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

SAND2013-8285C

4th East Asia Forum on Radwaste Management
Beijing, China, October 14-16, 2013

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SAND2013-8285C

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ACKNOWLEDGEMENTS

- This research is funded by Waste Isolation Pilot Plant (WIPP) programs administered by the US Department of Energy.

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OUTLINE OF PRESENTATION

- Introduction
- Waste Isolation Pilot Plant (WIPP)
- The WIPP Actinide Oxidation State Analogies Model at 298.15 K
- The Strategy for the Extension of the Existing Thermodynamic Model to 373.15 K
- Summary and Future Work

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INTRODUCTION

- Accurate prediction of actinide solubilities in various solutions is important to the performance assessment (PA) of geological repositories for nuclear waste.
- Some repositories are in salt formations (e.g., WIPP in U.S.A.; Asse in Germany), and therefore associated brines are of high ionic strength in nature.
- Activity coefficient models employed in common geochemical codes: Davies equation ($I \leq 0.1$ m); B dot equation ($I \leq 1.0$ m); Pitzer equation (from very dilute solutions to solutions with high ionic strengths, up to saturation of most salts).

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Overview of WIPP Thermodynamic Model at 298.15 K

The WIPP thermodynamic model with actinide chemistry developed at Sandia National Laboratories featuring:

- **Pitzer equations for calculation of activity coefficients of aqueous species**
- **Major ion chemistry include: H-Na-K-Mg-Ca-$B(OH)_3$-Cl-SO_4-CO_3**
- **Actinide complexes with organic ligands expected in WIPP (acetate, citrate, EDTA, and oxalate)**
- **Actinide oxidation state analog model: Nd(III), Am(III) and Cm(III) are used to predict actinide solubilities in +III state; Th(IV) is employed to predict actinide solubilities in +IV state; Np(V) is utilized to predict actinide solubilities in +V state**
- **The WIPP thermodynamic model has been approved by U.S. EPA for predicting actinide solubilities for the PA of the WIPP, including:**
  - **The WIPP Compliance Certification Application in 1996 ,**
  - **The WIPP Compliance Re-Certification Applications in 2004, 2009, and 2014**
- **The WIPP thermodynamic model will be upgraded to include Fe and Pb chemistry, and high precision borate sub-model in approximately March of 2014.**

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THE WASTE ISOLATION PILOT PLANT (WIPP)

- The WIPP is a U.S. Department of Energy geological repository being used for the permanent disposal of defense-related transuranic waste, located about 40 km east of Carlsbad, southeastern New Mexico, U.S.A.

