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Sandia National Laboratories
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to: Laurence H. (Larry) Brush
Geochemistry Team Lead
Org. 6822, MS-1395
Carlsbad Programs Group

from: Emily R. Giambalvo
Performance Assessment
Org. 6821, MS-1395
Carlsbad Programs Group

Emily Giambalvo

subject: Recommended Parameter Values for Modeling An(IV) Solubility in WIPP Brines

1. Introduction

Parameter values for modeling speciation and solubility of Th(IV) from the recent literature (Felmy and Rai, 1999) offer the opportunity to improve the speciation and solubility model for actinides in the +IV oxidation state (An(IV)) that is implemented in the Fracture Matrix Transport (FMT) geochemical database. The newly available parameters are the ternary ion interaction parameters (θ and ψ) describing the interaction of $Th(CO_3)_5^{6-}$ with Cl^- and Na^+.

This memo describes the implementation of the An(IV) speciation and solubility model in the version of the FMT database used for compliance baseline performance assessment (PA) calculations (baseline database)*, and recommends modifications to the two parameters listed above. It also recommends modification of the value used for the normalized chemical potential (μ^0/RT, where R is the ideal gas constant and T is temperature in Kelvin) of $Th(OH)_{4(aq)}$.

2. An(IV) Model in the Baseline Database

The An(IV) speciation and solubility model in the current baseline database is that described by Novak (1996; 1997). Parameters are derived from Th solubility data and electromotive force measurements. The WIPP actinide solubility model assumes that Th(IV) solubilities predicted by the An(IV) model are representative of Pu(IV) and U(IV) solubility in addition to Th(IV) solubility (DOE, 1996). This assumption is conservative, i.e. Th(IV) is more soluble than Pu(IV) and U(IV) (e.g., Neck and Kim, 2001; Wall et al., 2002). The parameters used in the baseline An(IV) model are derived as follows:

1. Hydrolysis species (except $Th(OH)_{4(aq)}$) and polynuclear complexes of Th are neglected. The solubility product constant (K_{sp}) for $ThO_{2(am)}$ was calculated by Felmy et al. (1991) from Th solubility data collected in dilute solution at pH <7 (Ryan and Rai, 1987). Felmy et al. (1991)

* The baseline database is identical to the database used in the Performance Assessment Verification Test (PAVT), and is the most recent documented version of the database (Novak, 1997). It is stored in the CHEMDAT file FMT_970407.CHEMDAT in Sandia National Laboratories' Configuration Management System on the WIPP Alpha Cluster in the library WP$NONPA_CMSROOT:[FMT].

WIPP:1.3.5.1.2.1:PA:QA:FMT Database for CRA

neglected all hydrolysis species in their calculation of K_{sp}. They successfully simulated Th solubility in NaCl solutions up to 3 mol/L using their calculated K_{sp} and Pitzer parameters describing the interaction of Th^{4+} and Cl^- from Pitzer and Mayorga (1973).

In order to model $ThO_{2(am)}$ solubility at pH > 7, Novak (1996) added $Th(OH)_{4(aq)}$ to the model. In the pH range 7-14, Th solubility is pH-independent and $Th(OH)_{4(aq)}$ is the dominant Th species in solution (in the absence of carbonate) (Ryan and Rai, 1987; Neck and Kim, 2001). Novak (1996) cites only "new work by PNL [Pacific Northwest National Laboratory]" as the source for μ^0/RT of $Th(OH)_{4(aq)}$. I was unable to discover the data set from which this value is derived.

2. Th-carbonate complexes include $Th(CO_3)_5^{6-}$ and $Th(OH)_3CO_3^-$. Novak (1996) determined μ^0/RT values for these species by comparing $ThO_{2(am)}$ solubility in the presence of carbonate (Felmy et al., 1997) to $ThO_{2(am)}$ solubility in the absence of carbonate (Felmy et al., 1991). Felmy et al. (1997) determined the solubility of $ThO_{2(am)}$ in the presence of carbonate from solubility experiments run in dilute to moderately concentrated (<2 mol/L) $NaHCO_3$, Na_2CO_3, and $NaClO_4/CO_{2(g)}$ solutions. Pitzer parameters describing interaction of $Th(CO_3)_5^{6-}$ with Na^+ ($\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ}) and with ClO_4^- (θ) are from Felmy et al. (1997). Pitzer parameters describing the ternary interaction of $Th(CO_3)_5^{6-}$, Cl^-, and Na^+ (θ, ψ) result from A. Felmy's preliminary analysis of $ThO_{2(am)}$ solubility in mixed $NaCl/Na_2CO_3$ solutions (Novak, 1997).

