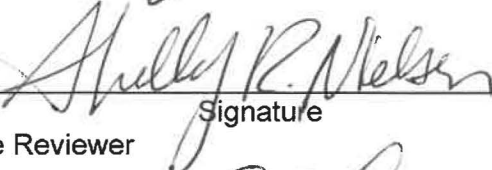# SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

AP-167
Revision 0

Analysis Plan for the Evaluation of Humic-Actinide Complexation for WIPP Conditions

Task 4.4.2.2.1

Effective Date: August 6, 2014

Authored by:	Paul E. Mariner	*Rel...*		8/6/2014
	Print Name	Signature		Date
Reviewed by:	Larry H. Brush	*Shelly R. Nielsen for*		8-6-14
	Print Name	Signature		Date
	Technical Reviewer			
Reviewed by:	Shelly R. Nielsen	*Shelly R. Nielsen*		8-6-14
	Print Name	Signature		Date
	Quality Assurance Reviewer			
Approved by:	Christi D. Leigh			8-6-14
	Print Name	Signature		Date
	Department Manager			

Table of Contents

1   Introduction and Objectives

1.1   Introduction

Humic colloids contribute substantially to calculated actinide releases in WIPP performance assessment (PA) calculations. They account for major contributions to the total mobile concentrations of Th, Pu, and Am in brine release scenarios (Mariner and Sassani 2014, Section 4.3 and Table 5-3).

The humic colloids model has not changed from its original version used in the Compliance Certification Application (CCA) (DOE 1996, SOTERM.6.3.3). At low values of dissolved actinide concentrations, the actinide concentration associated with humic substances is assumed to be proportional to the dissolved concentration and is calculated by multiplying the total dissolved actinide concentration by the PHUMSIM proportionality constant for the Salado Formation (Fm.) brine or by PHUMCIM for the Castile Fm. brine. If this product exceeds the maximum actinide concentration allowed to be bound to humic colloids, defined by the CAPHUM parameter, then the CAPHUM value is used in place of the product. The established value for CAPHUM is 1.1×10^{-5} M and is based on a site-binding capacity of 5.56 meq g^{-1}. The humic colloid concentration is assumed to be 2.0 mg L^{-1}.

Since the CCA, experimental work by Wall and Mathews (2005) on the stability of humic acids in 95% Salado and Castile formation brine simulants showed that humic acid concentrations will decrease below detection (< ~2 mg L^{-1}) within 60 days of MgO addition. If realistic humic colloid concentrations under WIPP conditions are significantly lower than the assumed concentration of 2 mg L^{-1}, then the concentration of humic colloids used in the WIPP PA is conservative. To confirm that a decrease in the humic colloid concentration is appropriate, definitive data are needed from studies that include fulvic acids and lower detection limits (around 0.1 mg L^{-1} or lower). Such work is under consideration for the future.

In addition to the likely conservative representation of humic colloid stability in the WIPP PA, the representation of complexation of actinides with humic substances may also be conservative. The humic-actinide stability constants ($\beta_{1:An}$) used in the WIPP model to calculate the PHUMSIM and PHUMCIM values for An(III) and An(VI) are based on observations in concentrated NaCl solutions at pH 6 (DOE 1996, Section SOTERM.6.3.3.1). Cations that form stable negatively-charged carbonate species at high pH often exhibit reduced humic complexation at pH values above 7 to 8 in the presence of carbonate (e.g., Pourret et al. 2007, Figure 8). In addition, the calculation of PHUMSIM and PHUMCIM uses the products of the stability constants and total actinide concentrations instead of the products of the stability constants and free actinide cation concentrations. For actinides with free cation concentrations that are much lower than the total actinide concentrations, the resulting PHUMSIM and PHUMCIM values will be overestimated.

This analysis plan directs the recalculation of PHUMSIM and PHUMCIM values based on an updated literature review of available humic complexation data studies and a reevaluation of the derivation and application of PHUMSIM and PHUMCIM. Because the PHUMSIM and PHUMCIM parameter values are used in performance assessment, this is a compliance decision analysis.

1.2   Objectives

The objectives of this work are (1) to evaluate the humic-actinide complexation model used to derive PHUMSIM and PHUMCIM for the WIPP PA based on knowledge gained from recent publications, reports, and analyses, and (2) to calculate updated values for PHUMSIM and PHUMCIM based on the results of the evaluation.

