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Reevaluation of Actinide(IV)-Humic Complexation in the WIPP Performance Assessment

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ABSTRACT

The legacy humic colloid model for tetravalent actinides (Th(IV), U(IV), Np(IV), and Pu(IV)) in the performance assessment (PA) of the Waste Isolation Pilot Plant (WIPP) is highly conservative. The model structure is feasible, but substantial reductions are needed for two constants, PHUMSIM and PHUMCIM, that represent the equilibrium aqueous concentration ratio of humic-bound An(IV) to non-colloidal An(IV) for the Salado and Castile formations. In the WIPP PA model, both constants are set at 6.3 based on observed colloidal partitioning of Th(IV) in seawater. Humic partitioning in WIPP brines is expected to be significantly lower than in seawater because the pH of WIPP brines (~9) is higher, concentrations of competing cations (e.g., Mg^{2+}) are higher, and concentrations of aqueous humic substances may be lower.

In this work, competitive humic complexation is simulated under WIPP conditions. The resulting PHUMSIM and PHUMCIM values are calculated to be well below 0.01. These values would reduce mobile An(IV) concentrations in the WIPP PA by as much as 85%.

INTRODUCTION

In the current performance assessment (PA) of the Waste Isolation Pilot Plant (WIPP), humic colloids are substantial contributors to the mobility of tetravalent actinides, An(IV) (i.e., Pu(IV), Th(IV), Np(IV), and U(IV)).[1] An(IV)-humic complexation is currently based on Baskaran et al. (1992) which reported concentrations of colloidal and non-colloidal Th(IV) in seawater.[2, 3] Assuming analogous behavior in WIPP brines, a proportionality constantsof 6.3 was adopted. This constant in the WIPP PA is known as PHUMSIM for brine from the Salado formation and PHUMCIM for brine from the Castile formation.

The legacy 6.3 proportionality constant is highly conservative.:

1. Aqueous humic substances may be unstable under WIPP conditions;[4]
2. The brines in the repository are expected to be more alkaline than seawater, [6] and
3. Mg^{2+} from the MgO buffer will strongly compete with actinides for humic complexation sites.

Since the mid-1990s when the original humic colloids model was developed, a number of studies of An(IV)-humic complexation have been published.[5, 7-12] These studies examine complexation over a broad range of pH and include laboratory measurements of humic complexation with Th(IV), Pu(IV), and U(IV). In addition, studies of the humic complexation of Ca and Mg over broad ranges of pH and salinity have been published.[13, 14] These studies were used in this work to assess Th(IV)-humic complexation for WIPP conditions. This work is documented in detail in Mariner (2016).[15]

MODEL

The WIPP humic colloids model calculates the aqueous humic-bound actinide concentration $(AnHs)$ from the non-colloidal aqueous concentration (An) and a proportionality constant H:

$$(\mathrm{AnHs}) = H(\mathrm{An})$$

The proportionality constant H is PHUMSIM or PHUMCIM in the WIPP PA.[3] To calculate the "mobile" actinide concentration in the WIPP PA, $(AnHs)$ is added to (An) and to the concentrations of actinides in other colloids (intrinsic, microbial, and mineral fragment).

A conservative assumption of the WIPP PA 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.[6] Solubility can vary broadly due to the broad ranges of solubility measurements reported in the literature.

In this work, humic complexation is simulated using a traditional model.[15] Actinide-humic complexation is described by the reaction:

$$\mathrm{An}^{m+} + \mathrm{Hs}^{-} \Leftrightarrow \mathrm{AnHs}$$

where An^{m+} is the free actinide species (e.g., Th^{4+}) and Hs^{-} is an available humic substance complexation site. The conditional stability constant ($\beta_{1:\mathrm{An}^{m+}}$) for this reaction is represented by the following equation:

$$\beta_{1:\mathrm{An}^{m+}} = \frac{(\mathrm{AnHs})}{(\mathrm{An}^{m+})(\mathrm{Hs}^{-})}$$

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. This approach is acceptable when stability parameters such as $\beta_{1:\mathrm{An}^{m+}}$ are conditional.[8]

The calculation of $(AnHs)$ accounts for competition by Ca^{2+} and Mg^{2+} and assumes that Ca^{2+} and Mg^{2+} behave similarly:

$$(\mathrm{AnHs}) = \frac{\beta_{1:\mathrm{An}^{m+}}(\mathrm{An}^{m+})(\mathrm{Hs}_{\mathrm{tot}})}{\beta_{1:\mathrm{An}^{m+}}(\mathrm{An}^{m+}) + \beta_{1:\mathrm{Ca}^{2+}}[(\mathrm{Ca}^{2+}) + (\mathrm{Mg}^{2+})] + 1}$$

METHODS

Databases

The non-humic reaction database used in this analysis are shown in TABLE I. The humic reactions adopted (HsH), conservatively assumed (CaHs+ and MgHs+), or fitted (ThHs+) for this analysis are shown in TABLE II.

