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Waste Isolation Pilot Plant

Actinide(III)-Humic Complexation in the WIPP Performance Assessment

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Abstract

In the Waste Isolation Pilot Plant (WIPP) performance assessment (PA), the stability of humic colloid complexation with An(III) (trivalent actinides) requires an update. Increases are needed for two proportionality constants, PHUMSIM and PHUMCIM. These parameters represent the equilibrium aqueous concentration ratios of humic-bound An(III) to non-colloidal An(III) for brines of the Salado and Castile formations, respectively. At low An(III) loadings, humic partitioning of An(III) in WIPP brines is expected to be significantly higher than previously modeled. The primary reason for this difference is that An(III)-humic complexation in alkaline pH water is more stable than previously modeled.

In this work, results of cumulative studies of An(III)-humic and Ca^{2+}-humic complexation are used to simulate competitive humic complexation for the WIPP PA and to estimate new An(III) PHUMSIM and PHUMCIM values. The new calculations are 30 and 80, respectively. At low An(III) loadings these values significantly increase humic-bound An(III) concentrations in WIPP brines and therefore increase An(III) mobility. Importantly, however, low loadings correspond with low total mobile An(III) concentrations. At high An(III) loadings, An(III) mobility remains unchanged because humic-bound An(III) concentrations continue to be limited by the maximum concentration of aqueous humic complexation sites.

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TABLES

NOMENCLATURE

An	Actinide
Am(III)	Americium
An(III)	Trivalent actinide
AnHs	Actinide-humic site complex (also shown as AnHS in figures)
AP	Analysis plan
BCHA	Belgian Boom clay humic acid
CAPHUM	Maximum concentration of humic-bound actinide in the PA abstraction model
CCA	Compliance Certification Application
CFR	Code of Federal Regulations
DBR	Direct brine release
DOE	U.S. Department of Energy
EDTA	Ethylenediaminetetraacetic acid (also shown as Edta when symbolizing a ligand)
EHA	Elliot soil humic acid
Eq.	Equation
ERDA-6	Energy Research and Develop Administration WIPP Well 6
FA	Fulvic acid
GWB	Generic Weep Brine
HA	Humic acid
LHA	Leonardite soil humic acid
M	Molarity
MgO	Magnesium oxide
Min	Minimum brine volume for a DBR from the repository (17,400 m^3)
NM	New Mexico
PA	Performance Assessment
pcH	Negative log of the calculated molar concentration of hydrogen ion
PDF	Adobe Acrobat file extension
pH	Negative log of the hydrogen ion activity
PHA	Pahokee peat humic acid
PHUMCIM	Proportionality constant for concentration of actinide associated with mobile humic colloids in Castile brine in the PA abstraction model
PHUMSIM	Proportionality constant for concentration of actinide associated with mobile humic colloids in Salado brine in the PA abstraction model
SNL	Sandia National Laboratories
SRFA	Suwannee River fulvic acid
WIPP	Waste Isolation Pilot Plant

1 INTRODUCTION

In performance assessment (PA) calculations of the Waste Isolation Pilot Plant (WIPP), humic colloids can significantly contribute to the mobility of trivalent actinides (e.g., DOE 2009, SOTERM-4.7). The trivalent actinides, An(III), of interest in the WIPP PA are Pu(III) and Am(III). The An(III)-humic colloid process and abstraction models used in the WIPP PA have not been updated since the original Compliance Certification Application (CCA). This analysis report provides an update of the humic colloid process model for An(III) and revises parameter values for the abstraction model.

When the An(III)-humic colloid process model was developed for the CCA, there were few published humic complexation data for trivalent actinides in saline, alkaline waters. A simple 1:1, single site complexation model was developed that allowed for competitive complexation of Ca^{2+} and Mg^{2+}. Log stability constants of 6.02 and 6.09 for An(III)-humic complexation were used for humic acid (HA) and 4.60 was used for fulvic acid (FA) (Mariner and Sassani 2014, Section 4.2.3). These stability constants were measured in experiments conducted at Florida State University on Lake Bradford HA, Gorleben HA, and Suwannee River FA, respectively, at pH 6 in NaCl solutions of 3 and 6 molal (DOE 1996, SOTERM.6.3.3.1). A log stability constant of 2.0 was assumed for Ca/Mg-humic complexation based on values reported in the literature for Ca/Mg-humic complexation experiments conducted at low ionic strength at pH values ranging from 3.5 to 5.0 (DOE 1996, SOTERM.6.3.3.1).

Since the CCA, many studies have published humic complexation data for alkaline pH and high ionic strength for trivalent metals and Ca. Studies involving trivalent cations (e.g., rare earth metals, Am) show that stability constants increase by more than a log unit for each unit increase in pH (Maes et al. 1988; Maes et al. 1991; Sonke and Salters 2006; Pourret et al. 2007; Stern et al. 2007; Janot et al. 2013). Two of the cited studies were published before the CCA, and it is not known why they were not used in the CCA. Perhaps the experimental procedure of those studies did not provide sufficient confidence at the time due to the assumptions inherent in the procedure (see Section 4.2.2). Studies involving Ca^{2+} and Mg^{2+} since the CCA indicate that stability constants for Ca/Mg-humic complexation under WIPP conditions are also higher than assumed for the CCA (Lead et al. 1994; Laszak and Choppin 2001; Lu and Allen 2002).

The stability constants reported in the literature are a function of the *free* concentrations of complexing cations. These studies confirm that the free concentrations of An(III), Ca, and Mg should be used in the application of the 1:1, single site complexation process model. To the contrary, the CCA process model assumes they are a function of the total non-colloidal aqueous concentrations of complexing cations. The current analysis report departs from the CCA process model by using free concentrations of An(III), Ca, and Mg (i.e., An^{3+}, Ca^{2+}, and Mg^{2+}) to calculate the An(III) PHUMSIM and PHUMCIM values.

This analysis report is completed under the Analysis Plan for the Evaluation of Humic-Actinide Complexation for WIPP Conditions, AP 167, Rev. 0 (Mariner 2014). This report completes the portion of the scope of AP 167 pertaining to An(III)-humic complexation. All four tasks are completed for An(III)-humic complexation. A previous report addressed all four tasks for An(IV)-humic complexation (Mariner 2016).

2 HUMIC SUBSTANCES IN THE WIPP PA

Aqueous humic substances are a mixture of humic and fulvic acids. Humic acid by definition is soluble only below pH 10. Fulvic acid is soluble at all pH values.

The structure of humic substances is far from uniform. The range of molecular weight of humic molecules that make up the aqueous humic fraction vary over three orders of magnitude up to approximately 100,000 atomic mass units. A typical humic macromolecule contains aromatic rings and aliphatic chains that host numerous carboxylic, hydroxyl, and other functional groups. Other characteristics are the presence of nitrogen groups, a highly polyelectrolyte nature, and inter-/intra-molecular aggregation (Buffle 1988).

In natural waters, humic substances originate from the decomposition of plant and animal tissues and residues. At the WIPP, they may largely be a product of biotic or abiotic degradation of emplaced organic materials. The WIPP humic colloid model assumes that humic colloids are present at a concentration of 2 mg L^{-1} in WIPP brines (Section 3) and consist of both humic and fulvic acid.

The aqueous stability of humic colloids is controlled by the solution composition and primarily by the cation concentrations and the solution pH. At higher ionic strength, the rates of aggregation and flocculation tend to increase, reducing stability. Wall and Mathews (2005) show that for WIPP brines in the presence of MgO, concentrations of humic colloids fall below detection within a matter of weeks. The detection limit in the Wall and Mathews (2005) study appears to be around 1 to 2 mg L^{-1} based on the error bars on the plotted data. However, without definitive evidence that humic colloid concentrations are much lower than 2 mg L^{-1} in WIPP brines in the presence of MgO, the calculations in this study will continue to assume that humic colloids are present at a concentration of 2 mg L^{-1} in WIPP brines.

Humic colloids are potentially important to the WIPP PA because they increase the concentrations of actinides in solution. Carboxylic and phenolic functional groups on humic substances act to chelate cations. Positively-charged actinides such as Am^{3+} and Pu^{3+} have a strong affinity for these functional groups. Thus, by providing additional aqueous complexation sites, humic colloids can increase the aqueous concentrations of actinides. Section 4 further addresses humic complexation of actinides and alkaline earth metals.

Humic colloids are assumed not to adsorb in the WIPP PA. Adsorption of humic colloids to stationary geologic media retards aqueous transport and can reduce mobile concentrations. Physical and chemical mechanisms are postulated to describe adsorption of humic substances. The principle physical mechanism for adsorption of humic substances is that the solid-liquid interface provides a state of lower energy for humic molecules resulting from the hydrophobic nature of various humic components. The chemical mechanism involves inner-sphere complexation of humic functional groups with mineral surface hydroxyl groups. Humic substances adsorb readily to the net positively charged surfaces of aluminum oxide clays and adsorb little to negatively-charged silica surfaces (Buffle 1988).

Should humic colloids not interact with geologic media, they have the potential for facilitated transport, i.e., mean velocities greater than the velocity of the average water molecule (Enfield et al. 1989). However, the possibility of facilitated transport of actinides bound to colloids is not pursued in the WIPP PA mainly because the direct brine release (DBR) scenario bypasses the porous media and deposits all releases on the ground surface.

3 WIPP ENVIRONMENT

The compositions of groundwater in the Salado and Castile formations are represented in the WIPP PA by GWB (Generic Weep Brine) and ERDA-6 (Energy Research and Develop Administration WIPP Well 6). The compositions of these brines after equilibration with halite (NaCl), anhydrite ($CaSO_4$), hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), and brucite ($Mg(OH)_2$) are shown in Table 1 for the minimum volume of brine (1 × Min) required for a DBR from the repository and for five times the minimum volume (5 × Min) (Domski and Xiong 2015). These volumes are conservatively assumed to contain the expected inventory of acetate, citrate, ethylenediaminetetraacetic acid (EDTA), and oxalate (Domski and Xiong 2015). For the calculations in Table 1, Domski and Xiong (2015) used the Pitzer ion interaction model of EQ3/6, Version 8.0a (Wolery and Jarek 2003; Wolery 2008; Wolery et al. 2010; Xiong 2011) and the thermodynamic database DATA0.FM2 (Domski 2015). Humic colloids are not included in the Domski and Xiong (2015) calculations.

Metal corrosion within the WIPP repository may serve to maintain reducing conditions. The kinetics of corrosion reactions will be controlled by the availability of H_2O at the metal surface. The predominant metals will be iron (Fe) in the form of low-carbon steel and chemical-grade lead (Pb). These metals are present within the waste itself, as well as in the containers used to hold the waste during emplacement.

In addition to the organic acids, Fe, and Pb, the waste disposed at the WIPP contains significant quantities of cellulosic, plastic and rubber materials. With time, microbial activity and abiotic reactions may consume a portion of these organic materials, resulting in the generation of carbon dioxide (CO_2), hydrogen sulfide (H_2S), hydrogen (H_2), nitrogen (N_2), methane (CH_4), and humic substances.