2   Approach

2.1   Calculation of PHUMSIM and PHUMCIM

The values of PHUMSIM and PHUMCIM for the WIPP humic colloids model as calculated for the CCA are shown in Table 1.

Table 1. PHUMSIM and PHUMCIM values for the CCA and subsequent WIPP PA calculations (DOE 1996, Appendix SOTERM, Table SOTERM-14).

Actinide Oxidation State	Actinides	PHUMSIM (Salado Fm. Brine)	PHUMCIM (Castile Fm. Brine)
An(III)	Pu(III) Am(III)	0.19	1.37[a]
An(IV)	Th(IV) U(IV) Np(IV) Pu(IV)	6.3	6.3
An(V)	Np(V)	9.1×10^{-4}	7.4×10^{-3}
An(VI)	U(VI)	0.12	0.51

[a] A cumulative distribution from 0.065 to 1.6 with a mean value of 1.1 was used.

The brine of the Salado Formation is represented by the Generic Weep Brine (GWB) and is based on fluids collected near the repository horizon (Krumhansl et al. 1991; Snider 2003). The brine of the Castile Formation is represented by the Energy Research and Development Administration well 6 (ERDA-6) brine (Popielak et al. 1983).

Two approaches were used to calculate PHUMSIM and PHUMCIM for the CCA. For actinides at the IV oxidation state (i.e., Th(IV), U(IV), Np(IV), and Pu(IV)), a single value of 6.3 was calculated based on the colloidal partitioning of Th(IV) in seawater reported in Baskaran et al. (1992) and an assumed humic substance concentration in seawater of 2.0 mg L^{-1} (DOE 1996, SOTERM.6.3.3.1). For all other actinide oxidation states, a model was developed based on binary complexation data involving isolated humic substances. This latter approach produced an analytical model that includes actinide-humic complexation reactions and the competition for complexation sites by dissolved calcium (Ca^{2+}) and magnesium (Mg^{2+}) as summarized in the derivation below.

The complexation of a dissolved actinide species (An^{m+}) with an available humic substance complexation site (HS^-) is described by the chemical reaction

$$An^{m+} + mHS^- \Leftrightarrow AnHS_m \qquad \text{(Eq. 1)}$$

where $AnHS_m$ is the actinide-humic substance complex. The stability constant ($\beta_{m:An}$) for this chemical reaction is represented by

$$\beta_{m:An} = \frac{[AnHS_m]}{[An^{m+}][HS^-]^m} \qquad \text{(Eq. 2)}$$

where brackets denote the equilibrium concentration of the species. For the CCA, $\beta_{m:An}$ values were determined for each actinide having oxidation states of III, V, and VI. Values for the III and VI oxidation states were derived from laboratory experiments conducted at Florida State University (Choppin et al. 1999). For the V oxidation state, a stability constant of $10^{3.67}$ reported for Np(V) and Gorleben humic acid in a pH 9 solution was used (Kim and Sekine 1991).

Ca^{2+} and Mg^{2+} and their affinity for humic complexation sites act to reduce the humic-bound concentrations of actinides. The calculation of PHUMSIM and PHUMCIM for actinides at the III, V, and VI oxidation states accounts for this effect by including terms for humic-bound calcium and magnesium in the calculation of $[HS^-]$. The model also assumes that (1) the concentration of An^{m+} is equal to the total dissolved non-colloidal concentration of An, (2) the combined total dissolved concentrations of Ca and Mg is equal to the combined concentrations of Ca^{2+} and Mg^{2+}, and (3) only 1:1 binding of An^{m+} and HS^- occurs (i.e., m is effectively assumed to be 1). These assumptions result in the following equation in the CCA for the concentration of HS^- (DOE 1996, Equation 6-20):

$$[HS^-] = \frac{[HS_{tot}]}{\beta_{1:An}[An] + \beta_{1:CaMg}[Ca + Mg] + 1} \qquad \text{(Eq. 3)}$$

$\beta_{1:CaMg}$ is the combined stability constant for the humic complexation of Ca^{2+} and Mg^{2+}, $[Ca + Mg]$ is the sum of the dissolved Ca and Mg concentrations, $[HS_{tot}]$ is the total concentration of humic complexation sites, and $[An]$ is the total dissolved non-colloidal concentration of actinide.