TABLE I. Th(IV)-Ca-Mg-EDTA-CO_2-H_2O reaction database.

Reaction	Log K (0 M) DATA0.FM2 [17]	Log K (0.1 M) for DATA0.FM2	Log K (0.1 M) Stern et al. (2014) [12]
$H_2O = OH^- + H^+$	-13.9967	-14.0	nr[a]
$HCO_3^- = CO_3^{2-} + H^+$	-10.3392	-10.0	nr
$HCO_3^- + H^+ = CO_2(aq) + H_2O$	6.3374	6.22	nr
$HCO_3^- + H^+ = CO_2(g) + H_2O$	7.8193	7.71	nr
$Th^{4+} + 4 H_2O = Th(OH)_4 + 4 H^+$	-17.5002	-19.2	-18.3
$Th^{4+} + 3 H_2O = Th(OH)_3^+ + 3 H^+$	na[b]	na	-12.7
$Th^{4+} + 2 H_2O = Th(OH)_2^{2+} + 2 H^+$	na	na	-7.7
$Th^{4+} + H_2O = ThOH^{3+} + H^+$	na	na	-2.8
$H^+ + Edta^{4-} = HEdta^{3-}$	10.5707	9.82	10.24
$2 H^+ + Edta^{4-} = H_2Edta^{2-}$	17.4500	16.2	16.25
$3 H^+ + Edta^{4-} = H_3Edta^-$	20.5374	18.9	19.05
$4 H^+ + Edta^{4-} = H_4Edta$	23.0393	21.3	21.54
$Th^{4+} + Edta^{4-} = ThEdta$	23.5570	20.1	23.19
$Th^{4+} + HEdta^{3-} = ThHEdta^+$	na	na	17.00
$Ca^{2+} + Edta^{4-} = CaEdta^{2-}$	11.1562	9.48	nr
$Mg^{2+} + Edta^{4-} = MgEdta^{2-}$	10.1260	8.50	nr
$Th^{4+} + CO_2(g) + 4 H_2O = Th(OH)_3CO_3^- + 5 H^+$	-21.8650	-23.5	-20.36[c]
$Th^{4+} + 5 HCO_3^- = Th(CO_3)_5^{6-} + 5 H^+$	-24.5828	-23.0	nr
$Mg^{2+} + HCO_3^- = MgCO_3(aq) + H^+$	-7.4108	-7.87	nr
$Ca^{2+} + HCO_3^- = CaCO_3(aq) + H^+$	-7.1880	-7.70	nr

[a] nr = not reported; [b] na = not applicable to DATA0.FM2 database; [c] see text
Note: Activities of H^+ and OH^- and molalities of all other species are used in log K values.

TABLE II. Th(IV)-Ca-Mg-Hs-H_2O reaction database.

Reaction	Log β (0.1 M)	Source
$Hs^- + H^+ = HsH$	4.3	Stern et al. (2014) [12]
$Ca^{2+} + Hs^- = CaHs^+$ $Mg^{2+} + Hs^- = MgHs^+$	3.0	Based on [13, 14, 19]
$Th^{4+} + Hs^- = ThHs^{3+}$	21.6 (pH 8.8) 22.3 (pH 9)	Fit to Stern et al. (2014) [12] model (Fig. 1)

Derivation of $ThHs^+$ Stability Constants

The $ThHs^+$ stability constants in TABLE II were calculated using a four-step process:

1. Reproduce the Th(IV)-humic-EDTA-CO_2-H_2O system of Stern et al. (2014) [12] using PHREEQC version 3.1.7.[18]
2. Remove CO_2 from the Stern et al. (2014) [12] system.
3. Calculate proportionality coefficient H over pH range.
4. Derive log $\beta_{1:Th^{4+}}$ values vs. pH for DATA.FM2 database by fitting to observed H values.

Application to WIPP Brines

With the complete set of reactions in TABLES I and II, PHREEQC was used to predict humic complexation in the WIPP brines of Brush and Domski (2013) whose compositions are shown in TABLE III.[6] The results were used to provide new estimates for proportionality constants PHUMSIM and PHUMCIM.