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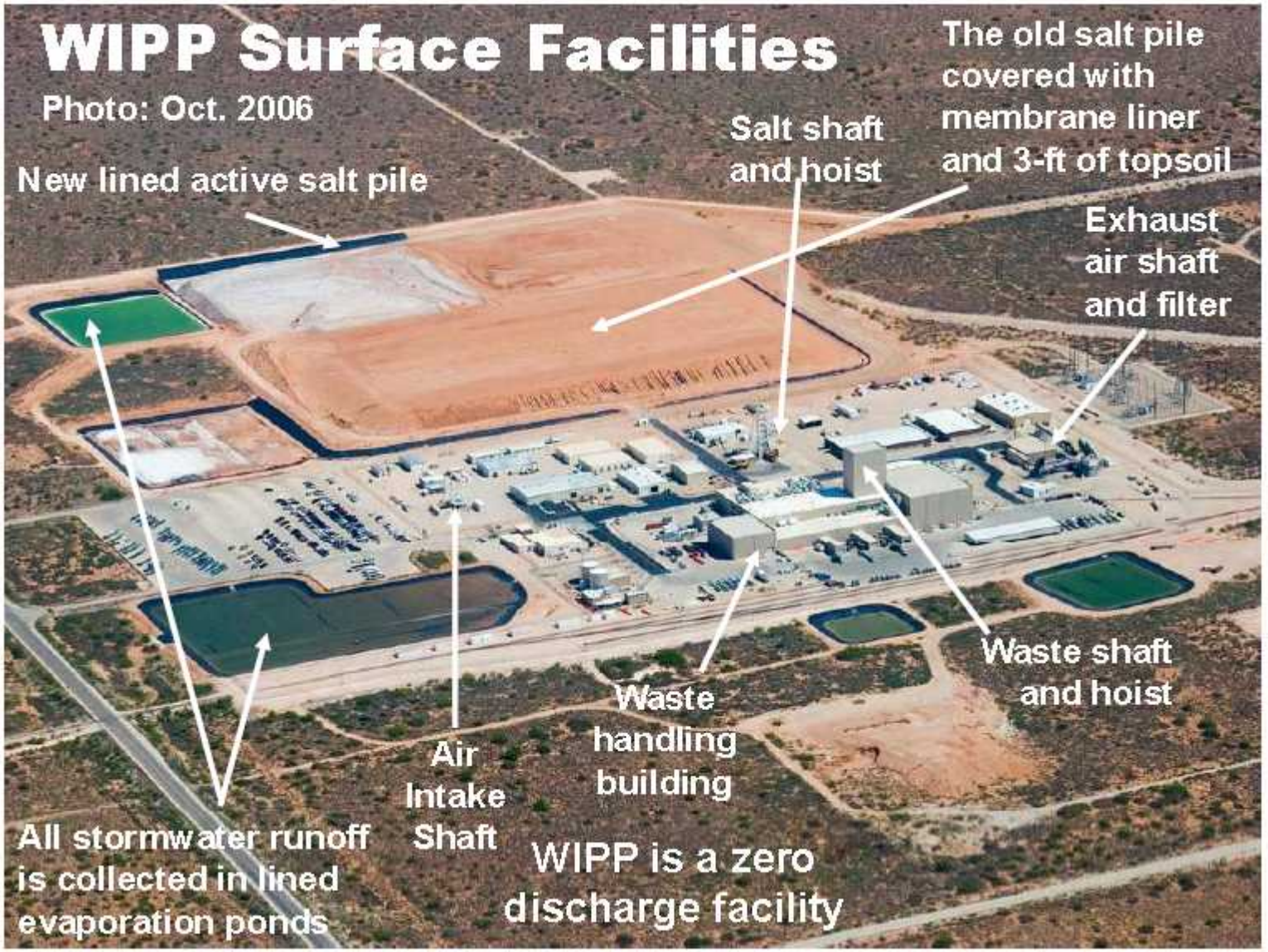

