Reevaluation of Actinide(IV)-Humic Complexation in the WIPP Performance Assessment — 16547

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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. These constants are proportionality constants representing 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. This value greatly enhances the mobile An(IV) concentration in the WIPP PA. Actual humic partitioning of An(IV) 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, the results of recent studies of Th(IV)-humic and Ca^{2+}-humic complexation are used to simulate competitive humic complexation under WIPP conditions. The PHUMSIM and PHUMCIM values calculated for these simulations are in the range of 0.0013-0.0016 and 0.0047-0.0056, respectively. These values reduce humic-bound An(IV) to less than 1% of aqueous non-colloidal concentrations and 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] At the time the humic colloid model was developed, there were few published humic complexation data for An(IV) in saline, alkaline waters. Consequently, An(IV)-humic complexation in the WIPP PA model was based on a study by Baskaran et al. (1992) that reported colloidal and non-colloidal Th(IV) concentrations in seawater.[2, 3] Assuming analogous behavior in WIPP brines and a humic colloid concentration of 2 mg L^{-1}, a proportionality constant of 6.3 for the ratio of humic-bound aqueous concentration (AnHs) to non-colloidal aqueous concentration (An) 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 6.3 proportionality constant is highly conservative. For one, aqueous humic substances may be unstable under WIPP conditions;[4] thus, the assumed 2 mg L^{-1} humic colloid concentration in WIPP brines may be much too high. Lower humic colloid concentrations would reduce the fraction of An(IV) bound to humic colloids.[5] Second, whereas the pH of seawater is around 8, the pH of brines in the repository is predicted to be around 9.[6] Increases in pH in the alkaline range

reduce overall An(IV)-humic complexation.[5(Fig.8)] Third, WIPP brines will equilibrate with MgO, a chemical buffer emplaced with the waste. Mg^{2+} will compete with actinides for humic complexation sites and thereby reduce the concentration of humic-bound An(IV). Aqueous Mg^{2+} concentrations in WIPP brines are expected to be 3 to 11 times higher than in seawater.[1]

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 and analysis of U(IV)-humic complexation under WIPP conditions are documented in detail in Mariner (2016).[15]

DESCRIPTION

Humic Complexation Model for WIPP PA

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:

$$(AnHs) = H(An) \qquad\qquad (Eq. 1)$$

The proportionality constant H is called PHUMSIM or PHUMCIM in the WIPP PA.[3] PHUMSIM is used for the Salado brine, represented by GWB (Generic Weep Brine), and PHUMCIM is used for the Castile brine, represented by ERDA-6 (Energy Research and Develop Administration WIPP Well 6). 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) in the direct brine release scenario (DBR) 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 [16] and the DATA0.FM2 [17] Pitzer ion interaction database are used to calculate solubility probabilistically for each brine.[6] Calculated solubility can vary broadly among realizations due to the broad ranges of solubility measurements reported in the literature.

In this work, humic complexation is simulated using a traditional model and recent data from the literature. Actinide-humic complexation is described by the reaction

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

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 ($\beta_{1:An^{m+}}$) for this reaction is represented by

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

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 $\beta_{1:An^{m+}}$ are conditional.[8] This treatment is nearly the same as the model used in the original WIPP model for actinides at the III, V, and VI oxidation states. The main difference is that the model 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 WIPP colloid model for actinides at the III, V, and VI oxidation states accounts for this effect by including terms for humic-bound Ca^{2+} and Mg^{2+} in the calculation of (Hs^-) [3(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

$$(Hs^-) = \frac{(Hs_{tot})}{\beta_{1:An^{m+}}(An^{m+}) + \beta_{1:Ca^{2+}}[(Ca^{2+}) + (Mg^{2+})] + 1} \qquad \text{(Eq. 4)}$$

where $\beta_{1:Ca^{2+}}$ is the stability constant for Ca^{2+}-humic complexation (and Mg^{2+}-humic complexation) and (Hs_{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):

$$(AnHs) = \frac{\beta_{1:An^{m+}}(An^{m+})(Hs_{tot})}{\beta_{1:An^{m+}}(An^{m+}) + \beta_{1:Ca^{2+}}[(Ca^{2+}) + (Mg^{2+})] + 1} \qquad \text{(Eq. 5)}$$

With appropriate values for free ion concentrations and stability constants, PHUMSIM and PHUMCIM can be calculated from Eq. 5 and Eq. 1.

Stability constants for complexation reactions with humic and fulvic acids typically represent equilibrium concentration ratios. Therefore, these constants are conditional not only to pH but also to ionic strength. For the actinide-humic

complexation studies used in this work, reported stability constants are mostly for systems at an ionic strength of 0.1 M (mole L^{-1}) (e.g., 0.1 M NaCl).