In the WIPP PA brines, the ionic strength is around 6 M, much higher than the ionic strength in most humic complexation studies. Such high ionic strength and high concentrations of Mg^{2+} may destabilize humic colloids in the aqueous phase (Wall and Mathews 2005). However, as in the original WIPP humic colloids model, the concentration of humic substances in the Salado and Castile brines is assumed to be 2.0 mg L^{-1}. This concentration was adopted based on the solubility range observed in systems containing Ca^{2+} and Mg^{2+} at concentrations of at least 0.01 M (DOE 1996, SOTERM.6.3.3.1). This concentration is expected to be conservative.

The site binding capacities of humic substances for the WIPP PA were estimated from experiments using Lake Bradford humic acid, Gorleben humic acid, and Suwannee River fulvic acid (DOE 1996, SOTERM.6.3.3.1). The experiments involved NaCl solutions of 3 and 6 molal, and fixed pH values of either 4.8 or 6. The site binding capacities were determined to be 4.65, 5.38, and 5.56 meq g^{-1}, respectively. Multiplying these values by the humic colloid concentration gives the following values for the total humic complexation site concentration (Hs_{tot}): 9.3×10^{-6} M, 1.1×10^{-5} M, and 1.1×10^{-5} M. The concentration of humic colloid complexation sites adopted in the present work is 1.1×10^{-5} M.

Table 1. Predicted compositions of GWB and ERDA-6 in the minimum volume (1 × Min) and five times the minimum volume (5 × Min) of brine required for a DBR from the repository (Domski and Xiong 2015)

Element or Property	**Units**	**GWB (1 × Min[a])**	**GWB (5 × Min)**	**ERDA-6 (1 × Min)**	**ERDA-6 (5 × Min)**
B(III) (aq)	M	0.167	0.168	0.0622	0.0623
Na(I) (aq)	M	4.70	4.71	5.38	5.40
Mg(II) (aq)	M	0.518	0.498	0.134	0.113
K(I) (aq)	M	0.531	0.530	0.0958	0.0959
Ca(II) (aq)	M	0.0213	0.0214	0.0134	0.0126
S(VI) (aq)	M	0.220	0.209	0.181	0.171
Cl(-I) (aq)	M	5.65	5.68	5.31	5.33
Br(-I) (aq)	M	0.0302	0.0302	0.0109	0.0109
CO_2 fugacity	atm	5.84×10^{-7}	5.84×10^{-7}	5.84×10^{-7}	5.84×10^{-7}
Ionic strength	M	6.08	6.08	5.80	5.79
pcH[b]	-log(M)	9.59	9.60	9.94	9.98
pH[c]	-log(M)	8.84	8.84	9.22	9.26
Total inorganic carbon	M	0.0694	0.0142	0.0603	0.0123
Acetate	M	2.30×10^{-2}	4.61×10^{-3}	2.30×10^{-2}	4.61×10^{-3}
Citrate	M	2.33×10^{-3}	4.65×10^{-4}	2.33×10^{-3}	4.65×10^{-4}
EDTA	M	7.40×10^{-5}	1.48×10^{-5}	7.40×10^{-5}	1.48×10^{-5}
Oxalate	M	1.18×10^{-2}	2.36×10^{-3}	1.18×10^{-2}	2.36×10^{-3}
Am(III)	M	2.32×10^{-7}	2.15×10^{-7}	6.03×10^{-8}	5.51×10^{-8}
Am^{3+}	M	1.11×10^{-11}	1.09×10^{-11}	6.14×10^{-13}	4.59×10^{-13}
Activity of water[d]	-	0.73358	0.73416	0.74787	0.74844
Solution density[d]	g mL^{-1}	1.2458	1.2446	1.2218	1.2204
Ca^{2+}[d]	molal	0.0225	0.0232	0.0131	0.0131
Mg^{2+}[d]	molal	0.226	0.222	0.0414	0.0343

[a] Min = minimum brine volume for a DBR from the repository (17,400 m^3)

[b] Negative log of the hydrogen ion concentration (M)

[c] Negative log of the hydrogen ion activity (M) on the Pitzer scale

[d] From gwb_ 1 x.60, gwb_5x.6o, erda_ 1x.6o, and erda_5x.6o EQ6 output files of Domski and Xiong (2015)

4 AN(III)-HUMIC COMPLEXATION MODEL

The WIPP humic colloids model for An(III) consists of a An(III)-humic complexation process model and an abstraction model. Section 4.1 describes both models and how the process model was upgraded. Section 4.2 presents the thermodynamic data used for the process model and describes how the humic complexation stability constants were selected or derived. Humic-complexation data are addressed for H^+, Ca^{2+}, and Mg^{2+} in Section 4.2.1 and for An(III) in Section 4.2.2.

Simulation of the process model is facilitated at low ionic strength in this report using PhreeqcI (version 2.12.5-669), a code developed at the U.S. Geological Survey for chemical speciation, batch reaction, and one-dimensional reactive transport (Parkhurst 1995; Parkhurst and Appelo 1999; USGS 2002; USGS 2005). PhreeqcI is used in Section 4.2.2 to simulate subsets of the An(III)-humic-Ca-Mg-EDTA-CO_2-H_2O system. The database used in the PhreeqcI calculations is the YMP_R2.dat database that comes with the PhreeqcI version 2.12.5-669 software package; however, all of the reactions that produce aqueous species that are relevant to this analysis are entered into the PhreeqcI input files to ensure quality control of thermodynamic data. Final PhreeqcI calculations were executed by Paul Domski on a qualified installation on a personal computer with Intel® Xeon® CPU E5-2620 v4 at 2.10GHz, 2101 MHz (S1014343) and Microsoft Windows 10 Enterprise.

EQ3/6 version 8.0a, not PhreeqcI, was planned for this analysis (Mariner 2014). PhreeqcI was used instead of EQ3/6 largely because PhreeqcI has more flexibility in its ion activity models for handling humic species. In addition, unlike EQ3/6, PhreeqcI allows modification and addition of reactions and equilibrium constants within the input file, which is convenient for many of the tasks involved in this analysis and provides a more straightforward means for tracing and reproducing the calculations. All calculations in this report are stored on the CVS (Concurrent Versioning System) in /nfs/data/CVSLIB/WIPP_EXTERNAL/ap167/Files.

4.1 Model Equations

The abstraction model used in the WIPP PA for calculating the aqueous humic-bound actinide concentration (AnHs) is described by the following equation:

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

(An) is the non-colloidal aqueous actinide concentration, H is a proportionality constant (either PHUMSIM or PHUMCIM), and CAPHUM is the total humic complexation site concentration (DOE 1996, SOTERM.6.3.3). Because CAPHUM is constant at 1.1×10^{-5} M, (AnHs) cannot exceed CAPHUM. PHUMSIM is used for the Salado brine, represented by GWB, and PHUMCIM is used for the Castile brine, represented by ERDA-6. To calculate the "mobile" actinide concentration in the WIPP PA, (AnHs) is added to (An) along with the concentrations of actinides bound to other colloids (intrinsic, microbial, and mineral fragment).

A conservative assumption of the WIPP PA calculations is that (An) is at chemical saturation with respect to a controlling mineral phase. Thus, (An) is the calculated solubility of the actinide in WIPP brines in the presence of MgO and organic acid wastes, excluding colloids. EQ3/6 (Wolery and Jarek 2003) and the DATA0.FM2 Pitzer ion interaction database (Domski 2015) are used to calculate the baseline (An) for each brine (Domski and Xiong 2015).

In the process model, actinide-humic complexation is described by the reaction

$$\mathrm{An}^{m+} + \mathrm{Hs}^{-} \Leftrightarrow \mathrm{AnHs} \qquad \text{(Eq. 2)}$$

where An^{m+} is the free actinide species (e.g., Am^{3+}) and Hs^{-} is an available humic substance complexation site. The conditional stability constant ($\beta_{1:\mathrm{An}^{m+}}$) for this reaction is represented by

$$\beta_{1:\mathrm{An}^{m+}} = \frac{(\mathrm{AnHs})}{(\mathrm{An}^{m+})(\mathrm{Hs}^{-})} \qquad \text{(Eq. 3)}$$

Only 1:1 binding of An^{m+} and Hs^{-} is assumed to occur. This treatment of the reaction does not conserve charge and assumes homogeneous complexation sites with no acido-basic properties; however, this approach is acceptable when stability parameters such as $\beta_{1:\mathrm{An}^{m+}}$ are conditional (Reiller et al. 2008). This equation is nearly the same as the equation used in the original process model (DOE 1996, Eq. 6-17). The difference is that the equation defined here uses the free ion actinide concentration (An^{m+}) as the reactant instead of the aqueous non-colloidal actinide concentration (An).

Ca^{2+} and Mg^{2+} are abundant in WIPP brines and compete with actinides for humic complexation sites. The process model accounts for this effect by including terms for humic-bound Ca^{2+} and Mg^{2+} in the calculation of (Hs^{-}) (DOE 1996, Eq. 6-20). A similar approach is used here to account for competition by Ca^{2+} and Mg^{2+} except, as in the case of actinide-humic complexation above, free ion concentrations are used as reactants instead of aqueous non-colloidal concentrations. The concentration of available humic complexation sites is calculated from

$$(\mathrm{Hs}^{-}) = \frac{(\mathrm{Hs}_{\mathrm{tot}})}{\beta_{1:\mathrm{An}^{m+}}(\mathrm{An}^{m+}) + \beta_{1:\mathrm{Ca}^{2+}}\left((\mathrm{Ca}^{2+}) + (\mathrm{Mg}^{2+})\right) + 1} \qquad \text{(Eq. 4)}$$

where $\beta_{1:\mathrm{Ca}^{2+}}$ is the stability constant for Ca^{2+}-humic complexation (used also for Mg^{2+}-humic complexation) and ($\mathrm{Hs}_{\mathrm{tot}}$) is the total concentration of aqueous humic complexation sites.

The concentration of AnHs is calculated by solving Eq. 3 for (Hs^{-}), substituting the result into Eq. 4, and solving for (AnHs). This gives the following expression for (AnHs):

$$(\mathrm{AnHs}) = \frac{\beta_{1:\mathrm{An}^{m+}}(\mathrm{An}^{m+})(\mathrm{Hs}_{\mathrm{tot}})}{\beta_{1:\mathrm{An}^{m+}}(\mathrm{An}^{m+}) + \beta_{1:\mathrm{Ca}^{2+}}\left((\mathrm{Ca}^{2+}) + (\mathrm{Mg}^{2+})\right) + 1} \qquad \text{(Eq. 5)}$$

With appropriate values for free ion concentrations and stability constants, PHUMSIM and PHUMCIM can be calculated by dividing the result from Eq. 5 by the non-colloidal actinide concentration (An).