TABLE III. Compositions (mole L^{-1}) of GWB and ERDA-6 predicted by Brush and Domski (2013) in the repository.[6]

Element or Property	Units	GWB (1 × Min[a])	GWB (5 × Min)	ERDA-6 (1 × Min)	ERDA-6 (5 × Min)
Na(I) (aq)	M	4.77	4.78	5.30	5.33
Mg(II) (aq)	M	0.330	0.313	0.136	0.111
K(I) (aq)	M	0.550	0.549	0.0960	0.0960
Ca(II) (aq)	M	0.0111	0.0113	0.0116	0.0119
S(VI) (aq)	M	0.216	0.205	0.182	0.171
Cl(-I) (aq)	M	5.36	5.39	5.24	5.26
CO_2 fugacity	atm	3.14×10^{-6}	3.14×10^{-6}	3.14×10^{-6}	3.14×10^{-6}
Ionic strength	M	6.44	6.41	5.99	5.94
pcH[b]	-log(M)	9.54	9.54	9.69	9.72
pH[c]	-log(M)	8.82	8.82	8.99	9.02
Total inorganic carbon	M	3.79×10^{-4}	3.80×10^{-4}	4.55×10^{-4}	4.75×10^{-4}
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}
Th(IV)	M	6.05×10^{-8}	6.07×10^{-8}	7.02×10^{-8}	7.20×10^{-8}
Th^{4+}	M	3.45×10^{-25}	3.01×10^{-25}	1.26×10^{-25}	8.53×10^{-26}
Activity coeff. of Th^{4+} [d]	-	$10^{-0.1278}$	$10^{-0.0708}$	$10^{-0.3785}$	$10^{-0.3343}$

[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_1x.6o, gwb_5x.6o, erda_1xb.6o, and erda_5xb.6o EQ6 output files of [6]

RESULTS

Four-Step Calculation of Th-Humic Stability Constants for DATA.FM2

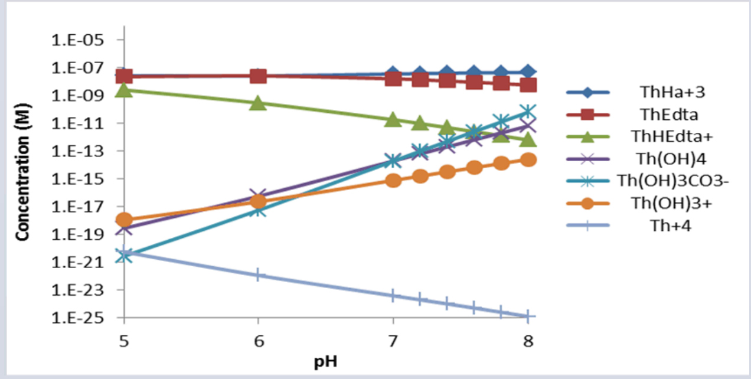

Fig. 1. Reproduction of Stern et al. (2014) [12]