In the CCA the log value for $\beta_{1:CaMg}$ was set to 2.0 based on literature values from experiments investigating complexation of Ca^{2+} and Mg^{2+} with humic and fulvic acids under acidic conditions in low-ionic-strength solutions (DOE 1996, SOTERM.6.3.3.1). The values for $[Ca + Mg]$ were taken from representative Salado Fm. and Castile Fm. brine compositions, 0.542 M and 0.0576 M, respectively (Papenguth 1996, Tables 1a and 1b).

The values used for $\beta_{1:An}$ and $[HS_{tot}]$ in Eq. 3 were determined from experiments using Lake Bradford humic acid (HAal-LBr), Gorleben humic acid (HAal-Gor), and Suwannee River fulvic acid (FA-Suw) (Choppin et al. 1999). These experiments involved Am(III) and U(VI) in NaCl solutions of 3 and 6 molal. The pH values of these experiments were fixed in the acidic range at either 4.8 or 6 to maximize actinide complexation. Data from the 6 molal NaCl solutions at pH 6 were used in the derivation of the PHUMSIM and PHUMCIM proportionality constants. The site binding capacities of these humic substances were determined to be 4.65, 5.38, and 5.56 meq g^{-1}, respectively. The concentration of humic substances in the Salado Fm. and Castile Fm. brines

was set at the upper value (2.0 mg L^{-1}) of the solubility range observed in systems containing Ca^{2+} and Mg^{2+} at concentrations of at least 10 mM (DOE 1996, SOTERM.6.3.3.1). Multiplying this value by the site binding capacities gives the following values for [HS$_{tot}$]: 9.3×10^{-6} M (HAal-LBr), 1.1×10^{-5} M (HAal-Gor), and 1.1×10^{-5} M (FA-Suw).

Table 2 shows the values of $\beta_{1:An}$ and [An] used in the derivation of the PHUMSIM and PHUMCIM values. The concentration of [AnHS] in Table 2 is calculated by solving Eq. 2 for [HS$^-$], substituting the result into Eq. 3, and solving for [AnHS]. This gives the following expression for [AnHS] (Mariner and Sassani 2014, Section 4.2.3):

$$[AnHS] = \frac{\beta_{1:An}[An][HS_{tot}]}{\beta_{1:An}[An] + \beta_{1:CaMg}[Ca + Mg] + 1} \qquad \text{(Eq. 4)}$$

This expression, which conservatively assumes that actinide species are monovalent and that there is no competition between actinides for binding sites, is used to calculate the [AnHS] values shown in Table 2. The values in this table for [An] are those assumed in the CCA for the brines in the Salado and Castile formations in the presence of MgO backfill (Papenguth 1996, Tables 1a and 1b).

The PHUMSIM and PHUMCIM values in Table 1 for actinides at the III, V, and VI oxidation states were obtained by selecting the highest (most conservative) values of [AnHS]/[An] in Table 2. Only the III oxidation state in the Castile brine was defined as a distribution.

Table 2. Calculated values of humic-bound actinide concentrations [AnHS] and proportionality constants (i.e., PHUMSIM and PHUMCIM) for U(VI), Np(V), and Am(III). Inputs from Papenguth (1996, Tables 1a, 1b, and 3). Table from Mariner and Sassani (2014).

Brine	Actinide	[An] (M)	Humic Substance	[HS$_{tot}$] (M)	log $\beta_{1:An}$	[AnHS] (M)	[AnHS]/[An]
Salado	U(VI)	1.00×10^{-5}	HAal-LBr	9.3×10^{-6}	5.91	1.2×10^{-6}	0.12
			HAal-Gor	1.1×10^{-5}	5.35	4.2×10^{-7}	0.042
			FA-Suw	1.1×10^{-5}	4.60	8.0×10^{-8}	0.0080
	Np(V)	2.64×10^{-6}	HAal-Gor	1.1×10^{-5}	3.67	2.4×10^{-9}	9.1×10^{-4}
	Am(III)	4.39×10^{-6}	HAal-LBr	9.3×10^{-6}	6.09	8.3×10^{-7}	0.19
			HAal-Gor	1.1×10^{-5}	6.02	8.3×10^{-7}	0.19
			FA-Suw	1.1×10^{-5}	4.60	3.5×10^{-8}	0.0080
Castile	U(VI)	1.00×10^{-5}	HAal-LBr	9.3×10^{-6}	5.91	5.1×10^{-6}	0.51
			HAal-Gor	1.1×10^{-5}	5.35	2.7×10^{-6}	0.27
			FA-Suw	1.1×10^{-5}	4.60	6.2×10^{-7}	0.062
	Np(V)	2.53×10^{-6}	HAal-Gor	1.1×10^{-5}	3.67	1.9×10^{-8}	7.4×10^{-3}
	Am(III)	4.12×10^{-7}	HAal-LBr	9.3×10^{-6}	6.09	6.5×10^{-7}	1.6
			HAal-Gor	1.1×10^{-5}	6.02	6.5×10^{-7}	1.6
			FA-Suw	1.1×10^{-5}	4.60	2.7×10^{-8}	0.065