4.2 Model Reactions

Two sets of chemical reaction databases are used when a chemical speciation code like PhreeqcI is used to simulate the process model. One is a set of intrinsic aqueous reactions with log K values, shown in Table 2, and the other is a set of humic complexation reactions with both log K values and log β values, shown in Table 3. Recall that K is an equilibrium *activity* quotient, and β is an equilibrium *concentration* quotient at the specified ionic strength. Thus,

$$\beta_{1:\mathrm{An}^{m+}} = \mathrm{K}_{1:\mathrm{An}^{m+}} \frac{(\gamma_{\mathrm{Hs}^{-}})(\gamma_{\mathrm{An}^{m+}})}{(\gamma_{\mathrm{AnHs}})} \qquad \text{(Eq. 6)}$$

where γ_i is the activity coefficient of species i. Because the WIPP PA DATA0.FM2 database only uses log K values, log β values are converted to log K values, as described at the end of this section.

Table 2 gives the reactions of the An(III)-Ca-Mg-EDTA-CO_2-H_2O system for modeling WIPP brines in the absence of humic colloids. The first column of data lists the log K values provided in Sonke and Salters (2006) and the assumed reactions for the other non-humic aqueous reactions in the Sonke and Salters (2006) model. EDTA is included in this table because it is a component in the Sonke and Salters (2006) laboratory experiments and is assumed to be prevalent in WIPP PA brines (Domski and Xiong 2015). The second column of data shows the WIPP PA DATA0.FM2 database log K values (Domski 2015). These log K values are used in the input files cited in Sections 4.2.2 and 5 (Table 4 and Table 7).

Table 3 shows the humic complexation reactions simulated in the calculations. The first column of data shows the log β values taken from Sonke and Salters (2006) except where noted. The log K values at infinite dilution (0 M ionic strength) and log β values achieve the same partitioning observed in the source studies when combined with the DATA0.FM2 database in Table 2. This is demonstrated in each of the simulations in Step 4 of Section 4.2.2.

The data adopted for An(III)-humic complexation in Table 3 are borrowed from studies of Eu(III)-humic complexation. Eu(III) is a lanthanide that shares the same column in the periodic table as Am(III) and has an affinity for humic complexation sites similar to Am(III), as demonstrated in Step 1 of Section 4.2.2.

The coefficients a, b, c, and d in Table 3 correspond to an equation developed by Sonke and Salters (2006). Sonke and Salters (2006) performed a non-linear regression on their experimental data to generate an empirical relationship to estimate log $\beta_{1:An^{3+}}$ for Leonardite soil humic acid (LHA) and Suwannee River fulvic acid (SRFA). The general empirical equation is:

$$\log \beta_{1:An^{3+}} = \exp(a \times AN + b \times \mathrm{pH} + c \times (-\log IS) + d) \qquad \text{(Eq. 7)}$$

where AN is the atomic number (63 for Eu) and IS is the ionic strength. The coefficients ($a, b, c,$ and d) for this equation are shown in Table 3 for LHA for the Sonke and Salters (2006) model and for WIPP humic colloids for use with the DATA0.FM2 database.

The determination of the log β and log K values in Table 3 is described in Sections 4.2.1 and 4.2.2. The activity coefficients γ_i of all humic species i defined in the PhreeqcI model are fixed at a value of one. This is done by entering "`-gamma 1e6 0.0`" in the PhreeqcI input files where the humic species are defined. Log $K_{1:An^{3+}}$ values are calculated from log $\beta_{1:An^{3+}}$ values by subtracting the log of the An^{3+} activity coefficient at the given ionic strength. Activity coefficients are calculated using the Davies equation. The Davies equation calculates activity coefficients as a function of ionic strength and species charge. Above 0.1 M ionic strength, specific ion interactions become important and the accuracy of the Davies equation deteriorates.

Table 2. An(III)-Ca-Mg-EDTA-CO_2-H_2O reaction database

Reaction	**Log K (0 M) Used for Eu(III) Sonke and Salters (2006) Model**	**Log K (0 M) of DATA0.FM2 (Domski 2015) for Am(III) System**
$H^+ + Edta^{4-} = HEdta^{3-}$	11.12	10.5707
$2\ H^+ + Edta^{4-} = H_2Edta^{2-}$	17.80	17.4500
$3\ H^+ + Edta^{4-} = H_3Edta^-$	21.04	20.5374
$4\ H^+ + Edta^{4-} = H_4Edta(aq)$	23.76	23.0393
$An^{3+} + Edta^{4-} = AnEdta^-$	19.89	23.550
$An^{3+} + 4\ H_2O = An(OH)_4^- + 4\ H^+$	-34.51[a]	na
$An^{3+} + 3\ H_2O = An(OH)_3(aq) + 3\ H^+$	-25.41[a]	-25.6905
$An^{3+} + 2\ H_2O = An(OH)_2^+ + 2\ H^+$	-16.37[a]	-15.6915
$An^{3+} + H_2O = AnOH^{2+} + H^+$	-7.90[a]	-7.5556
$An^{3+} + HCO_3^- = AnHCO_3^{2+}$	2.10[a]	na
$An^{3+} + HCO_3^- = AnCO_3^+ + H^+$	-2.43[a]	-2.2388
$An^{3+} + 2\ HCO_3^- = An(CO_3)_2^- + 2\ H^+$	-7.76[a]	-7.6766
$An^{3+} + 3\ HCO_3^- = An(CO_3)_3^{3-} + 3\ H^+$	-18.49[a]	-15.8157
$An^{3+} + 4\ HCO_3^- = An(CO_3)_4^{5-} + 4\ H^+$	na[b]	-28.3586
$H_2O = OH^- + H^+$	-13.9967[c]	-13.9967
$HCO_3^- = CO_3^{2-} + H^+$	-10.3392[c]	-10.3392
$HCO_3^- + H^+ = CO_2(aq) + H_2O$	6.3374[c]	6.3374
$HCO_3^- + H^+ = CO_2(g) + H_2O$	7.8193[c]	7.8193
$Ca^{2+} + Edta^{4-} = CaEdta^{2-}$	na	11.1562
$Mg^{2+} + Edta^{4-} = MgEdta^{2-}$	na	10.1260
$Mg^{2+} + HCO_3^- = MgCO_3(aq) + H^+$	na	-7.4108
$Ca^{2+} + HCO_3^- = CaCO_3(aq) + H^+$	na	-7.1880

[a] reaction set equivalent to Eu^{3+} reaction in Zavarin et al. (2005, Table 1)

[b] na = not applicable

[c] reaction set equivalent to reaction in DATA0.FM2

Table 3. An(III)-Ca-Mg-humic reaction database

Reaction	Log β for Sonke and Salters (2006) Model	Log K (0 M) for DATA0.FM2
$Hs^- + H^+ = HsH(aq)$	4.59 (LHA, 0 M *IS*)[a] 3.80 (SRFA, 0 M *IS*)[a]	4.59 (LHA and WIPP)[a] 3.80 (SRFA)[a]
$Ca^{2+} + Hs^- = CaHs^+$ $Mg^{2+} + Hs^- = MgHs^+$	na[b]	3.35[c]
LHA $An^{3+} + Hs^- = AnHs^{2+}$	14.30 (pH 8.95, 0.076 M *IS*)[d] 13.09 (pH 8.02, 0.0928 M *IS*)[d] 12.23 (pH 7.11, 0.103 M *IS*)[d] 10.71 (pH 5.98, 0.100 M *IS*)[d]	15.193 (pH 8.95)[e] 14.025 (pH 8.02)[e] 13.195 (pH 7.11)[e] 11.667 (pH 5.98)[e]
SRFA $An^{3+} + Hs^- = AnHs^{2+}$	13.798 (pH 9, 0.1 M *IS*)[f]	14.765 (pH 9, 0.1 M *IS*)[f]
Regressed coefficients for Log $\beta_{1:An^{3+}}$ $An^{3+} + Hs^- = AnHs^{2+}$	a = 0.01416 (LHA)[g] b = 0.09256 (LHA)[g] c = 0.08661 (LHA)[g] d = 0.86019 (LHA)[g]	a = 0.01416 (WIPP)[h] b = 0.09256 (WIPP)[h] c = 0.08661 (WIPP)[h] d = 0.87011 (WIPP)[h]

[a] Log K (not log β) from Sonke and Salters (2006, Table 1)

[b] na = not applicable

[c] Log $K_{1:Ca^{2+}}$ derived as described in Section 4.2.1

[d] Log $\beta_{1:An^{3+}}$ from Sonke and Salters (2006, Table 4, Appendix A, file mmc2.xls) for Eu(III); *IS* = ionic strength

[e] Log $K_{1:An^{3+}}$ fitted as described in Step 2 of Section 4.2.2

[f] Values derived as described in Step 4 of Section 4.2.2 (Table 6)

[g] Sonke and Salters (2006, Table 5) coefficients for log β regression equation (Eq. 7)

[h] Coefficients for log $\beta_{1:An^{3+}}$ regression equation (not log $K_{1:An^{3+}}$) as determined in Section 4.2.2 (Eq. 8)

4.2.1 Humic Complexation of H^+, Ca^{2+}, and Mg^{2+}

The stability constants for the humic complexation reactions in Table 3 are either selected from the literature or derived. The complexation of H^+ and the alkaline earths are selected.

For the protonation of the humic complexation site, log $\beta_{1:H^+}$ is set at 4.59 as in the LHA Sonke and Salters (2006) model. This value implies that the site becomes largely deprotonated above pH 4.59. Because WIPP brines are alkaline and there is little affinity of the modeled humic site for protons in alkaline waters, this reaction has a negligible effect on the dominant speciation of humic sites in the WIPP calculations. Therefore, no adjustment to the log $\beta_{1:H^+}$ value is made.

In the original process model the log $\beta_{1:Ca^{2+}}$ value for the humic complexation of Ca^{2+} and Mg^{2+} was conservatively set to 2.0 (DOE 1996, SOTERM.6.3.3.1). That value was based on experimental data on humic and fulvic acids. In this work, the value is increased to 3.0 but is still likely conservative based on studies over a broad range of pH, ionic strength, and concentrations of Ca^{2+} (Lead et al. 1994, Fig. 4b; Laszak and Choppin 2001, Fig. 4; Lu and Allen 2002, Table 5). At pcH 9, log $\beta_{1:Ca^{2+}}$ is found to be in the range of 3.3 to 4.3 for Aldrich humic acid (Laszak and Choppin 2001, Table 3). As the concentration of Ca^{2+} increases from 10^{-8} M in a 0.1 M NaCl solution (Laszak and Choppin 2001) to 0.033 M in a 0.033 M $CaCl_2$ solution (Lead et al. 1994), the log $\beta_{1:Ca^{2+}}$ is found to remain above 3.0 (approximately 3.4). Lu and Allen (2002) show a strong competitive effect of Ca^{2+} and Cu^{2+} to at least 0.001 M Ca (pH 6-7). Compared to $\beta_{1:An^{3+}}$ the pH dependence of $\beta_{1:Ca^{2+}}$ is weak (Laszak and Choppin 2001; Lu and Allen 2002). For this work the simplifying conservative assumption is that log $\beta_{1:Ca^{2+}}$ is 3.0 for all humic complexation of Ca^{2+} regardless of pH. This value is also used for Mg^{2+}-humic complexation due to the similar humic complexation behavior of Mg^{2+} (Lead et al. 1994). The value of 3.35 for the log K at 0 M ionic strength gives a log $\beta_{1:Ca^{2+}}$ of 3.0 at 0.1 M ionic strength. This is a direct result of the log activity coefficient for Ca^{2+} at 0.1 M ionic strength in the simulations being -0.35 while the log activity coefficients of Hs^- and $CaHs^+$ are held at zero.