TABLE I presents the reactions of the Th-Ca-Mg-EDTA-CO_2-H_2O system relevant to WIPP brines in the absence of humic colloids. The log K values in the first column are from the DATA0.FM2 database [17] of the WIPP PA and are for infinite dilution. These values are converted in the second column to log K values at 0.1 M ionic strength using the Davies equation as implemented in PHREEQC version 3.1.7.[18] The third column lists the log K values provided in Stern et al. (2014) [12], also at 0.1 M ionic strength. EDTA (ethylenediaminetetraacetic acid) is included in this table because EDTA is a reactant in the Stern et al. (2014) laboratory experiments and is assumed prevalent in WIPP PA brines.[6]

The humic complexation reactions are presented in TABLE II. These reactions correspond to the humic acid behavior observed and modeled in Stern et al. (2014).[12] As indicated by the first reaction, the humic complexation site is largely deprotonated above pH 4.3 and therefore does not significantly affect equilibrium calculations in the alkaline pH range. The log value for $\beta_{1:Ca^{2+}}$ was conservatively set to 2.0 in the original WIPP model based on experimental data on humic and fulvic acids.[3] 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+}.[13(Fig. 4), 14(Table 5), 19(Fig. 4b)] 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.[13(Table 3)] As the concentration of Ca^{2+} increases from 10^{-8} M in a 0.1 M NaCl solution [13] to 0.033 M in a 0.033 M $CaCl_2$ solution [19], 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).[14] Compared to $\beta_{1:Th^{4+}}$ the pH dependence of $\beta_{1:Ca^{2+}}$ is weak.[13, 14] 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+}.[19]

The $ThHs^{3+}$ species in TABLE II represents the humic-bound actinide species AnHs of Eq. 2. The associated stability constant is a function of pH and was calculated using a four-step process. This process is described and documented in detail in Mariner (2016).[15] First, PHREEQC was used to reproduce the system presented in Stern et al. (2014) [12] over a pH range of 5 to 8. The results in Figure 5 of Stern et al. (2014) were reproduced almost exactly using the Stern et al. (2014) database without modification. The only difference was that the $Th(OH)_3CO_3^-$ species was overestimated. An excellent match could be obtained by changing the reactant for the $Th(OH)_3CO_3^-$ species from $CO_2(g)$ (as published) to $CO_2(aq)$. Second, the partial pressure of CO_2 was removed from the system to produce analogous results using the Stern et al. (2014) model in the absence of CO_2 and to eliminate the $Th(OH)_3CO_3^-$ issue. In this simulation, the pH range was extended to 9 to include pH values calculated for equilibrated WIPP brines.[6] Third, the proportionality constant H was calculated from the model results in step 2 at multiple pH values from 7 to 9. Fourth, the system was modeled over the pH range

of 7 to 9 using the DATA0.FM2 database with the humic complexation reactions in TABLE II. The log K values in DATA0.FM2 for the $ThHs^{3+}$ complexation reaction was fitted at each pH to the corresponding proportionality constant calculated in step 3. This fitted model was not extended below pH 7 because the DATA0.FM2 database does not include Th hydrolysis products $Th(OH)_3^+$, $Th(OH)_2^{2+}$, and $ThOH^{3+}$, which could become important below pH 7. The fitted log K values in the DATA0.FM2 database use the activity of Th^{4+}. These log K values are converted to stability constants $\beta_{1:Th^{4+}}$ (0.1 M) in TABLE II and Fig. 1.

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.

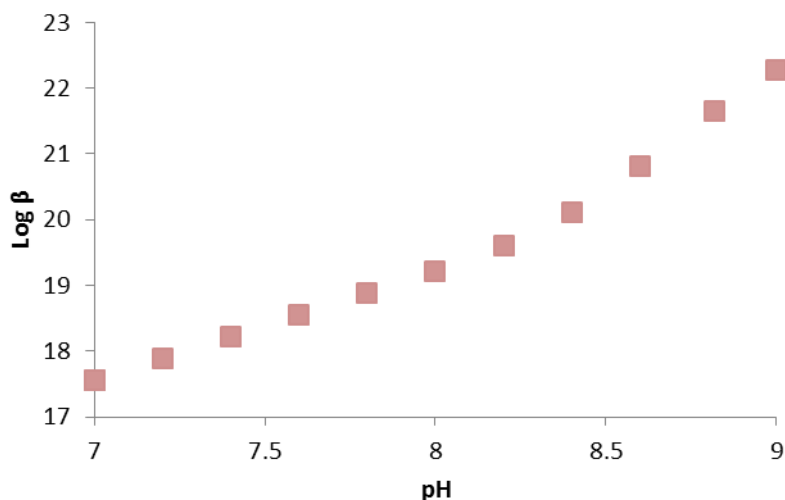| Reaction	Log β (0.1 M)	Source
$Hs^- + H^+ = HsH$	4.3	Stern et al. (2014) [12]
$Ca^{2+} + Hs^- = CaHs^+$ $Mg^{2+} + Hs^- = MgHs^+$	3.0	Based on [13, 14, 19]
$Th^{4+} + Hs^- = ThHs^{3+}$	21.6 (pH 8.8) 22.3 (pH 9)	Fit to Stern et al. (2014) [12] model (Fig. 1)

Fig. 1. Log $\beta_{1:Th^{4+}}$ values (0.1 M) fit to DATA0.FM2 and the Th(IV)-Hs-EDTA-H_2O system of Stern et al. (2014) [12].