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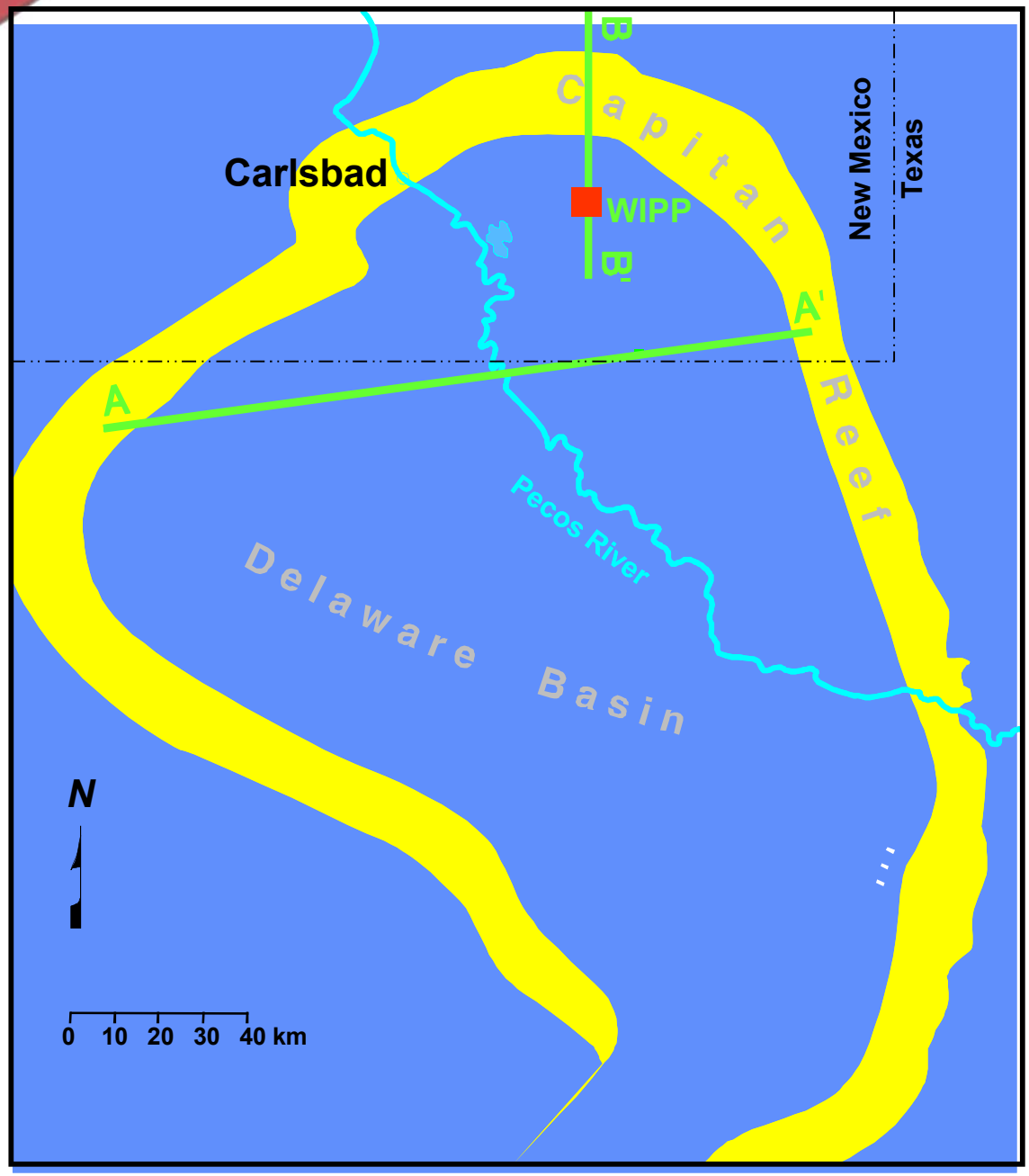