4.2.2 An(III)-Humic Complexation

The $AnHs^{2+}$ species in Table 3 represents the humic-bound radionuclide species AnHs of Eq. 2. The first column of data in Table 3 contains the log stability constants reported by Sonke and Salters (2006). The second column contains the log K and log β values selected or derived for use with the WIPP PA DATA0.FM2 database. The steps involved in the determination of these log K values are described in detail below.

Due to the nature of the available relevant data, several steps had to be taken to derive the log $K_{1:An^{3+}}$ values for DATA0.FM2. The humic colloid model of the WIPP PA simulates humic colloids for Am(III) and Pu(III). The WIPP thermodynamic database, DATA0.FM2, uses Am(III) to represent all chemical reaction calculations for Am(III) and Pu(III). Therefore, the derived log $K_{1:An^{3+}}$ values for use with DATA0.FM2 must be appropriate for Am(III) as defined in the database. Unfortunately, the available studies of Am(III)-humic complexation in the alkaline pH range (Maes et al. 1988; Maes et al. 1991) do not provide the most useful data for this analysis because they do not present direct experimental data; instead, they report stability constants and ranges that are difficult to interpret and verify. In addition, Maes et al. (1988) and Maes et al. (1991) used an adsorption separation method that necessitates assumptions that complicate interpretation of the results. A highly uncertain assumption in the method is that humic acids adsorbed to the resin have the same affinity for the trivalent metal as the humic acid that remains aqueous.

A more sensitive examination of trivalent actinide or lanthanide complexation with humic substances in the alkaline pH range is presented in Sonke and Salters (2006). Sonke and Salters (2006) measured the humic complexation of a set of lanthanides including Eu(III) at high pH using an EDTA-ligand competition method. This method avoids the complications caused by adsorption separation and more closely mimics expected EDTA-contaminated WIPP brines. In addition, Sonke and Salters (2006) includes direct experimental measurements of the proportion of Eu(III) bound to humic or fulvic acids in the various batch systems, which allows for robust model calibration in the current report.

Given the available data for Eu(III) and Am(III), determining the log $K_{1:An^{3+}}$ values for use with the DATA0.FM2 thermodynamic database required the following four steps:

1. Assess the differences in humic complexation between Eu(III) and Am(III)
2. Reproduce the Eu(III)-LHA-EDTA-CO_2-H_2O system of Sonke and Salters (2006)
3. Examine the empirical log $\beta_{1:An^{3+}}$ relationship of Sonke and Salters (2006) for LHA
4. Derive log $K_{1:An^{3+}}$ values for use with the DATA0.FM2 database

Each step involves one or more process model simulations using PhreeqcI. The simulations and their results are described in detail below. Table 4 lists the simulations along with their associated input/output files and post-processing files.

Table 4. Phreeqcl input/output files and Excel spreadsheets used in the derivation of the log $K_{1:An^{3+}}$ values for DATA0.FM2 (/nfs/data/CVSLIB/WIPP_EXTERNAL/ap167/Files).

Simulation	Files
Step 1 – Assess the differences in humic complexation between Am(III) and Eu(III)	1a. Am-HA alpha Maes 1991 pH 9.pqi 1a. Am-HA alpha Maes 1991 pH 9.pqo 1a. Eu-HA alpha Maes 1991 pH 9.pqi 1a. Eu-HA alpha Maes 1991 pH 9.pqo Sonke-mmc2.xls
Step 2 – Reproduce the Eu(III)-LHA-EDTA-CO_2-H_2O system of Sonke and Salters (2006)	1. Eu-LHA Sonke reproduction pH 6-9.pqi 1. Eu-LHA Sonke reproduction pH 6-9.pqo 1. EuHA Sonke reproduction.xlsx
Step 3 – Examine the empirical log $\beta_{1:An^{3+}}$ relationship of Sonke and Salters (2006, Table 5) for LHA	1c. Eu-LHA Sonke regression pH 6-9.pqi 1c. Eu-LHA Sonke regression pH 6-9.pqo 1c-high. Eu-LHA Sonke regression pH 6-9.pqi 1c-high. Eu-LHA Sonke regression pH 6-9.pqo 1c-low. Eu-LHA Sonke regression pH 6-9.pqi 1c-low. Eu-LHA Sonke regression pH 6-9.pqo 1c. EuHA Sonke regression.xlsx 1d. Eu-LHA Sonke regression pH 6-9 0.08 mu.pqi 1d. Eu-LHA Sonke regression pH 6-9 0.08 mu.pqo 1d. EuHA Sonke regression with 0.08 mu.xlsx
Step 4 – Derive log $K_{1:An^{3+}}$ values for the DATA0.FM2 database	2a. Fit FM2 model to Sonke LHA data.pqi 2a. Fit FM2 model to Sonke LHA data.pqo 2c. SRFA FM2 model fit to Sonke Fig 2C.pqi 2c. SRFA FM2 model fit to Sonke Fig 2C.pqo 2. Am-humic Log K derivation for DATA0.FM2.xlsx

Step 1 – Assess the differences in humic complexation between Am(III) and Eu(III)

As noted above, the WIPP PA uses Am(III) in the DATA0.FM2 database to simulate the behavior of trivalent actinides Am(III) and Pu(III). However, literature data involving Am(III)-humic complexation is not as reliable as those for Eu(III)-humic complexation (also as noted above). Therefore, it is necessary to assess whether Eu(III)-humic complexation data can be used as a surrogate for Am(III)-humic complexation.

The clearest comparison of humic complexation of Am(III) and Eu(III) is provided in Maes et al. (1991). In that study, both Am(III) and Eu(III) were examined in batch experiments containing Boom clay humic acid (BCHA) at a pH of 9.0 in the presence of 0.1 M $NaClO_4$ and either 0.01 M or 0.0135 M carbonate. For Am(III), the calculated log $\beta_{1:An^{3+}}$ is reported to be 13.219 ± 0.857 (Maes et al. 1991, Table 5). For Eu(III), four sets of measurements were performed for BCHA. The means of the log $\beta_{1:An^{3+}}$ values of these sets are tabulated as 13.47 ± 0.30, 13.24 ± 0.47, 13.82 ± 0.81, and 13.45 ± 0.50 (Maes et al. 1991, Table 4). The overall mean is approximately 13.5.

The log $\beta_{1:An^{3+}}$ values reported for Am(III) and Eu(III) do not indicate by themselves which metal has a greater affinity for BCHA because each metal has a slightly different set of aqueous chemical reactions with different equilibrium constants (Maes et al. 1991, Table 7). In addition, the actual log $\beta_{1:An^{3+}}$ values reported by Maes et al. (1991) are not expected to be as accurate as the log $\beta_{1:An^{3+}}$ values reported by Sonke and Salters (2006) for Eu(III) because of the difference in experimental methods (discussed earlier in this subsection). Nevertheless, the Maes et al. (1991) study does provide the means for a useful comparison of the relative affinity of Am(III) and Eu(III) to humic acid. The comparison requires simulating the two Maes et al. (1991) systems using the reported log $\beta_{1:An^{3+}}$ values and aqueous species reactions.

PhreeqcI was used to simulate each batch solution. For the Am(III) simulation, the Am(III) aqueous reactions in the next to last column of Table 7 ("I=0") of Maes et al. (1991) were used along with the 13.219 mean log $\beta_{1:An^{3+}}$ value for Am(III)-humic complexation. For the Eu(III) simulation, the Eu(III) aqueous reactions in the first and third columns of Table 7 ("I=0") were used along with a 13.5 log $\beta_{1:An^{3+}}$ value for Eu(III)-humic complexation. In addition, reactions and equilibrium constants for the Eu(III) hydroxide carbonate species were assumed to be identical to those of Am(III), which is consistent with how Maes et al. (1991, see p. 44) treated these species. In each simulation, the solution was set to have a pH of 9.0 and to contain 10^{-4} M humic complexation sites, 0.1 M NaCl, and 10^{-10} M of either Am(III) or Eu(III). In addition, the carbonate concentration was set at 0.0135 M as in the Am(III) the batch experiment.

The results are shown in Table 5. The similar fractions of humic-bound An(III) indicate that Am(III) and Eu(III) under these conditions have approximately the same affinity for BCHA. This finding supports the assumption that the Eu(III)-humic complexation data reported in Sonke and Salters (2006) can be used to approximate Am(III)-humic complexation.

Table 5. Simulation results of Maes et al. (1991) model for Am(III) and Eu(III)

Input or Output	Am(III)-BCHA Simulation of Maes et al. (1991) Model	Eu(III)-BCHA Simulation of Maes et al. (1991) Model
Log $\beta_{1:An^{3+}}$	13.22	13.50
Fraction of An(III) humic-bound	0.9953	0.9963

Note: Solutions contain 10^{-4} M BCHA, 10^{-10} M Am(III) or Eu(III), pH 9.0, 0.1 M NaCl, and 0.0135 M $NaHCO_3$

Step 2 – Reproduce the Eu(III)-LHA-EDTA-CO_2-H_2O system of Sonke and Salters (2006)

PhreeqcI was used to simulate Eu(III) complexation with Leonardite humic acid (LHA) as measured in experiments by Sonke and Salters (2006, Fig. 2) over a pH range of 6 to 9. As indicated in Appendix A of Sonke and Salters (2006), the system of interest contains 4.59×10^{-7} M EDTA, 4.54×10^{-5} M humic acid sites, 8.24×10^{-8} M Eu(III), and ~0.1 M $NaNO_3$ (Sonke and Salters 2006, Appendix A, file: mmc2.xls). The experiments were exposed to atmospheric partial pressures of $CO_2(g)$, assumed here to be $10^{-3.4}$ bar. For the PhreeqcI reproduction of the Sonke and Salters (2006) model, the reaction data in the first column of Table 2 were used along with the Sonke and Salters (2006) log $\beta_{1:An^{3+}}$ data in Table 3.

As shown in Figure 1, the PhreeqcI reproduction of the Sonke and Salters (2006) model closely approximates the experimental data. The slight underestimations may be due to small differences in the Eu(III) hydrolysis reactions used. The exact Eu(III)-CO_2-H_2O reactions used in the Sonke and Salters (2006) model are not clear.

