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subject: A summary of humic colloid parameter values to be implemented in the CRA-2019 Deferred Performance Assessment

Introduction

The set of of humic colloid parameter values to be used in the 2019 Compliance Recertification Application (CRA-2019) Deferred Performance Assessment (PA) is changed from the set used for the 2014 Compliance Recertification Application (CRA-2014). The values of the proportionality coefficients, PHUMSIM and PHUMCIM, for oxidation states III and IV are updated based on the analyses documented in Mariner (2018) and Mariner (2016) and revisions to the calculations in those analyses due to the adoption of a new WIPP thermodynamic database, DATA0.FM4. The values of PHUMSIM and PHUMCIM for oxidation states of V and VI are unchanged. The humic colloid parameter descriptions and their implementation in PA are unchanged for all oxidation states. This memo provides an updated listing of the humic colloid parameter values for use in the CRA-2019 Deferred PA.

Humic Colloids Implementation in PA

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

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

(An) is the non-colloidal aqueous actinide concentration, H is the proportionality coefficient (either PHUMSIM or PHUMCIM), and CAPHUM is the total humic complexation site concentration (DOE 2014, SOTERM-5.2). PHUMSIM and PHUMCIM are the humic colloid proportionality coefficients for brines from the Salado and Castile formations, respectively. These coefficients are equilibrium ratios of (AnHs) to (An). As indicated by Eq. 1, (AnHs) is the product of H and (An) if the product is less than CAPHUM; otherwise, (AnHs) is set at the value of CAPHUM.

PHUMSIM and PHUMCIM are defined by oxidation state (DOE 2014, Table SOTERM-20). Each actinide and its oxidation state apply individually to Eq. 1 and use the PHUMSIM and PHUMCIM values defined for the oxidation state (DOE 2014, SOTERM-5.2). Humic-bound concentrations of each

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actinide and its oxidation state have the same CAPHUM limit. CAPHUM is constant at 1.1×10^{-5} molar (M) (DOE 2014, Table SOTERM-21), as established in the Compliance Certification Application (CCA) (DOE 1996, SOTERM.6.3.3). A simplifying conservative assumption of the humic colloids implementation in PA is that actinides do not compete with other oxidation states of the actinide or other actinides for humic complexation sites (DOE 2014, SOTERM-5.2).

Humic Colloid Parameter Values for the CRA-2019 Deferred PA

The new humic colloid parameter values to be used in the CRA-2019 Deferred PA are presented in Table 1. The new values are for parameters PHUMSIM and PHUMCIM of PHUMOX3 and PHUMOX4, i.e., actinides with oxidation states of III and IV, respectively. These changes are discussed in more detail below. The PHUMSIM and PHUMCIM values for Np(V) and U(VI) (i.e., PHUMOX5 and PHUMOX6) are unchanged, as are the values for CAPHUM (DOE 2014, Table SOTERM-21).

Table 1: New humic colloid parameter values for the CRA-2019 Deferred PA.

Actinide	PHUMSIM[a]	PHUMCIM[a]
PHUMOX3	0.2	0.2
PHUMOX4	0.01	0.01

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

The changes in the PHUMSIM and PHUMCIM values for An(III) and An(IV) are based on analyses reported in Mariner (2018) and Mariner (2016), respectively, and on updated calculations for these analyses based on the new DATA0.FM4 database (Domski 2019) and new baseline solubility calculations (Domski and Sisk-Scott 2019). The Mariner (2018) and Mariner (2016) analyses drew from additional data reported in the literature since the CCA and developed an improved humic complexation process model for calculating PHUMSIM and PHUMCIM values for An(III) and An(IV). The values calculated by the improved humic complexation process model account for the alkaline conditions (pH 8.8) of predicted WIPP brines and incorporate the effects of free ion concentrations on humic complexation. The new values are expected to conservatively represent actinide-humic complexation in the predicted WIPP brines. These new values and their derivations are explained in more detail below.

Simulation of the process model for this memo was facilitated at low ionic strength 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). 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.