3. Values of μ^0/RT for Th-sulfate complexes, related Pitzer parameters, and K_{sp} values for Th-sulfate solid phases were derived from various data sets by Felmy and Rai (1992). Like Felmy et al. (1991), Felmy and Rai (1992) used the Pitzer and Mayorga (1973) Th^{4+}-Cl^- interaction parameters in their calculations.

4. Th-chloride complexes are not explicitly modeled. Instead they are accounted for through appropriate Pitzer ion interaction parameters. The Th^{4+}-Cl^- ion interaction parameters included in the baseline database were determined from electromotive force measurements in mixed $HCl/ThCl_4$ solutions (Roy et al., 1992). Although this set of Pitzer parameters is not identical to that used by Felmy et al. (1991) and Felmy and Rai (1992), Roy et al. (1992) used it to successfully simulate the systems studied by Felmy et al. (1991) and Felmy and Rai (1992) without altering μ^0/RT values or K_{sp}s.

5. Pitzer parameters describing the ternary interaction of Th^{4+}, H^+, and Cl^- are from the electromotive force measurements of Roy et al. (1992).

6. Pitzer parameters describing the interaction of Th^{4+} with Na^+ and Mg^{2+} were calculated from $ThO_{2(am)}$ solubility data collected in NaCl (up to 6 m) and $MgCl_2$ (up to 3 m) brines (Rai et al., 1997). Rai et al. (1997) used the K_{sp} determined by Felmy et al. (1991) and the Roy et al. (1992) Th^{4+}-Cl^- Pitzer parameters in their calculations.

Tables 1-4 list the parameter values used in the baseline An(IV) model.

3. Recommended An(IV) Model

The recommended An(IV) model improves on the baseline An(IV) model in two ways:

1. Pitzer parameters describing the ternary interaction of $Th(CO_3)_5^{6-}$, Cl^-, and Na^+ (θ, ψ) come from a peer-reviewed article (Felmy and Rai, 1999), rather than an informal communication (e-mail from A. Felmy cited in Novak, 1997). They are derived from $ThO_{2(am)}$ solubility data collected in mixed Na_2CO_3/NaCl solutions (2.33 and 4.67 mol/kg NaCl).

2. The μ^0/RT value for $Th(OH)_{4(aq)}$ is derived from a traceable data set (Ryan and Rai, 1987) as follows. From the low pH (<7) data of Ryan and Rai (1987) Felmy et al. (1991) calculated log K_{sp} = -45.5 for the dissolution reaction:

$$ThO_{2(am)} + 2H_2O = Th^{4+} + 4OH^- \qquad \log K_{sp} = -45.5.$$

In the pH range where $Th(OH)_{4(aq)}$ is the dominant Th species in solution (pH = 7-14), Ryan and Rai's (1987) data yield a Th solubility of $10^{-8.8}$ mol/L, or:

$$ThO_{2(am)} + 2H_2O = Th(OH)_{4(aq)} \qquad \log K_{sp} = -8.8.$$

Differencing these equations yields the complexation constant for $Th(OH)_{4(aq)}$, which is easily converted to μ^0/RT:

$$Th^{4+} + 4OH^- = Th(OH)_{4(aq)} \qquad \log K = 36.7.$$

This calculation assumes that all Pitzer parameters related to $Th(OH)_{4(aq)}$ are zero (i.e., the activity of $Th(OH)_{4(aq)}$ is independent of ionic strength). The complexation constant obtained in this way is similar to that used in the baseline An(IV) model and to that obtained from a similar analysis of the solubility data presented by Felmy et al. (1991) (log K = 36.9 and 37.0, respectively). The log K calculated from either the Ryan and Rai (1987) or the Felmy et al. (1991) data set results in a conservative prediction of Th solubility at neutral and alkaline pH, because, in both experiments, measured solubilities in the pH range 7-14 were at the detection limit of the measurement technique.

Tables 1-4 list the recommended parameter values and compare them to the values used in the baseline version of the database.

