalent to CAPHUM), it too is likely conservative because it assumes that humic colloids are stable at a concentration of 2 mg L^{-1} (DOE 1996, SOTERM.6.3.3). Humic acid is likely unstable in these brines in the presence of MgO (Wall and Mathews 2005; Mariner and Sassani 2014, Section 5.3.4.1).

PHUMSIM and PHUMCIM for An(IV)

The PHUMSIM and PHUMCIM values of 0.02 and 0.01 for An(IV), respectively, are a result of updating the CRA-2026 FS calculations of Mariner (2025) with the CRA-2026 IS baseline solubility calculations of Domski (2025). The free Th^{+4} species concentration calculated in the baseline solubility calculations increased significantly from FS to IS. This increase caused the process model calculation for PHUMSIM to exceed 0.01. Rounding up to the nearest single significant figure, in accordance with the previously established conservative methodology, caused the PHUMSIM value to change from 0.01 to 0.02.

The An(IV) humic colloids process model was updated as follows:

Information Only

1. An(IV)-humic complexation log K values (and their corresponding stability constants) were not recalculated for the process model because the thermodynamic database (DATA0.FM6) did not change from Mariner (2023) and the pH dependence of the humic complexation stability constant was established in Mariner (2025).
2. Process model ratios of humic-bound An(IV) concentration to An(IV) baseline solubility were calculated consistent with Mariner (2016, Section 5.4) and Mariner (2025). An example of this calculation is shown in Appendix 2. Speciation from the CRA-2026-IS Domski (2025) baseline solubility calculations and the pH dependent stability constant relationship established in Mariner (2025) were used to predict conservative equilibrium ratios of humic-bound An(IV) concentration to An(IV) baseline solubility.

The updated calculations are located at /nfs/data/CVSLIB/WIPP_EXTERNAL/ap167/CRA-2026-IS. The final step Th(IV)-humic calculations for the 1× minimum brine volume are shown in Appendix 2. The (AnHs):(An) ratios calculated by the process model for 1×, 3×, and 5× minimum brine volumes are 0.0112, 0.0054, and 0.0047 (PHUMSIM) and 0.0092, 0.0056, and 0.0051 (PHUMCIM), respectively.

The An(IV) PHUMSIM and PHUMCIM values of 0.02 and 0.01 in Table 1 are conservative for several reasons. First, they exceed the (AnHs):(An) ratios of the updated calculations of the An(IV)-humic complexation process model. In addition, the first three conservative assumptions identified above for the An(III)-humic complexation process model apply to the An(IV)-humic complexation process model. Regarding the second conservative assumption, pH-specific humic complexation stability constants were conservatively derived at 0.1 molar ionic strength. Additionally, as explained earlier, it is conservative to assume that humic colloids will persist at a concentration of 2 mg L^{-1} in WIPP brines equilibrated with MgO.

References

Buffle, J. (1988). Complexation Reactions in Aquatic Systems. New York, New York, John Wiley & Sons.

DOE (1996). Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant. DOE/CAO-1994-2184. U.S. Department of Energy, Carlsbad, New Mexico.

DOE (2014). Title 40 CFR Part 191 Subparts B and C Compliance Recertification Application 2014 for the Waste Isolation Pilot Plant, Appendix SOTERM-2014, Actinide Chemistry Source Term. DOE/WIPP 15-3503. U.S. Department of Energy, Carlsbad, New Mexico.

Domski, P. S. (2025). Prediction of Baseline Actinide Solubilities for the 2026 WIPP Compliance Recertification Application Performance Assessment Interim-State Analysis (CRA-2026 IS). Carlsbad, New Mexico, Sandia National Laboratories.

Laszak, I. and G. R. Choppin (2001). "Interaction study between Ca2+ and humic acids in brine media." Radiochimica Acta **89**(10): 653-659.

Mariner, P. E. (2016). Actinide(IV)-Humic Complexation in the WIPP Performance Assessment. ERMS 567222. Sandia National Laboratories, Carlsbad, New Mexico.

Mariner, P. E. (2018). Actinide(III)-Humic Complexation in the WIPP Performance Assessment. ERMS 569599. Sandia National Laboratories, Carlsbad, New Mexico.