PHUMSIM and PHUMCIM for An(III)

The new An(III) PHUMSIM and PHUMCIM values of 0.2 and 0.2 are a result of updating the calculations in Mariner (2018) with the new DATA0.FM4 database (Domski 2019) and new baseline solubility calculations (Domski and Sisk-Scott 2019). These values are near the 0.19 value for PHUMSIM and below the 1.37 median value for PHUMCIM used in previous PA calculations (DOE 2014, Table SOTERM-21). The 0.19 and 1.37 values were determined for the CCA using a process

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model that does not account for the effects of pH nor the effects of free ion concentrations of An(III). Also, the PHUMCIM values are no longer sampled from a distribution.

The new DATA0.FM4 EDTA aqueous reactions and EDTA reaction constants for the Na-Ca-Mg-Am-EDTA-H_2O system had a major effect on the Mariner (2018) calculations. The specific calculations that were affected involved Step 4 of Section 4.2.2 of Mariner (2018) and all of the calculations in Section 5 of Mariner (2018). That analysis derived a stability constant based on the earlier DATA0.FM2 database in which the $AmEDTA^-$ formation constant was much higher ($10^{20.55}$, as opposed to the DATA0.FM4 value of $10^{18.97}$). This is especially important because the AnHs stability constant was calibrated based on the results of laboratory experiments in which EDTA and humic and fulvic acids competed for Am^{3+}. Because the formation constant for $AmEDTA^-$ decreased by nearly 1.6 orders of magnitude, the stability constant for AnHs would need to be reduced by approximately the same amount to achieve the same degree of partitioning between EDTA and the humic/fulvic acids observed in the experiments. In fact, the AnHs stability constant needed to be reduced even more because of the new $NaEDTA^{3-}$ species added to the DATA0.FM4 database. With this additional species, the Na^+ in the model also competes for EDTA complexation sites, which further weakens the ability of EDTA to bind with Am^{3+}. In other words, the EDTA reactions in DATA0.FM2 overstated the affinity of Am^{3+} for EDTA, which caused the AnHs stability constant to be overestimated when it was fitted in Mariner (2018) to replicate the experimental observations.

The updated calculations are located at /nfs/data/CVSLIB/WIPP_EXTERNAL/ap167. Calculation of the pH-specific An(III)-humic complexation constants for DATA0.FM4 was done using PhreeqcI (files "2a. Fit FM4 model to Sonke LHA data.pqi" and "2c. SRFA FM4 model fit to Sonke Fig 2C.pqi") and Excel (file "2. Am-humic Log K derivation for FM4.xlsx"). The final step Am(III)-humic calculations for the 1x dilutions of (Domski and Sisk-Scott 2019) are shown in Appendix 1.

The An(III) PHUMSIM and PHUMCIM values of 0.2 and 0.2 are expected to be conservative due to four conservative assumptions built into the Am(III)-humic complexation process model. First, the process model conservatively assumes that the entire concentration of humic colloids is composed of humic acid. Humic acid has a significantly greater affinity for complexing actinides than fulvic acid (e.g., Sonke and Salters 2006; Stern et al. 2007; Mariner and Sassani 2014, Sections 4.2.3 and 5.3.4.2). Humic colloids in natural groundwater are a combination of humic and fulvic acids (Buffle 1988). Second, the values used for the stability constant for actinide-humic complexation were derived at one molar ionic strength and were not adjusted to the ~6 molar ionic strength of WIPP brines (Mariner 2016, Section 5.1). High ionic strength tends to reduce humic complexation (Laszak and Choppin 2001, Fig. 4; Sonke and Salters 2006, Eq. 9). Third, to guard against overestimation of competition by calcium and magnesium for the available humic complexation sites, the values used for the stability constants for Ca-humic and Mg-humic complexation were set significantly lower than observed at the expected high ionic strength and pH of the MgO-equilibrated brines (Laszak and Choppin 2001; Mariner 2016, Section 5.2). Fourth, the actual (AnHs):(An) ratios calculated by the process model based on the above conservative assumptions are 0.11 and 0.12, respectively; PHUMSIM and PHUMCIM values were established by rounding up to the nearest single significant figure. As for the value of the total concentration of humic complexation sites (equivalent to CAPHUM), it too is likely conservative because it assumes that humic colloids are stable at a concentration of 2 mg L^{-1} (DOE 1996, SOTERM.6.3.3). On the contrary, humic acid is likely unstable in these brines in the presence of MgO (Wall and Mathews 2005; Mariner and Sassani 2014, Section 5.3.4.1).