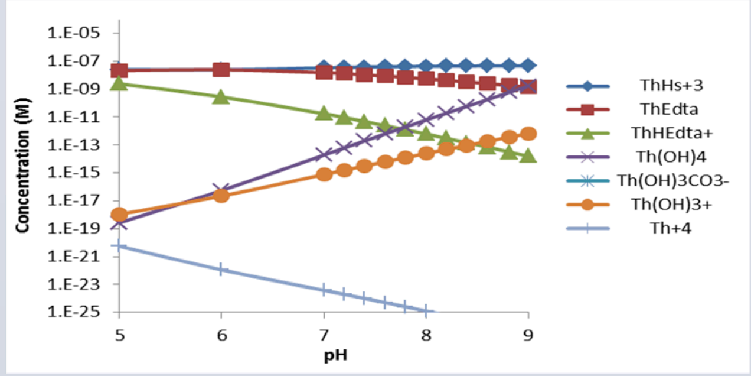

Fig. 2. Simulation of Stern et al. (2014) [12] in the absence of CO_2

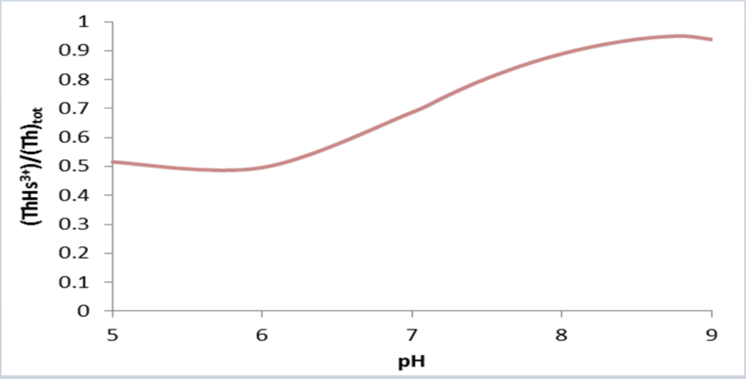

Fig. 3. Calculated proportionality constants for Step 2 results

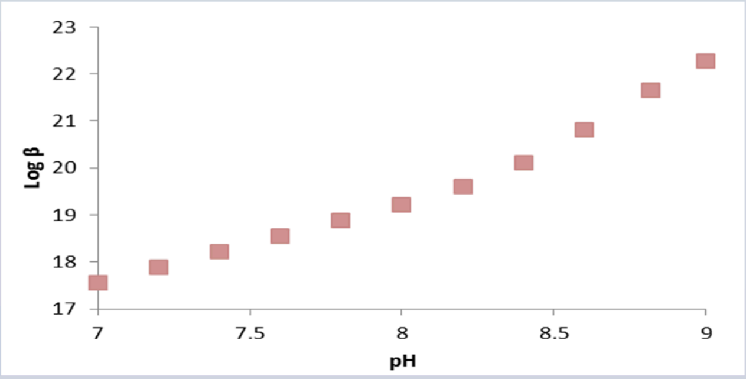

Fig. 4. Derived log $\beta_{1:Th^{4+}}$ values for DATA.FM2 database

Application to WIPP Brines

The databases of TABLES I and II were applied to the WIPP brines of TABLE III. The results are shown in TABLES IV and V.

TABLE IV. Predicted concentrations (mole L^{-1}) for WIPP PA.

Parameter	GWB (1 × Min)	GWB (5 × Min)	ERDA-6 (1 × Min)	ERDA-6 (5 × Min)
(Th)[a]	6.05×10^{-8}	6.07×10^{-8}	7.02×10^{-8}	7.20×10^{-8}
(Th^{4+})[a]	3.45×10^{-25}	3.01×10^{-25}	1.26×10^{-25}	8.53×10^{-26}
(Hs_{tot})	1.10×10^{-5}	1.10×10^{-5}	1.10×10^{-5}	1.10×10^{-5}
(Ca^{2+})[b]	0.010	0.010	0.011	0.011
(Mg^{2+})[b]	0.323	0.303	0.131	0.111
(Hs^-)	3.29×10^{-8}	3.50×10^{-8}	7.69×10^{-8}	8.94×10^{-8}
(CaHs)+(MgHs)	1.10×10^{-5}	1.10×10^{-5}	1.09×10^{-5}	1.09×10^{-5}
$(ThHs^+)$	8.38×10^{-11}	7.23×10^{-11}	4.20×10^{-10}	3.63×10^{-10}

[a] [6]
[b] From gwb_1x.6o, gwb_5x.6o, erda_1xb.6o and erda_5xb.6o EQ6 output files of [6]

TABLE V. PHUMSIM and PHUMCIM for Th(IV).

PHUMSIM	PHUMCIM	Source
6.3	6.3	DOE (1996) [3]
0.0016 (1 x Min[a]) **0.0013 (5 x Min)**	0.0056 (1 x Min) 0.0047 (5 x Min)	This work

[a] Min = minimum brine volume for a DBR from the repository

CONCLUSIONS

The ranges of Th(IV) PHUMSIM and PHUMCIM calculated in this work for the direct brine release scenario are 0.0013 to 0.0016 and 0.0047 to 0.0056, respectively. (TABLE V) These values are much lower than the legacy 6.3 value because new humic complexation data are available and WIPP conditions are applied. These values are lower because they account for:

1. A higher concentration of Mg^{2+} in WIPP brines compared to seawater (3 to 11 times higher),
2. A higher pH of WIPP brines (~9) compared to seawater (~8), and
3. The effect of a low free Th^{4+} concentration at high pH.

The calculated PHUMSIM and PHUMCIM values may still overestimate Th(IV)-humic complexation because the stability constant adopted for competing Mg-humic complexation likely underestimates the affinity of humic complexation sites for Mg^{2+} at the pH of WIPP brines. In addition, the assumption that humic colloids may be present in WIPP brines at a concentration of 2 mg L^{-1} may be conservative based on possible instability of humic colloids in WIPP brines in the presence of MgO.[4] Regardless, the newly calculated PHUMSIM and PHUMCIM values imply negligible Th(IV)-humic complexation in WIPP brines and would reduce mobile Th(IV) concentrations in the WIPP PA by as much as 85%. Details of this work and recommendations for An(IV) PHUMSIM and PHUMCIM values for future WIPP PA simulations are documented in Mariner (2016).[15]

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