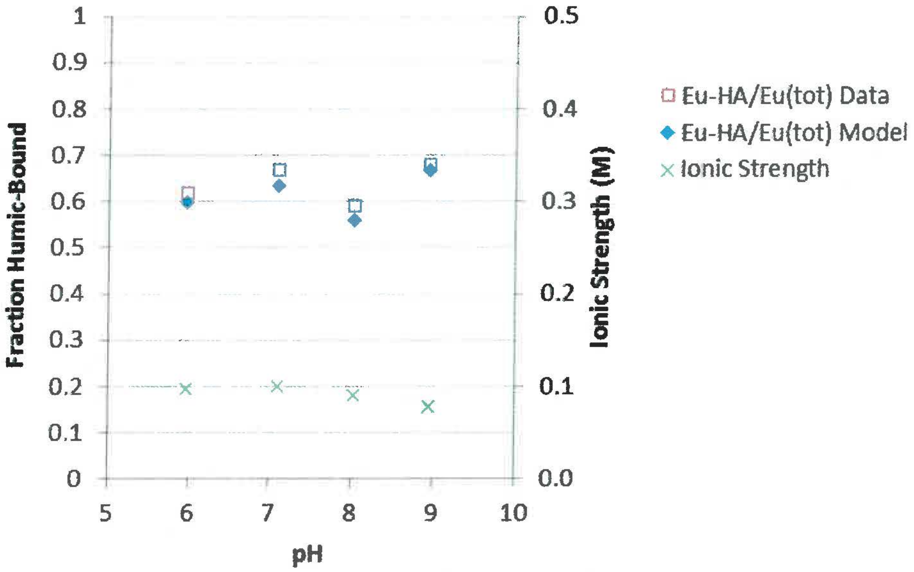

Figure 1. PhreeqcI reproduction of the Sonke and Salters (2006) model of the Eu(III)-LHA-EDTA-CO_2-H_2O system

The concentrations of relevant species of the Eu(III)-LHA-EDTA-CO_2-H_2O system, as calculated by the PhreeqcI model, are plotted in Figure 2. The dominant species in the alkaline range are $HEdta^{3-}$, $EuEdta^{-}$, and $EuHs^{2+}$. $Edta^{4-}$ and H_2Edta^{2-} are also abundant in the alkaline range. The concentrations of Eu-carbonate species are orders of magnitude lower than the dominant Eu species and therefore do not significantly affect the fraction of Eu bound to LHA and EDTA in these experiments. Thus, it can be concluded that the Eu-LHA fractions in these experiments (Figure 1) are negligibly affected by exposure to atmospheric carbon dioxide.

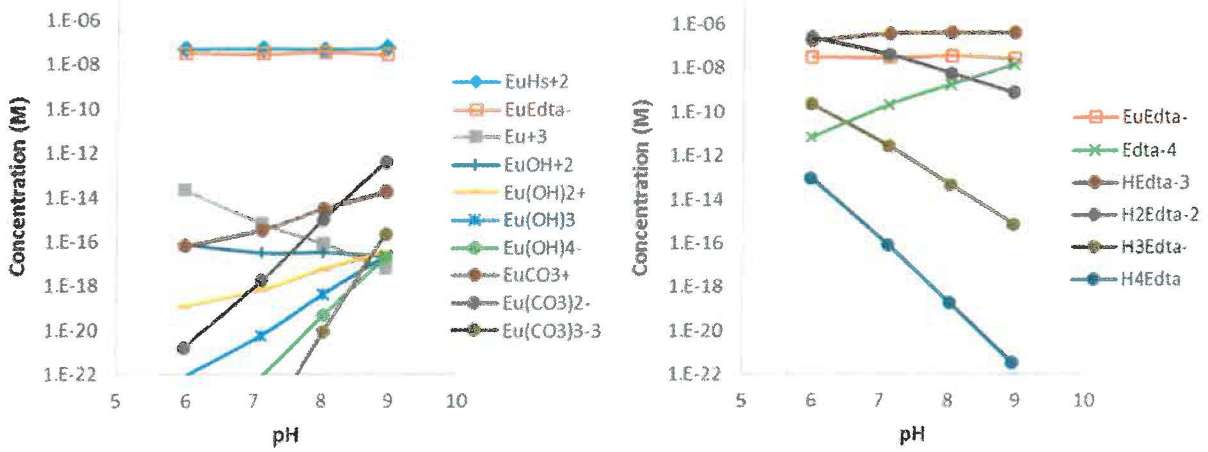

Figure 2. Calculated species concentrations in the Phreecqcl reproduction of the Sonke and Salters (2006) model of the Eu(III)-LHA-EDTA-CO_2-H_2O system

Step 3 – Examine the empirical log $\beta_{1:An^{3+}}$ relationship of Sonke and Salters (2006) for LHA

In Step 2, a PhreeqcI model was developed that uses the Eu-LHA log $\beta_{1:An^{3+}}$ values determined by Sonke and Salters (2006) to simulate individual Eu-LHA Sonke and Salters (2006) batch experiments. In Step 3, the PhreeqcI model is modified to use Eu-LHA log $\beta_{1:An^{3+}}$ values calculated from the empirical relationship in Eq. 9 and Table 5 of Sonke and Salters (2006). This equation is shown in Section 4.2 (Eq. 7) and its coefficients are given in Table 3. The average deviation of the equation calculations from experimental values for the lanthanides is ~0.11 (Sonke and Salters 2006).

In this step, the effects of ionic strength on Eu-HA complexation is examined. Figure 3 shows the results of using the log $\beta_{1:An^{3+}}$ regression equation (Eq. 7 and Table 3) in the PhreeqcI model developed in Step 2 at two different ionic strengths. In Figure 3, ionic strength isopleths for 0.08 M and 0.1 M ionic strength are compared to the experimental data points. The ionic strengths of the experimental data vary from 0.076 M at pH 8.95 to 0.103 M at pH 7.11 (Table 3). The isopleths indicate that as ionic strength increases, Eu-LHA complexation increases relative to Eu-EDTA complexation. It should be noted, however, that the Eu-LHA stability constant (log $\beta_{1:An^{3+}}$) decreases with increasing ionic strength (as indicated by the regression equation and its coefficients). Thus, to explain why Eu-LHA complexation increases relative to Eu-EDTA complexation as ionic strength increases (Figure 3), the affinity of Eu for EDTA decreases more rapidly than the affinity of Eu for LHA with increasing ionic strength.

To provide a rough measure of the effects of the uncertainty in the log $\beta_{1:An^{3+}}$ regression equation on the Eu fraction bound to LHA in the Eu-LHA experimental system, 95% confidence intervals are approximated for the 0.1 M ionic strength isopleth assuming that the log $\beta_{1:An^{3+}}$ standard deviation of ~0.11 reported for all lanthanide-LHA complexation (Sonke and Salters 2006, p. 1502) could be directly applied to the isopleth. The results, shown in Figure 4, indicate a 95% confidence interval range of around 0.2 in the Eu fraction bound to LHA for this system.

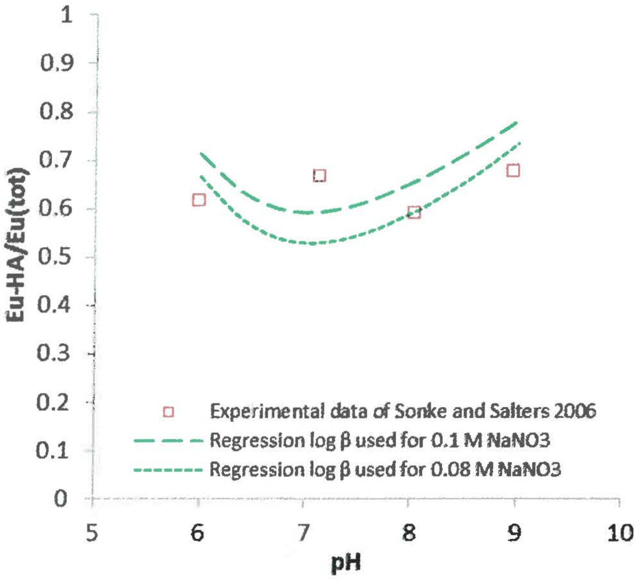

Figure 3. Eu-LHA complexation predicted using Sonke and Salters (2006) log $\beta_{1:An^{3+}}$ regression equation at 0.08 M and 0.1 M ionic strength, as compared to Eu-LHA experimental data of Sonke and Salters (2006, Appendix A, file mmc2.xls)

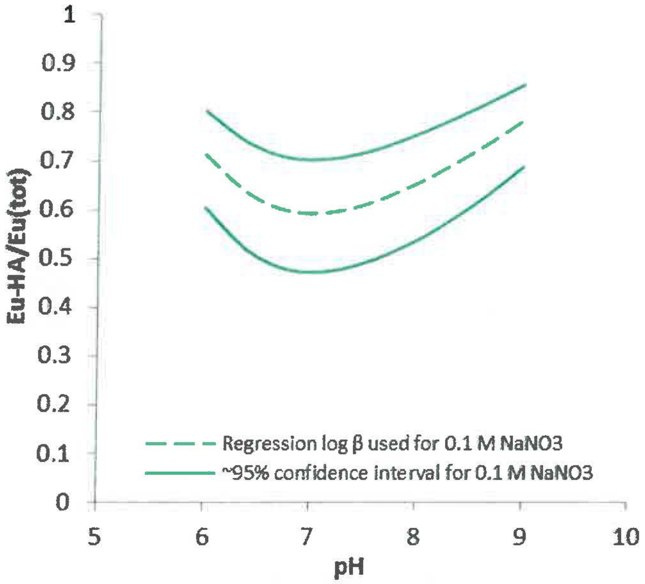

Figure 4. Approximated 95% confidence interval for 0.1 M ionic strength isopleth using Sonke and Salters (2006) log $\beta_{1:An^{3+}}$ regression equation for the Sonke and Salters (2006) experimental Eu-LHA system

Step 4 – Derive log $K_{1:An^{3+}}$ values for use with the DATA0.FM2 database

In Step 4, log $K_{1:An^{3+}}$ values are determined for the WIPP DATA0.FM2 database. It is assumed in this step that Am(III) and Eu(III) have equal overall affinities for humic substances in alkaline waters. This assumption is supported by the results of Step 1.

In the first calculation for this step, a log $K_{1:An^{3+}}$ value is effectively fitted to DATA0.FM2 to be consistent with the humic complexation observed at pH 8.95 for Eu(III) and Leonardite humic acid (LHA), as observed in Sonke and Salters (2006, Appendix A, file mmc2.xls). Fitting to DATA0.FM2 was done by replacing all aqueous reactions in the PhreeqcI model from Step 2 with the DATA0.FM2 aqueous reactions for Am(III) listed in Table 2 and replacing the $EuHs^{2+}$ reaction with one for $AmHs^{2+}$. The log $K_{1:An^{3+}}$ was adjusted by trial and error to achieve the same degree of humic complexation observed for Eu(III) humic complexation in Sonke and Salters (2006, Appendix A, file mmc2.xls). These actions produced a log $K_{1:An^{3+}}$ value of 16.39, which corresponds to a log $\beta_{1:An^{3+}}$ value of 15.50 at the ionic strength of the system modeled. This simulation is summarized in the first row of Table 6 below.