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PHUMSIM and PHUMCIM for An(IV)

The new PHUMSIM and PHUMCIM values of 0.01 for An(IV) are much lower than the 6.3 value used in previous PA calculations (e.g., DOE 2014, Table SOTERM-21). The 6.3 value was determined for the CCA based on a study by Baskaran et al. (1992) in which colloidal and non-colloidal Th(IV) concentrations were measured in seawater samples (Baskaran et al. 1992; DOE 1996, SOTERM.6.3.3.1). The physicochemical state of the colloidal Th(IV) in the Baskaran et al. (1992) study, e.g., the portion composed of humic colloids, was not determined. For the CCA, the colloidal Th(IV) in the seawater samples was assumed to be entirely humic. The majority of the Baskaran et al. (1992) seawater samples had measured ratios of colloidal to dissolved Th(IV) less than 1, and no samples had a ratio of 4 or greater (Mariner and Sassani 2014, Section 5.3.4.4).

The chemical composition of seawater is much different from that of likely brines in the WIPP repository. The pH of seawater is around 8, whereas the pH of brines in the repository is expected to be around 8.8 (Domski and Sisk-Scott 2019). Increases in pH in the alkaline range tend to markedly reduce overall An(IV)-humic complexation (e.g., Reiller et al. 2003, Fig. 8; Mariner 2016, Section 5.1). In addition, Mg^{2+} from MgO will compete strongly with released actinides for humic complexation sites, reducing concentrations of humic-bound An(IV). Aqueous Mg^{2+} concentrations in WIPP brines equilibrated with MgO are expected to be approximately 7 times higher than in seawater (Mariner and Sassani 2014, Section 5.3.4.4; Domski and Sisk-Scott 2019).

To predict An(IV)-humic complexation in WIPP brines, the humic complexation process model developed in the CCA for An(III), An(V), and An(VI) was adapted and developed for application to An(IV) (Mariner 2016). The resulting process model indicates that An(IV)-humic complexation is quite weak in MgO-equilibrated WIPP brines. This result is consistent with studies published in the literature that show major reductions in An(IV)-humic complexation as pH increases in alkaline solutions (e.g., Reiller et al. 2003, Fig. 8 and 9).

The Mariner (2016) analysis used the DATA0.FM2 thermodynamic database and produced recommended value distributions for PHUMSIM and PHUMCIM that were much lower than the legacy 6.3 value. Rerunning the Mariner (2016) calculations for DATA0.FM4 and for the new CRA-2019 baseline solubility calculations resulted in approximately the same results for the (AnHs):(An) ratios for Salado brine, represented by equilibrated GWB, but it further decreased these ratios for Castile brine, represented by equilibrated ERDA-6. Unlike the equilibrated GWB brine, which changed slightly, equilibrated ERDA-6 brine changed markedly from the CRA-2014 (Domski and Sisk-Scott 2019). The total Ca^{2+} and Mg^{2+} concentration in equilibrated ERDA-6 brine increased by a factor of 6 while the pH decreased from 9.2 to 8.8. Although lower pH tends to enhance An(IV)-humic complexation, this effect is low in this pH range and is small compared to the increased competition for humic complexation sites by the much higher total concentrations of Ca^{2+} and Mg^{2+} in the new equilibrated ERDA-6 brine.

The updated calculations are located at /nfs/data/CVSLIB/WIPP_EXTERNAL/ap167. Calculation of the pH-specific An(IV)-humic complexation constants for DATA0.FM4 was done using PhreeqcI (file "3b. ThHA Stern fit at low pCO2 to FM4 davies.pqi") and Excel (file "3b. ThHAstern fit Davies NO CO2 FM4.xlsx"). The final step Th(IV)-humic calculations for the 1x dilutions of (Domski and Sisk-Scott 2019) are shown in Appendix 2.