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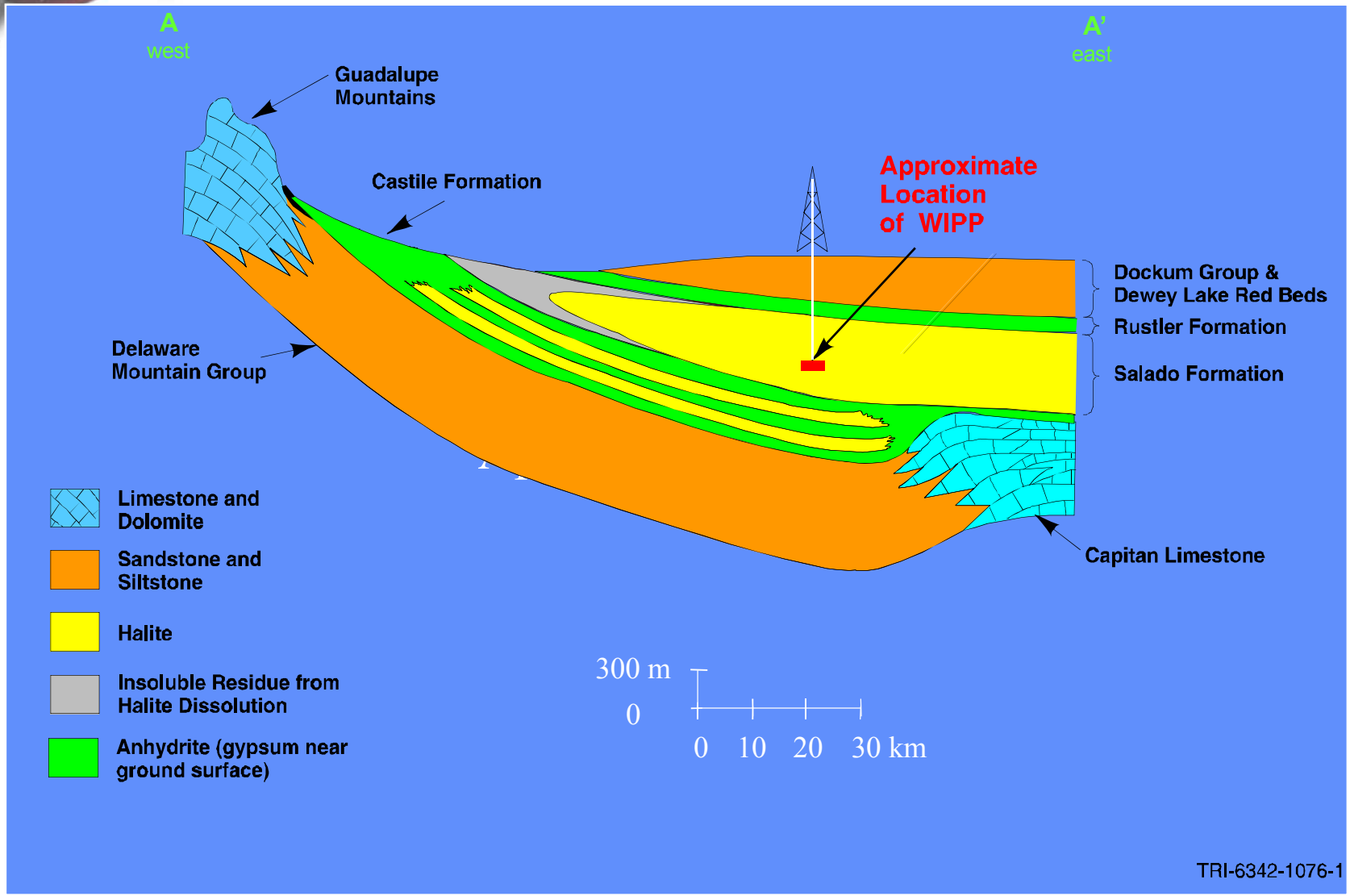

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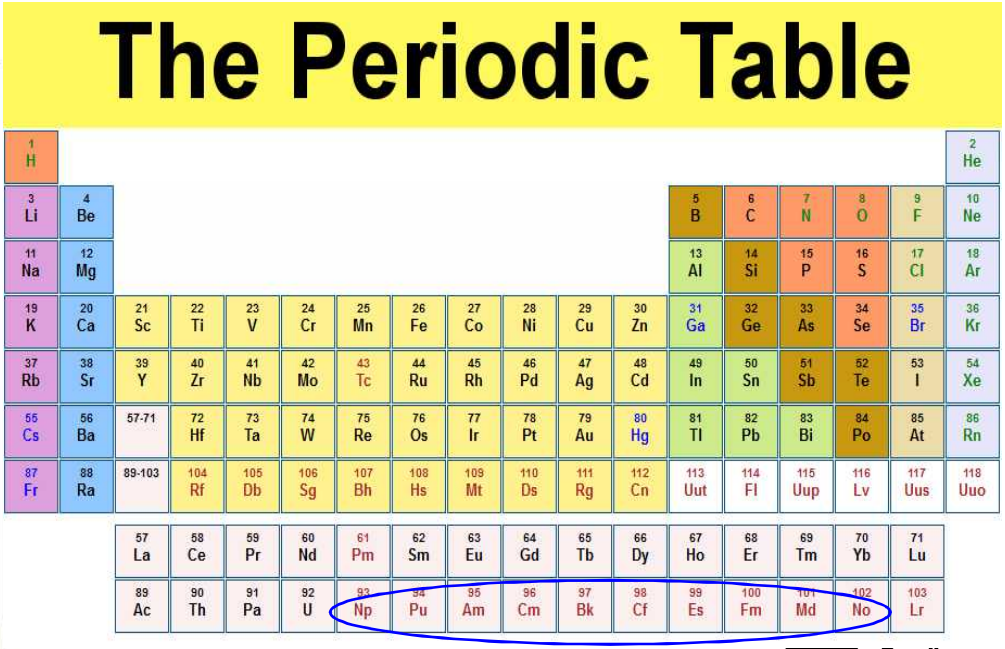
WASTE FOR WIPP

