EXTENSION OF THE WIPP ACTINIDE OXIDATION STATE ANALOG MODELS TO ELEVATED TEMPERATURES UNDER REDUCING CONDITIONS

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ABSTRACT

The Waste Isolation Pilot Plant (WIPP) is a U.S. DOE geological repository for the permanent disposal of defense-related transuranic (TRU) waste. The WIPP thermodynamic database uses oxidation state analogies, i.e., Am(III) being used to predict solubilities of actinides in +III oxidation state; Th(IV) being employed to predict solubilities of actinides in +IV state, and Np(V) being utilized to predict solubilities of actinides in +V state. This database has been approved by U.S. EPA for predicting actinide solubilities for the WIPP Compliance Certification Application in 1996, and Compliance Re-Certification Applications in 2004, 2009, and 2014. The database uses the Pitzer model for calculation of activity coefficients.

Accurate prediction of actinide solubilities is one of the key components for the safety case in geological disposal of high level nuclear waste (HLW) and used nuclear fuel (UNF). In deep geological repositories for HLW and UNF, actinides are expected to be speciated into two oxidation states, i.e., +III and +IV oxidation states, because of strong reducing conditions. As the WIPP database is well known to regulators, it provides an excellent platform for upgrading to elevated temperatures for HLW and UNF. The strategy for the potential upgrade of the WIPP database will be presented.

INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy geological repository for the permanent disposal of defense-related transuranic (TRU) waste [1-2]. This geological repository is located 42 km east of Carlsbad in southeastern New Mexico. The repository is 655 m below the surface, and is situated in the Salado Formation, a Permian salt bed composed mainly of halite, and lesser amounts of anhydrite, gypsum, polyhalite, magnesite, clays and quartz. The Salado Formation is approximately 600 m thick [3]. The Rustler Formation is immediately above the Salado Formation. It is 95 m thick at the WIPP and consists of anhydrite, halite, siltstone, sandstone, and dolomite. The Castile Formation underlies the Salado Formation, and is approximately 385 m thick at the WIPP [3]. It has three thick anhydrite units separated by halite layers [3]. There are brine reservoirs located in areas of structural deformation within the Castile Formation [4]. The in situ temperature at a depth of 655 m (the repository horizon) is 28 $^{\circ}$C, which is also the expected temperature after the repository is filled and sealed because the TRU waste to be emplaced in the WIPP will not produce enough heat to increase the temperature significantly. The brines associated with the Salado and Castile Formations are of high ionic strengths (up to 8.26 m) in nature [5].

In the WIPP performance assessment (PA) calculations, the baseline solubilities of actinide are predicted by the EQ3/6 version 8.0a using the WIPP thermodynamic database at 298.15 K. In this paper, the strategy for the extension of the WIPP thermodynamic database to 373.15 K is described.

THE WIPP THERMODYNAMIC MODEL AT 298.15 K

The WIPP thermodynamic model uses oxidation state analogies, i.e., Am(III) being used to predict solubilities of actinide in the +III oxidation state; Th(IV) being employed to predict solubilities of actinide in the +IV state, and Np(V) being utilized to predict solubilities of actinide in the +V state. In deep geological repositories for high level nuclear waste (HLW) and used nuclear fuel (UNF), actinides are expected to be speciated into two oxidation states, i.e., +III and +IV oxidation states, because of strong reducing conditions. The following descriptions focus on the WIPP Am(III) and Th(IV) models at 298.15 K first, and then the strategy to extend them to 373.15 K is discussed.

Am(III) and Th(IV) models

In Table I, the aqueous species of Am(III) and Th(IV) models incorporated into the database of the WIPP thermodynamic database are listed. The aqueous thermodynamic model of Am(III) includes Am^{3+}, americium carbonate complexes, chloride complexes, hydroxyl complexes, organic ligand complexes, and sulfate complexes. The aqueous thermodynamic model of Th(IV) includes Th^{4+}, thorium carbonate complex, hydroxyl complex, mixed carbonate and hydroxyl complex, organic ligand complexes, and sulfate complexes. The Pitzer interaction parameters of these Am(III) and Th(IV) species with major ions are listed in Table II. The sources of these thermodynamic parameters are detailed in [6] and [7].