2.2 Data Analysis

Data analysis for this AP will focus on the derivation of PHUMSIM and PHUMCIM and the data used to calculate the values for these two parameters for each actinide species. A literature review will be performed to gather published data and modeling relevant to PHUMSIM and PHUMCIM. This information will be used to evaluate and improve the complexation equations used to calculate PHUMSIM and PHUMCIM as needed. New data will be evaluated with previous data to identify the most relevant data for the PHUMSIM and PHUMCIM calculations. Based on these analyses, new PHUMSIM and PHUMCIM constants will be calculated.

3 Software List

The following computer code may be used for different tasks associated with this Analysis Plan:

- EQ3/6 version 8.0a, qualified under NP 19-1 for execution on platforms with Microsoft Windows 95, 98, 2000, NT4, XP, Vista, and Window 7 (Wolery and Jarek 2003; Wolery 2008; Wolery et al. 2010; Xiong 2011). Paul Domski will be the run master if this software is used for any calculations.

Commercial off-the-shelf spreadsheet programs, such as Excel, may also be used for calculations, data manipulation, and plotting.

4 Tasks

There are four tasks associated with this AP. The analyst for these tasks is Paul Mariner. All tasks associated with this AP are planned for completion by December 31, 2014.

4.1 Task 1 – Literature Review

Since the CCA in 1996, the study of humic-complexation with actinides and rare earth elements (REEs) has continued, as evidenced by a number of publications in the scientific literature. Two models that appear to be particularly popular are the Humic Ion Binding Model VI (Model VI) advanced by Tipping (1998) and the NICA-Donnan model advanced by Kinniburgh et al. (1996). In addition, many studies have been published in the past 18 years that include humic-complexation data for various actinides and REEs in aqueous solutions of various compositions. These studies include some of the work performed at FSU on humic-actinide complexation in high ionic strength solutions.

Task 1 will involve a review of the scientific literature for studies relevant to the prediction of humic complexation in WIPP PA brine release scenarios. This review will focus on new developments in the modeling of humic complexation and on identifying new humic complexation data that may be relevant.

4.2 Task 2 – Evaluation of PHUMSIM and PHUMCIM Model Equations

For Task 2, the model equations used to calculate PHUMSIM and PHUMCIM will be revisited to determine whether they should be improved. As shown in Section 2.1, the model equations

include the effects of dissolved calcium and magnesium that will compete for complexation sites. In addition, they assume 1:1 binding, no competition between actinides for complexation sites, and the substitution of dissolved concentrations for free ion concentrations. Task 2 will either result in recommended improvements to the model equations used to calculate PHUMSIM and PHUMCIM or confirmation that the existing model equations are sufficient.

4.3   Task 3 – Evaluation of Humic Complexation Data

For Task 3, humic complexation data collected since the CCA will be evaluated together with data used for the CCA to determine whether the humic complexation stability constants used in the calculation of PHUMSIM and PHUMCIM should be updated. This task will involve evaluating the applicability of available humic complexation data to WIPP brine conditions and predicting the effects of pH and ionic strength on stability constants. The result of Task 3 will be recommendations for changes to model stability constants or confirmation that the existing stability constants are sufficient.

4.4   Task 4 – Calculation of PHUMSIM and PHUMCIM

For Task 4, new values for PHUMSIM and PHUMCIM will be calculated if there are any recommended changes to model equations (Task 2) and/or stability constants (Task 3). All recommended changes will be implemented in the calculations, and the resulting PHUMSIM and PHUMCIM values for each actinide species will be determined. As part of Task 4, the effects of the new values on total mobile actinide concentrations will be assessed using CRA-2014 baseline actinide solubilities.

5   Special Considerations

No special considerations have been identified.