Information Only

Mariner, P. E. (2019). A summary of humic colloid parameter values to be implemented in the CRA-2019 Deferred Performance Assessment. Letter from P. Mariner to C. Camphouse, April 15, 2019. ERMS 571250. Sandia National Laboratories, Albuquerque, New Mexico.

Mariner, P. E. (2023). Updates to the WIPP humic colloids models for An(III) and An(IV). Letter from P. Mariner to Sandia National Laboratory WIPP Records Center, July 26, 2023. ERMS 580251. Albuquerque, New Mexico, Sandia National Laboratories.

Mariner, P. E. (2025). CRA-2026 FS updates to the WIPP humic colloids models for An(III) and An(IV). Letter from P. Mariner to Sandia National Laboratory WIPP Records Center, April 14, 2025. Albuquerque, New Mexico, Sandia National Laboratories.

Mariner, P. E. and D. C. Sassani (2014). Analysis report for WIPP colloid model constraints and performance assessment parameters. SAND2014-1961. Sandia National Laboratories, Carlsbad, New Mexico.

Sonke, J. E. and V. J. M. Salters (2006). "Lanthanide-humic substances complexation. I. Experimental evidence for a lanthanide contraction effect." Geochimica Et Cosmochimica Acta **70**(6): 1495-1506.

Stern, J. C., J. E. Sonke and V. J. M. Salters (2007). "A capillary electrophoresis-ICP-MS study of rare earth element complexation by humic acids." Chemical Geology **246**(3-4): 170-180.

Wall, N. A. and S. A. Mathews (2005). "Sustainability of humic acids in the presence of magnesium oxide." Applied Geochemistry **20**: 1704-1713.

Information Only

Appendix 1. Last step An(III)-humic complexation calculations for GWB and ERDA-6 brines (file: "5. Am-CaMg-HA Sonke 2006 1x FM6 CRA26IS.mcdx")

Am and Ca/Mg Complexation with HA in Brines

Brines (all brine values from CRA26-SOL and associated EQ3/6 I/O files (1x dilution))

H2O frac (g/g) $w := \begin{bmatrix} 0.70663 \\ 0.72374 \end{bmatrix}$

Brine density $\rho := \begin{bmatrix} 1.2323 \\ 1.2159 \end{bmatrix} \frac{kg}{L}$

$i := 0..1$

1. GWB
2. ERDA-6

$pH := \begin{bmatrix} 8.756 \\ 8.797 \end{bmatrix}$ $HAtot := 1.1 \cdot 10^{-5}$

(Ca+2 + Mg+2) (enter molalities)

$CaMgfree := \begin{bmatrix} (0.0122 + 0.9091) \cdot w_0 \cdot \rho_0 \\ (0.0125 + 0.5295) \cdot w_1 \cdot \rho_1 \end{bmatrix} = \begin{bmatrix} 0.802 \\ 0.477 \end{bmatrix}$ Conc. in M

Conc.(M) from EQ3/6 I/O files

$SolubAc := \begin{bmatrix} 1.452 \cdot 10^{-5} \\ 1.440 \cdot 10^{-5} \end{bmatrix}$

(enter molalities * $w \cdot \rho$) = Conc. in M

$Acfree := \begin{bmatrix} 1.273 \cdot 10^{-10} \cdot w_0 \cdot \rho_0 \\ 7.967 \cdot 10^{-11} \cdot w_1 \cdot \rho_1 \end{bmatrix} = \begin{bmatrix} 1.109 \cdot 10^{-10} \\ 7.011 \cdot 10^{-11} \end{bmatrix}$

Ca+2 and Mg+2 molalities and solution densities from gwb*.6o and erda*.6o of CRA26-SOL

$IS := \begin{bmatrix} 1 \\ 1 \end{bmatrix}$ (conservative)

Actinide-HA Stability Constant

$log\beta AcHA_i := e^{0.01416 \cdot 63 + 0.09256 \cdot pH_i + 0.08661 \cdot -\log(IS_i) + 0.7557}$