- **Defense related transuranic (TRU) waste**
  - **Contact-handled (CH) waste, <200 mrem/hr**
  - **Remote-handled (RH) waste, 0.2-1000 rem/hr**



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THE WIPP ACTINIDE OXIDATION STATE ANALOGIES MODEL IN DETAIL

- Am(III) Model
- Th(IV) Model
- Np(V) Model

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WIPP THERMODYNAMIC MODEL: Am(III) MODEL

Aqueous and solid species and their Gibbs free energies of formation at reference state (298.15 K and 1 bar) of Am(III) model

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
$Am(OH)_2^+$	-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
$AmOHCO_3$(cr)	-1,413.770
$Am(OH)_3$(s)	-1,227.809
$NaAm(CO_3)_2 \cdot 6H_2O$ (cr)	-3,461.597

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WIPP THERMODYNAMIC MODEL: Th(IV) MODEL

Aqueous and solid species and their Gibbs free energies of formation at reference state (298.15 K and 1 bar) of Th(IV) model

Species	$\Delta_f G$, kJ mol^{-1}
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
ThO_2 (am)	-1,118.959
$Th(SO_4)_2 \cdot 8H_2O$	-4,164.416
$Th(SO_4)_2 \cdot 9H_2O$	-4,402.135
$Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O$ (289.15 K)	-4,985.624
$Th(SO_4)_2 \cdot K_2SO_4 \cdot 4H_2O$ (289.15 K)	-4,555.004
$Th(SO_4)_2 \cdot 2K_2SO_4 \cdot 2H_2O$ (289.15 K)	-5,408.312
$Th(SO_4)_2 \cdot 3.5K_2SO_4$ (289.15 K)	-6,917.963

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WIPP THERMODYNAMIC MODEL: Np(V) MODEL

Aqueous and solid species and their Gibbs free energies of formation at reference state (298.15 K and 1 bar) of Np(V) model

Species	$\Delta_f G$, kJ mol^{-1}
NpO_2^+	-914.945
$NpO_2CO_3^-$	-1,471.429
$NpO_2(CO_3)_2^{3-}$	-2,007.427
$NpO_2(CO_3)_3^{5-}$	-2,528.926
NpO_2OH^o	-1,087.532
$NpO_2(OH)_2^-$	-1,254.872
NpO_2Ac^o	-1,288.032
NpO_2Cit^{2-}	-852.087
$NpO_2H_2EDTA^-$	-902.533
NpO_2EDTA^{3-}	-832.159
NpO_2Ox^-	-906.878
NpO_2OH(am)	-1,126.299
NpO_2OH(aged)	-1,122.303
$NaNpO_2CO_3 \cdot 3.5H_2O$(s)	-1,048.058
$Na_3NpO_2(CO_3)_2$(s)	-2,837.249
$KNpO_2CO_3$(s)	-1,802.919
$K_3NpO_2(CO_3)_2$(s)	-2,909.008

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WIPP THERMODYNAMIC MODEL:
PITZER INTERACTION PARAMETERS OF Am(III) MODEL

Pitzer interaction parameters involving Am(III) species

Binary interaction parameters

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

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

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WIPP THERMODYNAMIC MODEL:
PITZER INTERACTION PARAMETERS OF Th(IV) MODEL