The fitted log $K_{1:An^{3+}}$ for LHA will likely overestimate humic complexation for the type of humic colloids expected in the WIPP repository. LHA is derived from coal, is highly aromatic, and binds metals more strongly than typical soil and river humic acid (Sonke and Salters 2006, p. 1502). The humic and fulvic acids in WIPP brines are assumed to be generated from the degradation of organic materials emplaced in the repository (DOE 1996, SOTERM.6.3.3.1). They are not expected to be highly aromatic like LHA nor have an especially high affinity for metals. Fulvic acids typically have significantly lower affinities for metals than humic acids (e.g., Lead et al. 1994).

To assess the effect of a different type of humic material on An(III)-humic complexation, a second PhreeqcI simulation was performed for Suwannee River fulvic acid (SRFA). Sonke and Salters (2006) measured the complexation of lanthanides with SRFA at pH values ranging from 6 to 9. The fraction of

Eu(III) complexed with SRFA is not reported for pH 9, but the trend observed for lanthanides at pH 9 as a function of atomic number indicates that this fraction would be approximately 0.45 for the experimental conditions (Sonke and Salters 2006, Fig. 2C). For the DATA0.FM2 PhreeqcI model, a log $K_{1:An^{3+}}$ value of 14.765 (log $\beta_{1:An^{3+}}$ of 13.797) was needed to simulate the approximate humic complexation expected for Eu(III) (Table 6).

Table 6. Log $K_{1:An^{3+}}$ and log $\beta_{1:An^{3+}}$ values fitted to DATA0.FM2 database

Experimental Conditions	**pH**	**Ionic Strength (M)**	**Fraction of Eu(III) or Am(III) Complexed to Humic Substance**[a]	**Log $K_{1:An^{3+}}$ for WIPP DATA0.FM2**	**Log $\beta_{1:An^{3+}}$ Consistent with WIPP DATA0.FM2**
LHA experiment for Eu(III)[b]	8.95	0.0776	0.678	16.389	15.497
SRFA experiments for lanthanides[c]	9.00	0.101	0.45[d]	14.765	13.798

[a] Am(III) humic complexation assumed equivalent to Eu(III) complexation based on analysis in Step 1

[b] Sonke and Salters (2006, Appendix A, file mmc2.xls); 0.0454 mM LHA, 82.4 nM Eu(III), and 459 mM EDTA (model output file: 2a. Fit FM2 model to Sonke data.pqo)

[c] 100 nM Eu(III), 130 mM EDTA, 20 mg L^{-1} SRFA, 5.99 mEq g^{-1} (Sonke and Salters 2006, p. 1497 and Fig. 2C) (model output file: 2c. SRFA FM2 model fit to Sonke Fig 2C.pqo)

[d] Approximated based on trend observed at pH 9 in Sonke and Salters (2006, Fig. 2C)

The difference in log $K_{1:An^{3+}}$ values between LHA and SRFA (Table 6) is large. This difference reflects the much higher affinity LHA has for metals than SRFA. It is also consistent with the difference in log $\beta_{1:An^{3+}}$ values calculated using the Sonke and Salters (2006, Table 5 and Eq. 9) empirical relationships, which are 14.55 for LHA and 12.89 for SRFA. The fraction complexed in the two systems modeled in Table 6 is not much different (0.678 vs. 0.45) because the ratio of concentrations of humic complexation sites to EDTA is much higher in the SRFA system.

As mentioned above, WIPP colloids are assumed to be a mixture of humic and fulvic acids potentially generated from degrading organic materials in the repository. Their overall affinity for complexing metals is expected to be between that of SRFA and LHA. At this point it is assumed that the log $K_{1:An^{3+}}$ for WIPP humic colloids at pH 9 and 0.1 M ionic strength is approximately midway between the log $K_{1:An^{3+}}$ values of SRFA and LHA, i.e., a log $K_{1:An^{3+}}$ of 15.58. This assumption implies that WIPP humic colloids have a greater affinity for Am(III) than does Elliot soil humic acid. Elliot soil humic acid has a log $\beta_{1:An^{3+}}$ that is much closer to SRFA than to LHA at pH 9 (Sonke and Salters 2006, Fig. 5), which suggests that a log $K_{1:An^{3+}}$ for WIPP humic colloids that is midway between that of LHA and SRFA may be conservative.

A log $K_{1:An^{3+}}$ of 15.58 in the WIPP DATA0.FM2 model at a pH of 9 and an ionic strength of 0.1 M corresponds to a log $\beta_{1:An^{3+}}$ of 14.61, after accounting for the log of the activity coefficient for Am^{3+} (-0.967). With this log $\beta_{1:An^{3+}}$ as a basis at pH 9 and 0.1 M ionic strength, it is further assumed that the LHA log $\beta_{1:An^{3+}}$ empirical relationship of Sonke and Salters (2006, Table 5) may be used to adjust for pH and ionic strength once the *d* parameter is fitted to the 14.61 log $\beta_{1:An^{3+}}$ value at pH 9 and 0.1 M ionic strength that corresponds to the selected intermediate log K value of 15.58. Doing so provides the following equation for log $\beta_{1:An^{3+}}$ for DATA0.FM2:

$$\log \beta_{1:An^{3+}} = \exp(0.01416\,AN + 0.09256\,\mathrm{pH} + 0.08661(-\log IS) + 0.87011) \qquad \text{(Eq. 8)}$$

AN is the atomic number, taken as 63 for Eu(III). Eq. 8 is derived from data in the ionic strength range of 0.001 to 0.1 M and the pH range of 6 to 9. Care must be taken when using this equation to extrapolate outside these ranges (Sonke and Salters 2006, p. 1502).

Log $K_{1:An^{3+}}$ for the WIPP DATA0.FM2 model at a specific ionic strength and pH is determined by first using Eq. 8 to calculate log $\beta_{1:An^{3+}}$ and then subtracting the log of the An^{3+} activity coefficient at the given ionic strength:

$$\log K_{1:An^{3+}}\ (\text{at } IS) = \log \beta_{1:An^{3+}}(\text{at } IS) - \log \gamma_{An^{3+}}(\text{at } IS) \qquad \text{(Eq. 9)}$$

5 MODEL APPLICATION

In this section, the An(III)-humic complexation model described in Section 4 is used to simulate complexation in WIPP waters. In Section 5.1, Am(III)-humic complexation stability constants for WIPP brines are determined and the extent of Am(III)-humic complexation is calculated for baseline Am(III) solubilities. In Section 5.2, the model is used to determine Am(III)-humic complexation in WIPP brines and the effects on Am(III) mobility. In Section 5.3, Am(III)-humic colloid proportionality constants are recommended for the WIPP PA abstraction model.

The calculations in Section 5 were performed using Microsoft Excel 2016 and PTC Mathcad Prime 3.0, a commercial mathematical software tool. The Mathcad files are saved in PDF format for documentation so that they can be read using Adobe Acrobat. It is clear from these PDF files exactly what algebraic calculations were performed. The calculated values shown in these files are easily checked by reading the file and using a hand calculator, so there is no need to include the Mathcad MCDX files in the data record. The input/output and post-processing files associated with the various model applications are listed in Table 7.

Table 7. Input/output and post-processing files used in the model applications (/nfs/data/CVSLIB/WIPP_EXTERNAL/ap167/Files).

Simulation	Files
Section 5.1 – Am(III)-humic complexation in WIPP brines	4. Am-HA vs IS Sonke 2006 r0.xlsx 5. Am-CaMg-HA Sonke 2006 1x r0.pdf 5. Am-CaMg-HA Sonke 2006 5x r0.pdf
Section 5.2 – Effect of Am(III) concentration on Am(III)-humic complexation in WIPP brines	5. PHUM III calc comparison r3a.xlsx

5.1 Humic Complexation in WIPP Brines at Baseline Am(III) Solubility

WIPP brines equilibrated with MgO (Table 1) have high Mg^{2+} concentrations and high ionic strengths (~6 M). These brines cannot be simulated using the PhreeqcI model developed in Section 4 because the ionic strength far exceeds the range of the PhreeqcI ion activity model. However, the EQ3/6 Pitzer calculations of Domski and Xiong (2015), shown in Table 1, can be directly used as input to the humic complexation model equations in Section 4 to predict Am(III)-humic complexation in equilibrated WIPP brines.

The calculations of Domski and Xiong (2015) assume that the aqueous concentration of Am(III) is at saturation with the mineral phase $Am(OH)_3(s)$, which is consistent with the conservative WIPP source term approach. This assumption implies that the free Am^{3+} concentration in equilibrium with the controlling solid phase will not be affected by the addition of humic colloids to the system. Similarly, the free concentrations Ca^{2+} and Mg^{2+} will not change with the addition of humic colloids because their concentrations are also controlled by solubility. Thus, the fraction of Am(III) complexed by aqueous humic substances in the equilibrated WIPP brines of Table 1 can be calculated directly from equations in Section 4.1, concentrations in Table 1, and stability constants calculated from Eq. 8 if extrapolated to high ionic strength.

Eq. 8 was derived from the results of experiments conducted over a pH range of 6 to 9 and an ionic strength range from 0.001 to 0.1 M. The ionic strength of WIPP brines, however, is well beyond this range. Figure 5 shows that Eq. 8 is highly linear over an ionic strength range of 0.001 to 6 M. The high linearity of the effects of ionic strength in the 0.001 to 0.1 M range suggests that log $\beta_{1:An^{3+}}$ at an ionic strength of 6 M is likely around 12.5. However, using log $\beta_{1:An^{3+}}$ values calculated for 6 M ionic strength for WIPP brines could potentially be significantly non-conservative if actual trends level off above 0.1 M. Alternatively, not extrapolating, i.e., using log $\beta_{1:An^{3+}}$ values calculated at 0.1 M ionic strength for WIPP brines, would likely be overly conservative. Therefore, using log $\beta_{1:An^{3+}}$ values calculated at 1 M ionic strength (an intermediate value between 0.1 and 6 M) is thought to be reasonably conservative for WIPP brines. The log $\beta_{1:An^{3+}}$ values calculated for GWB (1 × Min) and ERDA-6 (1 × Min) at 1 M ionic strength are 13.203 and 13.675, respectively, and are likely conservative for these brines based on the trends in Figure 5. Regardless, the estimation of Am(III)-humic complexation in the updated model is expected to be conservative primarily because a conservatively low value of log $\beta_{1:Ca^{2+}}$ of 3.0 is used for competing Ca^{2+} and Mg^{2+} cations (Section 4.2.1).