Table I. Aqueous species and their Gibbs free energy of formation at reference state (298.15 K and 1 bar) of Am(III) and Th(IV) models in the WIPP thermodynamic database

Species	$\Delta_f G$, kJ mol^{-1}
Am^{3+}	-599.116
$AmCO_3^+$	-1,173.200
$Am(CO_3)_2^-$	-1,729.026
$Am(CO_3)_3^{3-}$	-2,269.433
$Am(CO_3)_4^{5-}$	-2,784.705
$AmOH^{2+}$	-793.123
Species	$\Delta_f G$, kJ mol^{-1}
$Am(OH)_2^+$	-983.819
$Am(OH)_3^o$	-1,163.880
$AmCl^{2+}$	-731.747
$AmCl_2^+$	-857.424
$AmSO_4^+$	-2,109.450
$Am(SO_4)_2^-$	-1,362.260
$AmAc^{2+}$	-980.016
$AmCit^o$	-566.517

AmEDTA$^-$	-575.889
AmOx$^+$	-601.989
Th^{4+}	-704.547
Th(CO$_3$)$_5^{-6}$	-3,498.551
Th(OH)$_3$(CO$_3$)$^-$	-1,922.639
Th(OH)$_4^{o}$	-1,553.192
Th(SO$_4$)$_2^{o}$	-2,259.915
Th(SO$_4$)$_3^{2-}$	-3,009.286
ThAc^{3+}	-1,111.812
ThCit$^+$	-708.689
ThEDTA^{o}	-707.502
ThOx^{2+}	-737.270

Ac: Acetate; Cit: Citrate; Ox: Oxalate

$\Delta_f G$ are converted from μ^{o}/RT using $\Delta_f G = (\mu^{o}/RT) \times 298.15 \times 8.314$

Table II. Pitzer interaction parameters involving Am(III) and Th(IV) species

Binary interaction parameters for Am(III) species				
Species i	Species j	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Am^{3+}	Cl$^-$	0.5856	5.6	-0.0166
Am^{3+}	SO$_4^{2-}$	1.792	15.04	0.600
AmCO$_3^+$	Cl$^-$	-0.072	0.403	0.0388
AmOH^{2+}	Cl$^-$	-0.055	1.6	0.05
Am(OH)$_2^+$	Cl$^-$	-0.616	-0.45	0.05
AmCl^{2+}	Cl$^-$	0.593	3.15	-0.006
AmCl$_2^+$	Cl$^-$	0.516	1.75	0.010
AmSO$_4^+$	Cl$^-$	-0.091	-0.39	0.048
AmAc^{2+}	Cl$^-$	0.3088	1.74	-0.132
AmOx$^+$	Cl$^-$	-0.9374	0.29	0.248
Na$^+$	Am(CO$_3$)$_2^-$	-0.240	0.224	0.0284
Na$^+$	Am(CO$_3$)$_3^{3-}$	0.125	4.73	0.0007
Na$^+$	Am(CO$_3$)$_4^{5-}$	2.022	19.22	-0.305
Na$^+$	Am(SO$_4$)$_2^-$	-0.345	0.40	0.051
Na$^+$	AmEDTA$^-$	-0.2239	0.29	0.095
Interaction parameters for neutral species and mixing parameters for Am(III) species				
Species i	Species j	λ_{ij}	θ_{ij}	
Am(OH)$_3^{o}$	Na$^+$	-0.2		
Am(OH)$_3^{o}$	Cl$^-$	-0.2		
AmCit^{o}	Cl$^-$	-0.406		
Am^{3+}	Ca^{2+}		0.2	
AmCl^{2+}	Ca^{2+}		-0.014	
AmCl$_2^+$	Ca^{2+}		-0.196	
Am^{3+}	Na$^+$		0.1	
Binary interaction parameters for Th(IV) species				
Species i	Species j	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}

|				
Th^{4+}	Cl^-	1.092	13.7; $\beta^{(2)}$= -160	-0.112
Th^{4+}	SO_4^{2-}	1.56	0	0
Th^{4+}	HSO_4^-	1.44	0	0
$ThAc^{3+}$	Cl^-	1.061	5.22	0.109
$ThCit^+$	Cl^-	-0.7467	0.29	0.319
$ThOx^{2+}$	Cl^-	-0.343	1.74	0.5
Na^+	$Th(CO_3)_5^{-6}$	1.31	30	0
Na^+	$Th(SO_4)_3^{2-}$	0.12	0	0
K^+	$Th(SO_4)_3^{2-}$	0.90	0	0
Interaction parameters for neutral species and mixing parameters for Th(IV) species				
Species i	Species j	Species k	λ_{ij} or θ_{ij}	Ψ_{ijk}
$Th(SO_4)_2^{\,0}$	Cl^-		0.29	
$Th(SO_4)_2^{\,0}$	HSO_4^-		0.68	
$ThEDTA^0$	Cl^-		0.1111	
Th^{4+}	Na^+	Cl^-	0.42	0.21
Th^{4+}	Mg^{2+}	Cl^-	0.60	0.21
Th^{4+}	H^+	Cl^-	0.60	0.37
Na^+	$Th(CO_3)_5^{-6}$	Cl^-	2.0	-0.08