The new An(IV) PHUMSIM and PHUMCIM values of 0.01 and 0.01 in Table 1 conservatively exceed, by factors of 6 or more, the (AnHs):(An) ratios newly calculated by the An(IV)-humic complexation process model. In addition to this conservatism, the first three conservative assumptions identified above

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for the An(III)-humic complexation process model apply to the An(IV)-humic complexation process model. Regarding the second conservative assumption, pH-specific humic complexation stability constants were conservatively derived at 0.1 molar ionic strength. Additionally, as explained earlier, it is conservative to assume that humic colloids will persist at a concentration of 2 mg L^{-1} in WIPP brines equilibrated with MgO.

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Appendix 1. Last step An(III)-humic complexation calculations for GWB and ERDA-6 brines (file: 5. Am-CaMg-HA Sonke 2006 1x FM4.mcdx)

Am and Ca/Mg Complexation with HA in Brines

Brines (all brine values from Domski & Sisk-Scott (D&SS) 2019 and associated EQ3/6 I/O files (1x dilution))

Brine density $dens := \begin{bmatrix} 1.2451 \\ 1.2454 \end{bmatrix}$ $\frac{kg}{L}$

$i := 0..1$

1. GWB
2. ERDA-6

$pH := \begin{bmatrix} 8.82 \\ 8.82 \end{bmatrix}$ $Acfree := \begin{bmatrix} 5.28 \cdot 10^{-12} \\ 7.11 \cdot 10^{-12} \end{bmatrix}$

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

$CaMgfree := \begin{bmatrix} (0.0095 + 0.322) \cdot dens_0 \\ (0.0103 + 0.354) \cdot dens_1 \end{bmatrix} = \begin{bmatrix} 0.413 \\ 0.454 \end{bmatrix}$

Conc. in M

$SolubAc := \begin{bmatrix} 1.63 \cdot 10^{-7} \\ 1.78 \cdot 10^{-7} \end{bmatrix}$

Conc.(M) from Tables 12&13, D&SS '19

Ca+2 and Mg+2 molalities and solution densities from gwb_1x.6o and erda_1x.6o of D&SS 2019

$IS := \begin{bmatrix} 1 \\ 1 \end{bmatrix}$

$HAtot := 1.1 \cdot 10^{-5}$ (conservative)

Ca/Mg-HA Stability Constant

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

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

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

Actinide-HA Stability Constant

$log\beta AcHA_i := e^{0.01416 \cdot 63 + 0.09256 \cdot pH_i + 0.08661 \cdot -\log(IS_i) + 0.69941}$

Sonke and Salters 2006 (table 5, SRFA)
<< parameter d adjusted for FM4 fit >>

$log\beta AcHA = \begin{bmatrix} 11.11 \\ 11.11 \end{bmatrix}$

$betaAcHA := 10^{log\beta AcHA} = \begin{bmatrix} 1.289 \cdot 10^{11} \\ 1.289 \cdot 10^{11} \end{bmatrix}$

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

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

Free HA binding site concentration

$$HAfreeHA_i := \frac{HAtot}{\left(1 + Acfree_i \cdot betaAcHA_i + CaMgfree_i \cdot betaCaMgHA_i\right)} = \begin{bmatrix} 2.654 \cdot 10^{-8} \\ 2.414 \cdot 10^{-8} \end{bmatrix}$$

Total Ca-HA plus Mg-HA concentration

$$CaMgHA_i := CaMgfree_i \cdot HAfreeHA_i \cdot betaCaMgHA_i = \begin{bmatrix} 1.096 \cdot 10^{-5} \\ 1.095 \cdot 10^{-5} \end{bmatrix}$$

Humic-bound actinide concentration

$$AcHA_i := Acfree_i \cdot HAfreeHA_i \cdot betaAcHA_i = \begin{bmatrix} 1.806 \cdot 10^{-8} \\ 2.213 \cdot 10^{-8} \end{bmatrix}$$

(AcHA conc. with Ca & Mg competition)