Sonke and Salters 2006 (table 5, SRFA)
<< parameter d adjusted for FM6 fit >>

$log\beta AcHA = \begin{bmatrix} 11.684 \\ 11.729 \end{bmatrix}$

$betaAcHA := 10^{log\beta AcHA} = \begin{bmatrix} 4.833 \cdot 10^{11} \\ 5.353 \cdot 10^{11} \end{bmatrix}$

Ca/Mg-HA Stability Constant

(both Ca and Mg behave similarly (Lead et al. 1994))

$log\beta CaMgHA_i := 3.0 = \begin{bmatrix} 3 \\ 3 \end{bmatrix}$

$betaCaMgHA_i := 10^{log\beta CaMgHA_i}$

(1) Conservatively assume 3.0 from Laszak and Choppin 2001 (Table 3) for WIPP humic colloids and (2) do not adjust for pH (though this might raise PHUMCIM relative to PHUMSIM due to pH difference).

Lu and Allen 2002 show strong competitive effect to at least 0.001 M Ca (pH 6-7): log beta rises from 3.5 (pH 6) to 4.4 (pH 8) (Sav. River DOM). Same trend in Laszak and Choppin 2001 (Fig. 4). Lead 1994 (Table 2) has values of low 3s for HA and low 2s for FA in 0.033 M CaCl2 (from peat in North Yorkshire). Laszak and Choppin 2001 indicates that Ca+2 can compete with actinides (bottom p. 657).

Free HA binding site concentration

$$HAfreeHA_i := \frac{HAtot}{\left(1 + Acfree_i \cdot betaAcHA_i + CaMgfree_i \cdot betaCaMgHA_i\right)} = \begin{bmatrix} 1.284 \cdot 10^{-8} \\ 2.134 \cdot 10^{-8} \end{bmatrix}$$

Total Ca-HA plus Mg-HA concentration

$$CaMgHA_i := CaMgfree_i \cdot HAfreeHA_i \cdot betaCaMgHA_i = \begin{bmatrix} 1.03 \cdot 10^{-5} \\ 1.018 \cdot 10^{-5} \end{bmatrix}$$

Humic-bound actinide concentration

$$AcHA_i := Acfree_i \cdot HAfreeHA_i \cdot betaAcHA_i = \begin{bmatrix} 6.877 \cdot 10^{-7} \\ 8.008 \cdot 10^{-7} \end{bmatrix}$$ (AcHA conc. with Ca & Mg competition)

Proportionality with Ca/Mg competition

$\frac{AcHA}{SolubAc} = \begin{bmatrix} 0.04736 \\ 0.05561 \end{bmatrix}$ GWB ERDA-6

$alpha_i := \frac{SolubAc_i}{Acfree_i} = \begin{bmatrix} 1.31 \cdot 10^5 \\ 2.054 \cdot 10^5 \end{bmatrix}$

Information Only

Appendix 2. Last step An(IV)-humic complexation calculations for GWB and ERDA-6 brines (file: "5. Th-CaMg-HA Stern fitted to FM6 (1xMin) CRA26-IS.mcdx")

Th and Ca/Mg Complexation with HA in Brines

Brines (all brine values from CRA26-SOL and associated EQ3/6 I/O files (1x dilution))

H2O frac (g/g) $w := \begin{bmatrix} 0.70663 \\ 0.72374 \end{bmatrix}$

Brine density $\rho := \begin{bmatrix} 1.2323 \\ 1.2159 \end{bmatrix} \frac{kg}{L}$

$i := 0..1$

1. GWB
2. ERDA-6

$pH := \begin{bmatrix} 8.756 \\ 8.797 \end{bmatrix}$ $HAtot := 1.1 \cdot 10^{-5}$

(Ca+2 + Mg+2) (enter molalities)

$CaMgfree := \begin{bmatrix} (0.0122 + 0.9091) \cdot w_0 \cdot \rho_0 \\ (0.0125 + 0.5295) \cdot w_1 \cdot \rho_1 \end{bmatrix} = \begin{bmatrix} 0.802 \\ 0.477 \end{bmatrix}$