DISCUSSION

Application to WIPP Brines

In the WIPP PA, brines are conservatively assumed to contain the expected inventory of acetate, citrate, EDTA, and oxalate.[6] TABLE III gives the predicted compositions in the minimum volume (1 × Min) of GWB and ERDA-6 brine and five times the minimum volume (5 × Min) of brine required for a direct brine release (DBR) from the repository. The ionic strength is around 6 M, much higher than the ionic strength in most humic complexation studies. Such high ionic strength may destabilize humic colloids in the aqueous phase.[4] 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.[3] The site binding capacities of humic substances for the WIPP humic colloids model were determined from experiments using Lake Bradford humic acid, Gorleben humic acid, and Suwannee River fulvic acid.[3] These 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 1.1×10^{-5} M concentration is adopted in this work.

WIPP brines have combined concentrations of Ca^{2+} and Mg^{2+} that are more than 10,000 times greater than the assumed total concentration of humic complexation sites. Because Ca^{2+} and Mg^{2+} bind fairly strongly to humic complexation sites, their high concentrations will cause Ca^{2+} and Mg^{2+} to compete strongly with Th^{4+} for the sites.

Studies show that as the ionic strength of a NaCl solution increases from 0.1 M to 5 M, the complexation of Ca^{2+} with humic acid decreases in the pH range of 8 to 9.[13] However, the log $\beta_{1:Ca^{2+}}$ does not change by more than about one unit in this pH range and remains above 3.0.[13, 19] Because data for Th-humic complexation are not available at ionic strength above 0.1 M, it is assumed for the WIPP PA that the stability constants at 0.1 M ionic strength also apply to high ionic strength. This assumption is expected to be conservative based on the trends discussed in the previous section for Ca-humic complexation. Combined with a conservative log $\beta_{1:Ca^{2+}}$ of 3.0, this assumption is expected to result in conservative overestimation of Th(IV)-humic complexation in WIPP brines.

Concentrations of humic-bound Th(IV) in WIPP brines are calculated by the new model to be less than 1% of total aqueous Th(IV). TABLE IV summarizes the calculations for the four WIPP brines in TABLE III. More than 99% of the humic complexation sites are predicted to be occupied by Ca and Mg. The very low concentration of Th^{4+} ($<10^{-24}$ M) at pH ~9 combined with the low concentration of Hs^- ($<10^{-7}$ M) severely limits the humic-bound Th(IV) concentration. The corresponding PHUMSIM and PHUMCIM values are shown in TABLE V.

CONCLUSIONS

Parameters PHUMSIM and PHUMCIM in the WIPP PA model represent the equilibrium aqueous ratio of the humic-bound actinide concentration to the non-colloidal actinide concentration for GWB and ERDA-6 brines, respectively. The legacy value is 6.3 for actinides in the IV oxidation state. This value was based on Th(IV) concentrations measured in different size fractions of ultra-filtered seawater.[3]

The ranges of An(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. 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) higher pH of WIPP brines compared to seawater, (2) higher affinity of humic substances for Ca^{2+} and Mg^{2+} than previously assumed, (3) higher concentration of Mg^{2+} in WIPP brines compared to seawater, and (4) the effect of a low free An^{4+} concentration at high pH.

The Th(IV) PHUMSIM and PHUMCIM values calculated in this work 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]

TABLE III. Predicted molar compositions (mole L^{-1}) of GWB and ERDA-6 for a DBR from the repository.[6][e]

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}
Act. coef. 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]
[e] Results are preliminary. Do not cite.

TABLE IV. Predicted molal concentrations in Th(IV)-Ca-Mg-Hs system for WIPP PA.[c]

Parameter	GWB (1 × Min)	GWB (5 × Min)	ERDA-6 (1 × Min)	ERDA-6 (5 × Min)
(An)[a] (M)	6.05×10^{-8}	6.07×10^{-8}	7.02×10^{-8}	7.20×10^{-8}
(An^{m+})[a] (M)	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}
(AnHs)	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]
[c] Results are preliminary. Do not cite.

TABLE V. PHUMSIM and PHUMCIM for Th(IV).[b]

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
[b] Results are preliminary. Do not cite.

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