6   Applicable Procedures

All applicable WIPP quality-assurance procedures will be followed when conducting these analyses. Training of personnel will be done in accordance with the requirements of NP 2-1, *Qualification and Training*. Analyses will be performed and documented in accordance with the requirements of NP 9-1, *Analyses* and NP 20-2, *Scientific Notebooks*. All software used will meet the requirements of NP 19-1, *Software Requirements* and NP 9-1, as applicable. The analyses will be reviewed following NP 6-1, *Document Review Process*. All required records will be submitted to the WIPP Records Center in accordance with NP 17-1, *Records*.

7   References

Baskaran, M., P. H. Santschi, G. Benoit, and B. D. Honeyman 1992. "Scavenging of thorium isotopes by colloids in seawater of the Gulf of Mexico." *Geochimica et Cosmochimica Acta*. 56(9):3375-3388.

Choppin, G. R., A. H. Bond, M. Borkowski, M. G. Bronikowski, J. F. Chen, S. Lis, J. Mizera, O. Pokrovsky, N. A. Wall, Y. X. Xia, and R. C. Moore 1999. *Waste Isolation Pilot Plant Actinide Source Term Test Program: Solubility Studies and Development of Modeling Parameters*. SAND99-0943. Sandia National Laboratories, Carlsbad, New Mexico.

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, NM.

Kim, J. L., and T. Sekine 1991. "Complexation of neptunium(V) with humic acid." *Radiochimica Acta*. 55(4):187-192.

Kinniburgh, D. G., C. J. Milne, M. F. Benedetti, J. P. Pinheiro, J. Filius, L. K. Koopal, and W. H. VanRiemsdijk 1996. "Metal ion binding by humic acid: Application of the NICA-Donnan model." *Environmental Science & Technology*. 30(5):1687-1698.

Krumhansl, J. L., K. M. Kimball, and C. L. Stein 1991. *Intergranular Fluid Compositions from the Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico*. SAND90-0584. Sandia National Laboratories, Albuquerque, New Mexico.

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.

Papenguth, H. W. 1996. *H.W. Papenguth to Christine T. Stockman: " Parameter Record Package for Colloidal Actinide Source Term Parameters" May 7, 1996: Attachment A: Rationale for Definition of Parameter Values for Humic Substances"*. Sandia National Laboratories, Carlsbad, New Mexico. ERMS 235850.

Popielak, R. S., R. L. Beauheim, S. R. Black, W. E. Coons, C. T. Ellingson, and R. L. Olsen 1983. *Brine Reservoirs in the Castile Formation, Waste Isolation Pilot Plant Project, Southeastern New Mexico*. TME 3153. Sandia National Laboratories, Carlsbad, New Mexico.

Pourret, O., M. Davranche, G. Gruau, and A. Dia 2007. "Rare earth elements complexation with humic acid." *Chemical Geology*. 243(1-2):128-141.

Snider, A. C. 2003. *Verification of the definition of Generic Weep Brine and the development of a recipe for this brine*. ERMS 527505. Sandia National Laboratories, Calrsbad, New Mexico.

Tipping, E. 1998. "Humic ion-binding model VI: An improved description of the interactions of protons and metal ions with humic substances." *Aquatic Geochemistry*. 4(1):3-48.

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

Wolery, T. W. 2008. *Analysis plan for EQ3/6 analytical studies*. AP-140, Rev. 0. Sandia National Laboratories, Carlsbad, New Mexico. ERMS 548930.

Wolery, T. W., and R. L. Jarek 2003. *Software User's Manual EQ3/6, Version 8.0*. Civilian Radioactive Waste Management System Management & Operations, Albuquerque, New Mexico.

Wolery, T. W., Y. L. Xiong, and J. J. Long 2010. *Verification and validation plan/validation document for EQ3/6 version 8.0a for actinide chemistry, document version 8.10*. Sandia National Laboratories, Carlsbad, New Mexico. ERMS 550239.

Xiong, Y. L. 2011. *WIPP verification and validation plan/validation document for EQ3/6 version 8.0a for actinide chemistry, revision 1. Supersedes ERMS 550239*. Sandia National Laboratories, Carlsbad, New Mexico. ERMS 555358.

This work of authorship was prepared as an account of work sponsored by an agency of the United States Government. Accordingly, the United States Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so for United States Government purposes. Neither Sandia Corporation, the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately-owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by Sandia Corporation, the United States Government, or any agency thereof. The views and opinions expressed herein do not necessarily state or reflect those of Sandia Corporation, the United States Government or any agency thereof.

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Parties are allowed to download copies at no cost for internal use within your organization only provided that any copies made are true and accurate. Copies must include a statement acknowledging Sandia Corporation's authorship of the subject matter.