Pitzer interaction parameters involving Th(IV) species

Binary interaction parameters				
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				
Species *i*	Species *j*	Species *k*	λ_{ij} or θ_{ij}	Ψ_{ijk}
$Th(SO_4)_2^o$	Cl^-		0.29	
$Th(SO_4)_2^o$	HSO_4^-		0.68	
$ThEDTA^o$	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

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WIPP THERMODYNAMIC MODEL: PITZER INTERACTION PARAMETERS OF Np(V) MODEL

Pitzer interaction parameters involving Np(V) species

Binary interaction parameters				
Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
NpO_2^+	Cl^-	0.1415	0.281	0
Na^+	$NpO_2CO_3^-$	0.1	0.34	0
Na^+	$NpO_2(CO_3)_2^{3-}$	0.48	4.4	0
Na^+	$NpO_2(CO_3)_3^{5-}$	1.80	22.7	0
Na^+	NpO_2Cit^{2-}	-0.4226	1.75	0.142
Na^+	$NpO_2H_2EDTA^-$	-0.8285	0.2575	0.256
Na^+	NpO_2EDTA^{3-}	0.683	5.911	0
Na^+	NpO_2Ox^-	-0.5418	0.29	0.095
K^+	$NpO_2(CO_3)_3^{5-}$	2.34	22.7; $\beta^{(2)}$= -96	-0.22
Mg^{2+}	$NpO_2CO_3^-$	0.1	0.34	0
Mg^{2+}	$NpO_2(CO_3)_2^{3-}$	0.48	4.4	0
Mg^{2+}	$NpO_2(CO_3)_3^{5-}$	2.07	22.7; $\beta^{(2)}$= -48	-0.11
Interaction parameters for neutral species and mixing parameters				
Species *i*	Species *j*	Species *k*	λ_{ij} or θ_{ij}	Ψ_{ijk}
NpO_2OH^o	Cl^-		-0.19	
$NpO_2CO_3^-$	Cl^-	Na^+	-0.21	0
$NpO_2(CO_3)_2^{3-}$	Cl^-	Na^+	-0.26	0
$NpO_2(CO_3)_3^{5-}$	Cl^-	Na^+	-0.26	0
$NpO_2(CO_3)_3^{5-}$	CO_3^{2-}	K^+	-1.9	0

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

- The existing database has been scrutinized carefully, and it provides an excellent platform for upgrading to elevated temperatures for accurate prediction of actinide solubilities for the safety case for geological disposal of high level nuclear waste (HLW), used nuclear fuel (UNF), and heat-generating waste.
- We realize that the extension of the existing thermodynamic model to 373.15 K requires tremendous experimental studies.
- A strategy to map out the important topics is needed.

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STRATEGY FOR THE EXTENSION OF THE EXISTING THERMODYNAMIC MODEL TO 373.15 K (Cont.)

The following strategy is proposed:

- **The model will be simplified to exclude the complexes with charges higher than three at elevated temperatures;**
- **It is assumed that Pitzer interaction parameters are constant over the temperature range from 298.15 K to 373.15 K;**
- **Using some extrapolation methods such as the isocoulombic approach guides experimental work to obtain thermodynamic properties at elevated temperatures;**
- **In deep geological repositories for HLW and UNF, actinides are expected to be speciated into two oxidation states (+III and +IV) at elevated temperatures, because of strong reducing conditions.**

EXTRAPOLATION METHODS

An example of the one-term isocoulombic approach for an ideal isocoulombic reaction:

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

We have

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

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

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EXTRAPOLATION METHODS: PREDICTED VALUES FOR Am(III) MODEL

- **Using the one-term isocoulombic approach, the following stability constants are predicted.**

Predicted stability constants for the selected species in the Am(III) model to 373.15 K (Xiong, 2013, SAND2013-6687C)

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

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SUMMARY AND FUTURE WORK

- The existing thermodynamic model uses actinide oxidation state analogies, and has been carefully scrutinized.
- Therefore, it provides an excellent platform for upgrading to elevated temperatures for use for PA for HLW and UNF geological disposal.
- The systematic planning for upgrading the existing thermodynamic model to elevated temperatures is currently under consideration.