THE STRATEGY FOR THE EXTENSION OF THE WIPP THERMODYNAMIC MODEL TO 373.15 K

The extension of the WIPP thermodynamic model to 373.15 K requires tremendous experimental studies. In order to conduct the necessary experimental investigations, the following strategy is proposed. First, the model will be simplified to exclude the complexes with charges higher than three at elevated temperatures. The justification for this simplification is that dielectric constants of water decrease significantly with increasing temperature. For example, the dielectric constant of water at 298.15 K is 78.38, and it decreases to 55.46 at 373.15 K. When dielectric constants of water decrease, highly charged complexes cannot be supported, and therefore are unimportant. Second, it is assumed that Pitzer interaction parameters are constant over the temperature range from 298.15 K to 373.15 K. This assumption is supported by other studies (e.g., [8-9]). The third strategy is to use some extrapolation methods such as the isocoulombic approach [10], to guide experimental work to obtain thermodynamic properties at elevated temperatures. As an example, the one-term isocoulombic approach is used below to predict stability constants for the Am(III) to 373.15 K to guide the future experimental work.

The one-term isocoulombic approach has been extensively used before (e.g., [11] and references therein). The one-term isocoulombic approach can be cast as,

$$\Delta_r G_T^0 = \Delta_r G_{298.15K}^0 ,$$

$$\log K_T = -\frac{\Delta_r G_{298.15K}^0}{\ln(10) \times RT} \tag{1}$$

The essence of the isocoulombic approach is that a reaction for extrapolation should be preferably ideally balanced. As an example, for the following reaction,

$$Am^{3+} + OH^- \leftrightarrows AmOH^{2+} \qquad\qquad (2)$$
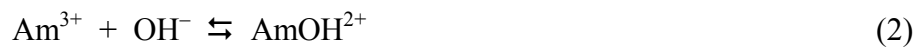
Using the formation of $NdAc^{2+}$ [12] as the model substance,

$$Nd^{3+} + Ac^- \leftrightarrows NdAc^{2+} \qquad\qquad (3)$$

Combination of Reactions 2 and 3 yields the following ideal isocoulombic reaction,

$$Am^{3+} + OH^- + NdAc^{2+} \leftrightarrows Nd^{3+} + Ac^- + AmOH^{2+} \qquad\qquad (4)$$

In this ideal isocoulombic reaction, Am^{3+} on the left side is balanced by Nd^{3+} on the right side, OH^- on the left side balanced by Ac^- on the right side, and $NdAc^{2+}$ on the left side balanced by $NdOH^{2+}$ on the right side.

RESULTS

In Table III, the stability constants for the selected species in the Am(III) model are predicted to 373.15 K. These species are selected because ideal or semi-ideal isocoulombic reactions can be written for them by using either $NdAc^{2+}$ or $Nd(Ac)_2^+$ from Wood et al. [12] as the model substances. In the near future, the stability constants for the other species in the Am(III) and Th(IV) models will also be predicted. When the model substances with reliable experimental stability constants at elevated temperatures to 373.15 K are available, this will permit us to produce the ideal or semi-ideal isocoulombic reactions for those species.

Table III. Predicted stability constants for the selected species in the Am(III) model to 373.15 K

Reaction	T, K	log K	Reaction	T, K	log K
$Am^{3+} + Cl^- = AmCl^{2+}$	298.15	0.24	$Am^{3+} + 2Cl^- = AmCl_2^+$	298.15	-0.74
	323.15	0.56		323.15	-0.25
	348.15	0.91		348.15	0.34
	373.15	1.29		373.15	1.03
$Am^{3+} + OH^- = AmOH^{2+}$	298.15	6.44	$Am^{3+} + 2OH^- = Am(OH)_2^+$	298.15	12.30
	323.15	6.28		323.15	11.78
	348.15	6.22		348.15	11.50
	373.15	6.24		373.15	11.45
$Am^{3+} + CO_3^{2-} = AmCO_3^+$	298.15	8.10	$Am^{3+} + SO_4^{2-} = AmSO_4^+$	298.15	3.25
	323.15	7.90		323.15	3.43
	348.15	7.91		348.15	3.75
	373.15	8.09		373.15	4.21
$Am^{3+} + Ac^- = AmAc^{2+}$	298.15	2.74	$Am^{3+} + Ox^{2-} = AmOx^+$	298.15	6.16
	323.15	2.87		323.15	6.11
	348.15	3.05		348.15	6.25
	373.15	3.29		373.15	6.54

CONCLUSIONS

In response to the need of upgrading the WIPP thermodynamic database to elevated temperatures for the potential use in investigation of the safe disposal of HLW and UFN in geological media associated with high ionic strength solutions, the strategy for the extension of the WIPP thermodynamic database to 373.15 K is presented in this work. In this strategy, the complexes with charges higher than three in the Am(III) and Th(IV) models are excluded because of their unimportance at elevated temperatures. Extrapolation methods such as the isocoulombic approach will be used to guide the necessary experimental studies.

ACKNOWLEDGMENTS

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