Proportionality with Ca/Mg competition

$\frac{AcHA}{SolubAc} = \begin{bmatrix} 0.11083 \\ 0.12431 \end{bmatrix}$ GWB ERDA-6

$$alpha_i := \frac{SolubAc_i}{Acfree_i} = \begin{bmatrix} 3.087 \cdot 10^4 \\ 2.504 \cdot 10^4 \end{bmatrix}$$

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Appendix 2. Last step An(IV)-humic complexation calculations for GWB and ERDA-6 brines (file: 5. Th-CaMg-HA Stern fitted to FM4 (1xMin).mcdx)

Th and Ca/Mg Complexation with HA in Brines

Brines (all brine values from Domski & Sisk-Scott (D&SS) 2019 and associated EQ3/6 I/O files (1x dilution))

$i := 0..1$

1. GWB
2. ERDA-6

$pH := \begin{bmatrix} 8.82 \\ 8.82 \end{bmatrix}$ $Acfree := \begin{bmatrix} 3.34 \cdot 10^{-25} \\ 8.40 \cdot 10^{-25} \end{bmatrix}$

$SolubAc := \begin{bmatrix} 5.45 \cdot 10^{-8} \\ 5.44 \cdot 10^{-8} \end{bmatrix}$ Conc.(M) from Tab8&9, D&SS '19

$HAtot := 1.1 \cdot 10^{-5}$

Brine density $dens := \begin{bmatrix} 1.2451 \\ 1.2454 \end{bmatrix}$ $\frac{kg}{L}$

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

$CaMgfree := \begin{bmatrix} (0.0095 + 0.322) \cdot dens_0 \\ (0.0103 + 0.354) \cdot dens_1 \end{bmatrix} = \begin{bmatrix} 0.413 \\ 0.454 \end{bmatrix}$

Conc. in M

Ca+2 and Mg+2 molalities and solution densities from gwb_1x.6o and erda_1x.6o of D&SS 2019

Actinide-HA Stability Constant

$betaAc := \begin{bmatrix} 10^{21.64} \\ 10^{21.64} \end{bmatrix}$ (FM4 fit, converted to beta)

$logbetaAc := \log(betaAc) = \begin{bmatrix} 21.64 \\ 21.64 \end{bmatrix}$

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

Ca/Mg-HA Stability Constant

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

$betaCaMg := 10^3$

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

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

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

Equilibrium Speciation

$$HAfreeComp := \frac{HAtot}{(1 + Acfree \cdot betaAc + CaMgfree \cdot betaCaMg)} = \begin{bmatrix} 2.659 \cdot 10^{-8} \\ 2.419 \cdot 10^{-8} \end{bmatrix}$$

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

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

$CaMgHA = \begin{bmatrix} 1.097 \cdot 10^{-5} \\ 1.098 \cdot 10^{-5} \end{bmatrix}$

(CaMgHA concentration with Ac competition)

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

$AcHAcomp = \begin{bmatrix} 3.8761 \cdot 10^{-11} \\ 8.8704 \cdot 10^{-11} \end{bmatrix}$ (AcHA conc. with Ca & Mg competition)

Proportionality constant with Ca/Mg competition

PHUMSIM
PHUMCIM

$$\frac{AcHAcomp}{SolubAc} = \begin{bmatrix} 0.00071 \\ 0.00163 \end{bmatrix}$$

Calculations if no Ca or Mg competition

$$HAfreeAc := \frac{HAtot}{(1 + Acfree \cdot betaAc)} = \begin{bmatrix} 1.098 \cdot 10^{-5} \\ 1.096 \cdot 10^{-5} \end{bmatrix}$$

(HA- concentration in presence of Ac only)

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

$AcHA = \begin{bmatrix} 1.601 \cdot 10^{-6} \\ 4.019 \cdot 10^{-8} \end{bmatrix}$

(AcHA concentration with no Ca or Mg competition)

Proportionality constant (no Ca/Mg competition)

PHUMSIM
PHUMCIM

$$\frac{AcHA}{SolubAc} = \begin{bmatrix} 0.294 \\ 0.739 \end{bmatrix}$$

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