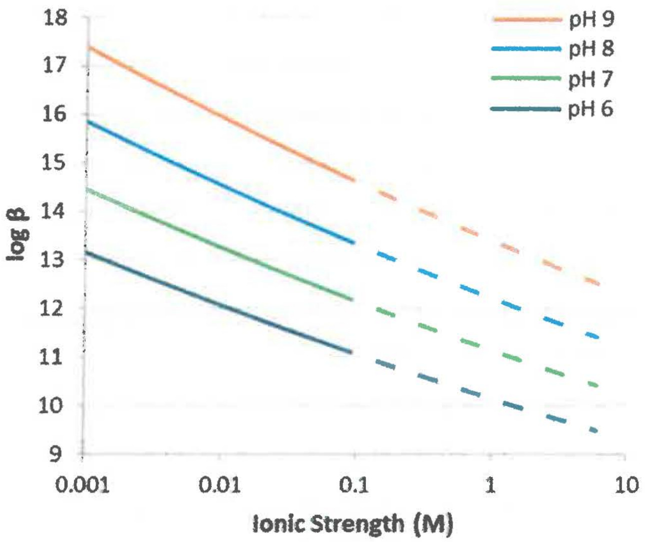

Figure 5. Behavior of log $\beta_{1:An^{3+}}$ regression equation (Eq. 8) over the range of supporting experimental data (solid) and beyond (dashed)

Table 8 summarizes the calculated speciation for each of the brines in Table 1. The concentrations of Hs^- and AnHs are calculated directly from Eq. 4 and 5. Concentrations of humic-bound Am(III) in WIPP brines are calculated to be quite high at baseline Am(III) solubility, much higher than the total aqueous non-colloidal concentrations. Hence, the presence of humic colloids (at a concentration of 1.10×10^{-5} M) is predicted to greatly increase the mobility of Am(III) at baseline Am(III) solubility in these brines. How the uncertainty in Am(III) solubility affects these calculations is addressed in the next section, along with how this uncertainty is used to determine the humic colloid proportionality constants PHUMSIM and PHUMCIM.

Table 8. Predicted concentrations (M) in Am(III)-Ca-Mg-Hs system for WIPP PA

Parameter	**GWB (1 × Min)**	**GWB (5 × Min)**	**ERDA-6 (1 × Min)**	**ERDA-6 (5 × Min)**
(An)[a]	2.32×10^{-7}	2.15×10^{-7}	6.03×10^{-8}	5.51×10^{-8}
(An^{m+})[a]	1.11×10^{-11}	1.09×10^{-11}	6.14×10^{-13}	4.59×10^{-13}
(Hs_{tot})[b]	1.10×10^{-5}	1.10×10^{-5}	1.10×10^{-5}	1.10×10^{-5}
(Ca^{2+})[c]	0.0280	0.0289	0.0160	0.0160
(Mg^{2+})[c]	0.282	0.276	0.0506	0.0419
(Hs^{-})	2.26×10^{-8}	2.29×10^{-8}	1.14×10^{-7}	1.32×10^{-7}
(CaHs)+(MgHs)	6.99×10^{-6}	6.99×10^{-6}	7.56×10^{-6}	7.64×10^{-6}
(AnHs)	3.99×10^{-6}	3.98×10^{-6}	3.23×10^{-6}	3.23×10^{-6}

[a] Domski and Xiong (2015); Am(III) at baseline solubility
[b] Assumed (Section 3)
[c] Molarity calculated from Table 1 (free cation molality multiplied by solution density)

5.2 Humic Complexation for Uncertain Am(III) Solubility

In Langmuir adsorption, the affinity of surface adsorption sites for adsorbing solutes decreases as the adsorbed concentration approaches the total adsorption site concentration. Like Langmuir adsorption, the affinity of humic complexation sites for Am(III) decreases as the humic-bound Am(III) concentration approaches the total concentration of humic complexation sites. When there is high loading of the sites with Am(III), the concentration of available sites becomes limited and the ratio of humic-bound to non-humic-bound Am(III) decreases. At low loading, the ratio of humic-bound to non-humic-bound Am(III) is not highly affected by the concentration of Am(III). An example of the loading effect is demonstrated in Figure 4 of Maes et al. (1988) for Eu(III) complexation with Podzol humic acid.

At low loading, a proportionality constant, such as PHUMSIM and PHUMCIM, provides a means of estimating the humic-bound concentration from the non-humic-bound concentration because at low loading the humic-bound concentration is negligibly affected by the total complexation site concentration. However, at high loading, the total humic complexation site concentration must be factored in (as in Eq. 5 of Section 4.1) to account for the decreasing availability of free complexation sites.

The calculations in the previous section predict that, assuming baseline Am(III) solubilities, a major portion (> 30%) of the humic complexation sites in WIPP brines will be occupied by Am(III). This high loading implies that the ratios of humic-bound to non-humic-bound Am(III) in these calculations should not be used to set the values of PHUMSIM and PHUMCIM. Doing so would cause underestimation of Am(III)-humic complexation when uncertainty in the solubility of Am(III) reduces non-colloidal Am(III) concentrations below baseline in given realizations.

Figure 6 shows the relationships between the concentrations of humic-bound actinide (shown as AnHS), total humic complexation sites (CAPHUM), and non-colloidal actinide (An) as a function of the non-colloidal actinide (An) concentration. These curves show the behavior and effects of the model equations and stability constants described in Sections 4 and 5.1. The dotted lines in Figure 6 show the Langmuir behavior of the An(III)-humic complexation model. At very low loading, the humic-bound An(III) concentration is proportional to the non-colloidal An(III) concentration. At very high loading, it is essentially equal to CAPHUM. In the (An) range of $\sim 10^{-7}$ to $\sim 10^{-6}$ M, the humic-bound An(III) concentration is highly affected by both (An) and CAPHUM. These curves are calculated in MS Excel file "PHUM III calc comparison r3a.xlsx".

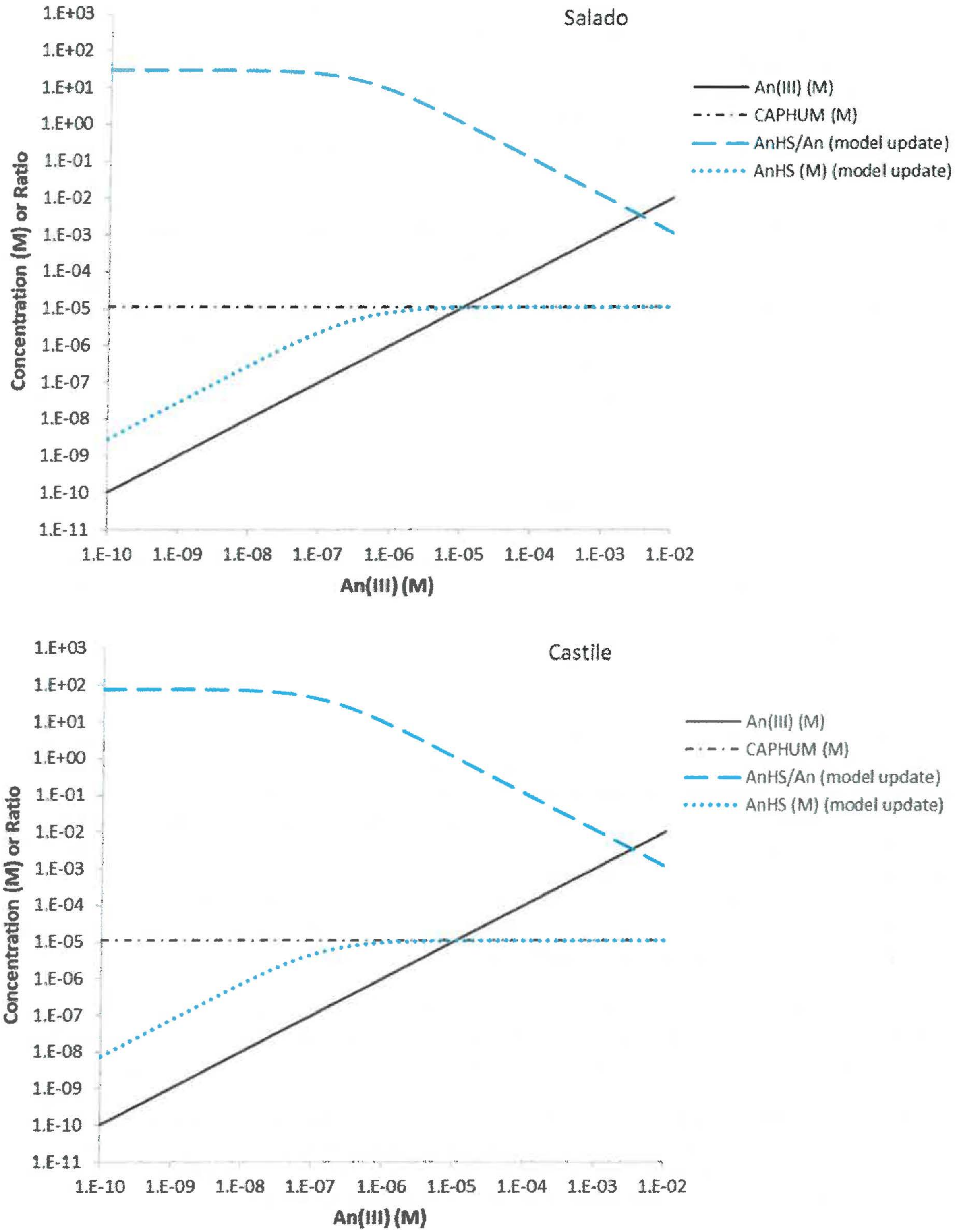

Figure 6. Effect of total non-colloidal An(III) concentration (denoted as “An(III) (M)”) on An(III)-humic complexation in simulated Salado (top) and Castile (bottom) brines

The curves in Figure 6 assume that the ratios of free An^{3+} to non-colloidal An(III), i.e., $(An^{3+})/(An)$, are constant over the entire uncertainty range of (An) and are consistent with the values calculated from the results in Table 8. In actuality, this ratio will change somewhat with (An) in the WIPP brines as uncertainties in An(III) solubility are applied to the non-colloidal An(III) concentration. It will change because of complexation with organic ligands, especially EDTA. For example, at the baseline An(III) solubility for GWB (i.e., 2.32×10^{-7} M for 1 × Min), loading effects are low for EDTA and extremely low for citrate and acetate (Domski and Xiong 2015, Tables 2, 11, and 12). Therefore, at lower An(III) solubility, i.e., lower (An), the $(An^{3+})/(An)$ ratio will not be much different than at baseline An(III) solubility because complexation with organic ligands will be approximately proportional to the free concentration of An^{3+} in this range. For An(III) solubility that is higher than baseline, loading effects on available EDTA will cause $(An^{3+})/(An)$ to increase as the loading capacity of EDTA is reached. However, the $(An^{3+})/(An)$ ratio quickly becomes irrelevant to calculating the AnHs concentration above the baseline solubility because the capacity of the humic colloids for An(III) is reached near the baseline An(III) solubility, causing the AnHs concentration to be controlled by CAPHUM. For these reasons, applying the $(An^{3+})/(An)$ ratios calculated from Table 8 to the full range of possible values for (An) is an acceptable simplification.