Conc. in M

Conc.(M) from EQ3/6 I/O files

(enter molalities * $w \cdot \rho$) = Conc. in M

$SolubAc := \begin{bmatrix} 5.3369 \cdot 10^{-8} \\ 5.6349 \cdot 10^{-8} \end{bmatrix}$ $Acfree := \begin{bmatrix} 2.0238 \cdot 10^{-23} \cdot w_0 \cdot \rho_0 \\ 7.3403 \cdot 10^{-24} \cdot w_1 \cdot \rho_1 \end{bmatrix} = \begin{bmatrix} 1.762 \cdot 10^{-23} \\ 6.459 \cdot 10^{-24} \end{bmatrix}$

Ca+2 and Mg+2 molalities and solution densities from gwb*.6o and erda*.6o of CRA26-SOL

Actinide-HA Stability Constant

$betaAc_i := 10^{3.6052 \cdot pH_i - 10.175}$ (FM6 fit, converted to 0.1 M beta; pH sensitive)

$logbetaAc := \log(betaAc) = \begin{bmatrix} 21.39 \\ 21.54 \end{bmatrix}$

Although these beta values are calculated for 0.1 M ionic strength, these beta values are expected to decrease with increasing ionic strength (e.g., Laszak and Choppin 2001 Table 3 for Ca-HA). Therefore, use of these beta values is conservative because lower beta values would decrease An-HA complexation and decrease An mobility in the WIPP PA.

Ca/Mg-HA Stability Constant

(both Ca and Mg behave similarly (Lead et a. 1994))

$betaCaMg := 10^3$

(though Laszak and Choppin 2001 (Tab3) says ~10^3.61)

3.61 might be too high for very high Ca and Mg. However, Lu and Allen 2002 show strong competitive effect to at least 0.001 M Ca (pH 6-7), beta rises to 4.4 at pH 8 (no ionic strength associated with these betas). Same trend observed by Laszak and Choppin 2001. Lead 1994 (Table 2) has values of low 3s for HA and low 2s for FA in 0.033 M CaCl2.

Laszak and Choppin 2001 indicates that Ca+2 can compete with actinides (bottom p. 657).

Equilibrium Speciation

$HAfreeComp := \frac{HAtot}{(1 + Acfree \cdot betaAc + CaMgfree \cdot betaCaMg)} = \begin{bmatrix} 1.369 \cdot 10^{-8} \\ 2.301 \cdot 10^{-8} \end{bmatrix}$

(HA- concentration in presence of Ac, Ca, and Mg)

$CaMgHA_i := CaMgfree_i \cdot HAfreeComp_i \cdot betaCaMg$

$CaMgHA = \begin{bmatrix} 1.099 \cdot 10^{-5} \\ 1.098 \cdot 10^{-5} \end{bmatrix}$

(CaMgHA concentration with Ac competition)

$AcHAcomp_i := Acfree_i \cdot HAfreeComp_i \cdot betaAc_i$

$AcHAcomp = \begin{bmatrix} 5.9527 \cdot 10^{-10} \\ 5.1533 \cdot 10^{-10} \end{bmatrix}$ (AcHA conc. with Ca & Mg competition)

Calculations if no Ca or Mg competition

$HAfreeAc_i := \frac{HAtot}{(1 + Acfree_i \cdot betaAc_i)} = \begin{bmatrix} 1.054 \cdot 10^{-5} \\ 1.076 \cdot 10^{-5} \end{bmatrix}$

(HA- concentration in presence of Ac only)

$AcHA_i := Acfree_i \cdot HAfreeAc_i \cdot betaAc_i$

$AcHA = \begin{bmatrix} 4.583 \cdot 10^{-7} \\ 2.409 \cdot 10^{-7} \end{bmatrix}$

(AcHA concentration with no Ca or Mg competition)

Proportionality constant with Ca/Mg competition

PHUMSIM
PHUMCIM

$\frac{AcHAcomp}{SolubAc} = \begin{bmatrix} 0.01115 \\ 0.00915 \end{bmatrix}$

Proportionality constant (no Ca/Mg competition)

PHUMSIM
PHUMCIM

$\frac{AcHA}{SolubAc} = \begin{bmatrix} 8.587 \\ 4.276 \end{bmatrix}$

Information Only