4. References

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Copy to:
MS-1395, M.K. Knowles [Dept. 6821]
MS-1395, D.E. Wall [Dept. 6822]
MS-1395, N.A. Wall [Dept. 6822]

MS-1395, Y. Xiong [Dept. 6822]
MS-1395, Y. Wang [Dept. 6823]
MS-0779, R.C. Moore [Dept. 6849]
MS-1395, E.R. Giambalvo [Dept. 6821]
MS-1395, Day File [Dept. 6821]

Table 1. Normalized Chemical Potential (μ^0/RT)

	Current Baseline		Recommended	
Species	μ^0/RT	Source	μ^0/RT	Source
Th^{4+}	-284.227	Fuger and Oetting (1976)		*same*
$Th(CO_3)_5^{6-}$	-1411.378	Novak (1996), based on Felmy et al. (1997)		*same*
$Th(OH)_3(CO_3)^-$	-775.627	Novak (1996), based on Felmy et al. (1997)		*same*
$Th(OH)_{4(aq)}$	-622.84	Novak (1996)	-622.47	Present work, based on Ryan and Rai (1987)
$Th(SO_4)_{2(aq)}$	-911.69	Felmy and Rai (1992)		*same*
$Th(SO_4)_3^{2-}$	-1214	Felmy and Rai (1992)		*same*
$ThO_{2(am)}$	-451.408	Felmy et al. (1991)		*same*
$Th(SO_4)_2 \cdot 9H_2O_{(s)}$	-1775.9	Felmy and Rai (1992)		*same*
$Th(SO_4)_2 \cdot 8H_2O_{(s)}$	-1680	Felmy and Rai (1992)		*same*
$Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O_{(s)}$ [a]	-2011.29	Felmy and Rai (1992)		*same*
$Th(SO_4)_2 \cdot K_2SO_4 \cdot 4H_2O_{(s)}$ [a]	-1837.57	Felmy and Rai (1992)		*same*
$Th(SO_4)_2 \cdot 2K_2SO_4 \cdot 2H_2O_{(s)}$ [a]	-2181.81	Felmy and Rai (1992)		*same*
$Th(SO_4)_2 \cdot 3.5K_2SO_{4(s)}$ [a]	-2790.83	Felmy and Rai (1992)		*same*

[a] μ^0/RT value is at 16°C. Unless noted, all values in the FMT geochemical database are at 25°C.

Table 2. Binary Pitzer Parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^{ϕ})[a]

Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Source
Na^+	$Th(SO_4)_3^{2-}$	0.12	0	0	0	Felmy and Rai (1992)
Na^+	$Th(OH)_3(CO_3)^-$	0	0	0	0	Felmy et al. (1997)
Na^+	$Th(CO_3)_5^{6-}$	1.31	30	0	0	Felmy et al. (1997)
K^+	$Th(SO_4)_3^{2-}$	0.9	0	0	0	Felmy and Rai (1992)
H^+	$Th(SO_4)_3^{2-}$	0.84	0	0	0	Felmy and Rai (1992)
Th^{4+}	Cl^-	1.092	13.7	-160	-0.112	Roy et al. (1992)
Th^{4+}	SO_4^{2-}	1.56	0	0	0	Felmy and Rai (1992)
Th^{4+}	HSO_4^-	1.44	0	0	0	Felmy and Rai (1992)
Th^{4+}	ClO_4^-	1.19	27.3	0	-0.057	Novak (1996)[b]

[a]Recommended values are identical to those used in the current baseline model.

[b]Novak (1996) references "new work, SNL/FSU" for these values. Although the exact source is unclear, I did not re-evaluate Th^{4+}-ClO_4^- parameters, because ClO_4^- is not a component in simulations of WIPP brines.

Table 3. Neutral-Ion Interaction Parameter (λ)[a]

Neutral	Ion	λ	Source
$Th(SO_4)_{2(aq)}$	Cl^-	0.29	Felmy and Rai (1992)
$Th(SO_4)_{2(aq)}$	HSO_4^-	0.68	Felmy and Rai (1992)

[a]Recommended values are identical to those used in the current baseline model.

Table 4. Ternary Interaction Parameters (θ, ψ)

			Current Baseline			Recommended		
ion *i*	ion *j*	ion *k*	θ_{ij}	ψ_{ijk}	Source	θ_{ij}	ψ_{ijk}	Source
Na^+	Th^{4+}	Cl^-	0.42	0.21	Rai et al. (1997)			*same*
Mg^{2+}	Th^{4+}	Cl^-	0.60	0.21	Rai et al. (1997)			*same*
H^+	Th^{4+}	Cl^-	0.60	0.37	Roy et al. (1992)			*same*
$Th(CO_3)_5^{6-}$	Cl^-	Na^+	2.0	-0.08	Novak (1997)	1.8	0.3	Felmy and Rai (1999)
$Th(CO_3)_5^{6-}$	ClO_4^-	Na^+	5.5	0	Felmy et al. (1997)			*same*