Figure 6 also plots the ratio of humic-bound to non-humic-bound actinide concentration, i.e., $(AnHs)/(An)$. This ratio levels off and becomes constant at very low loading when (An) is low. In this range, a proportionality constant like PHUMSIM and PHUMCIM does well at predicting the humic-bound actinide concentration from the non-colloidal actinide concentration. The model calculations at low loading result in the following PHUMSIM and PHUMCIM values (one significant figure, rounded up):

- An(III) PHUMSIM = 30
- An(III) PHUMCIM = 80

These values for PHUMSIM and PHUMCIM are much higher than the nominal values determined for the original WIPP PA model (0.19 and 1.37, respectively). The original process model uses An(III)-humic complexation stability constants measured at pH 6 to predict complexation at pH 9 (DOE 1996, SOTERM.6.3.3), which is a significantly non-conservative assumption. Stability constants for humic complexation of trivalent metals increase by orders of magnitude from pH 6 to 9 (Maes et al. 1991; Sonke and Salters 2006). Partially offsetting this non-conservative assumption in the original model is the use of total dissolved, non-colloidal actinide (An) in the model equations (DOE 1996, SOTERM.6.3.3, equations 6-17, 6-19, and 6-20) to calculate PHUMSIM and PHUMCIM. The appropriate input in these equations is the free actinide concentration (An^{3+}), as in Eq. 5 of Section 4.1.

Figure 7 shows a comparison of the effects of PHUMSIM and PHUMCIM values on the humic-bound and total mobile An(III) concentrations. The PHUMSIM and PHUMCIM values from the original WIPP PA model cause the humic-bound An(III) concentrations to have negligible (Salado) or relatively small (Castile) contributions to the total mobile An(III) concentrations, as indicated by the negligible or small deviations of the red dashed lines from non-colloidal An(III) concentrations. The updated PHUMSIM and PHUMCIM values, however, cause major increases to total mobile An(III) concentrations at low to mid-range values of (An), as indicated by the blue dashed lines. At high non-colloidal An(III) concentrations (> $\sim 10^{-5}$ M), effects are minimal or nonexistent because of the CAPHUM limit.

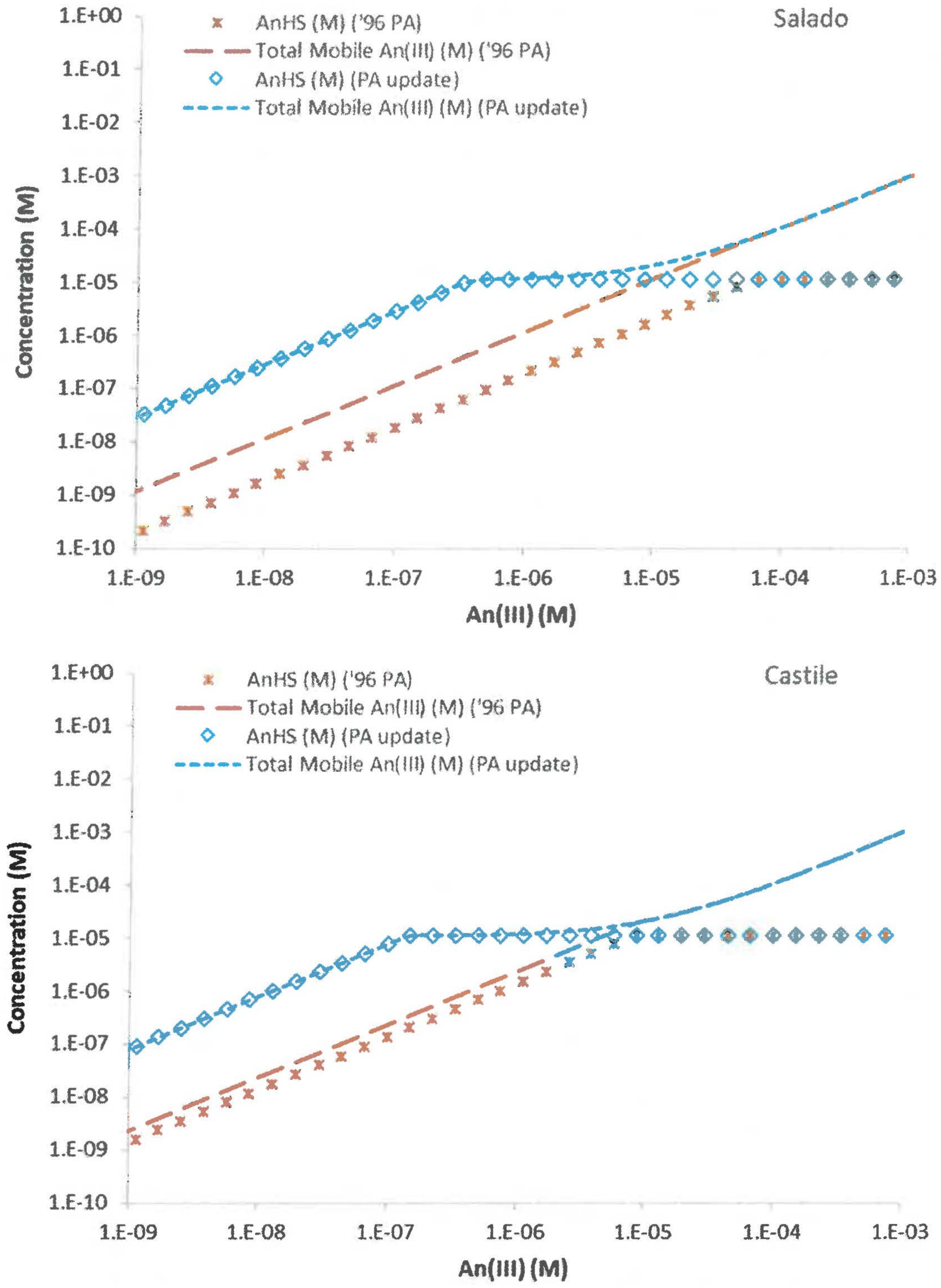

Figure 7. Comparison of original and new representations of An(III)-humic complexation in Salado (top) and Castile (bottom) brines

5.3 Recommendations for PHUMSIM and PHUMCIM for An(III)

The WIPP PA implementation of the effects of humic colloids on total An(III) mobile concentrations, as abstracted using the parameters PHUMSIM, PHUMCIM, and CAPHUM, requires no modification at this time, and hence no modification of the equations implemented in the WIPP PA model. These parameters and their use in the WIPP PA adequately represent the current understanding of the potential impact that humic colloids have on total An(III) mobile concentrations in projected WIPP brines. Major improvements to this representation would require new laboratory work focused on WIPP conditions. (The EDTA-ligand competition method used by Sonke and Salters (2006) would be especially suited for this work. Any new laboratory work, however, should first examine whether humic substances are sufficiently stable under WIPP conditions (Section 2).)

Improvements and updates are made, however, to the process model and process model inputs used to calculate PHUMSIM and PHUMCIM for the WIPP PA model. The major improvement to the process model is to use the free An(III), Ca, and Mg concentrations in the model equations instead of the total concentrations. The improved process model is described in Section 4.1. An additional change to the process model is to require low loading when it is used to calculate PHUMSIM and PHUMCIM. The input values of the stability constants $\beta_{1:Ca^{2+}}$ and $\beta_{1:An^{m+}}$ and the concentrations of An^{3+}, Ca^{2+} and Mg^{2+} are updated as described in Sections 4.2 and 5.1.

Based on the results of the improved process model and updated inputs, the recommended values for PHUMSIM and PHUMCIM are:

- An(III) PHUMSIM = 30
- An(III) PHUMCIM = 80

These values are expected to be conservative due to the following conservative assumptions used in their derivation:

- The stability constants for An(III)-humic complexation ($\beta_{1:An^{m+}}$) are calculated assuming an ionic strength of 1 M instead of 6 M (Section 5.1).
- The stability constant of 1000 for Ca/Mg-humic complexation ($\beta_{1:Ca^{2+}}$) is likely conservative (Section 4.2.1).
- There is no competition among different actinides for humic complexation sites.

Because the recommended values for PHUMSIM and PHUMCIM are expected to be conservative, distributions for these parameters are not determined.

The recommended PHUMSIM and PHUMCIM values depend not only on the available humic complexation data and assumptions described in this report, they also depend on the equilibrated WIPP brine compositions and free An^{3+}, Ca^{2+}, and Mg^{2+} concentrations calculated using the WIPP thermodynamic database. If the calculated brine compositions or the reactions of relevant species in the thermodynamic database change significantly from those used in Domski and Xiong (2015), the PHUMSIM and PHUMCIM values calculated in this report may require updating.

6 CONCLUSIONS

In accordance with the Analysis Plan for the Evaluation of Humic-Actinide Complexation of WIPP Conditions, AP 167, Rev. 0 (Mariner 2014), an analysis of the humic complexation of An(III) (i.e., trivalent actinides) in WIPP brines was performed. A literature search of humic complexation studies of trivalent metals (e.g., rare earth metals, Am), Ca, and different humic substances was used to evaluate and update the process model for predicting An(III)-humic complexation in WIPP brines. This report summarizes key findings, modifications to the process model, and revised calculations of inputs to the abstraction model used in PA. All calculations in this report are stored on the CVS (Concurrent Versioning System) in /nfs/data/CVSLIB/WIPP_EXTERNAL/ap167/Files.

PHUMSIM and PHUMCIM are proportionality constants in the WIPP PA humic colloid abstraction model. They represent the equilibrium aqueous ratios of the humic-bound actinide concentration to the non-colloidal actinide concentration for Salado and Castile formation brines, respectively. The nominal legacy values for these parameters for An(III) are 0.19 and 1.37, respectively.

PHUMSIM and PHUMCIM calculated using the updated process model are 30 and 80, respectively. These values are much higher than legacy values primarily because the effects of high pH on An(III)-humic complexation were not included in the original model. With the revised values, much higher An(III)-humic complexation is predicted at low loading compared to legacy WIPP PA calculations. Importantly, however, low loadings correspond with low total mobile An(III) concentrations. At high An(III) loadings, An(III) mobility remains unchanged because humic-bound An(III) concentrations continue to be limited by the maximum concentration of aqueous humic complexation sites, which is set at 1.1×10^{-5} M.

No uncertainty distributions are provided for the new PHUMSIM and PHUMCIM calculations. There are insufficient data upon which to quantify uncertainty in these values. Regardless, these calculations are expected to be conservative. Stability constants for the process model were calculated conservatively assuming 1 M ionic strength instead of 6 M (Section 5.1). The stability constant for Ca/Mg-humic complexation was conservatively set at 1000, though significantly higher complexation is likely (Section 4.2.1). Additionally, it is conservatively assumed in the process model that there is no competition among different actinides for humic complexation sites. However, the largest conservatism may be that humic colloids are assumed to be stable in WIPP brines in the presence of MgO. The work of Wall and Mathews (2005) indicates that humic colloids may be unstable under these conditions. Lab work similar to that of Wall and Mathews (2005), but employing lower detections limits, may show that humic colloids do not persist in significant concentrations in WIPP brines in the presence of MgO.

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