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A Pitzer Model for Na^+—Nd^{3+}—SO_4^{2-}—H^+—OH^- System to High Ionic Strengths

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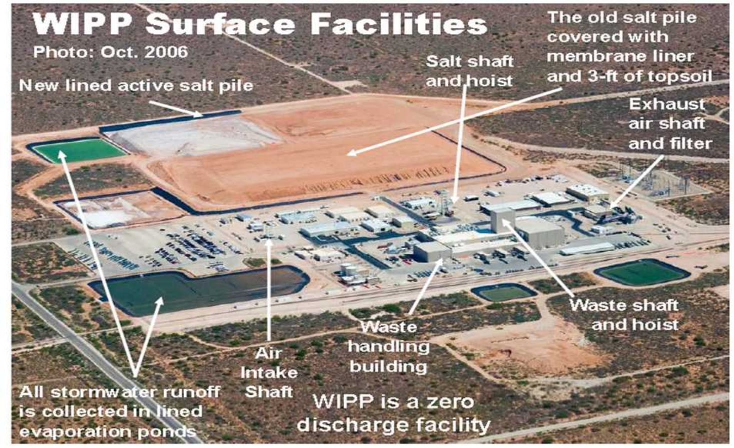
U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

INTRODUCTION

- The accurate knowledge of actinide solubilities that could be dissolved in natural brines is important to safe disposal of nuclear waste.
- Sulfate is a major species in natural brines and nuclear waste:
  - The sulfate concentrations in the Waste Isolation Pilot Plant (WIPP) brines
    - Generic Weep Brine (GWB): 0.203 mol•kg^{-1} and
    - U.S. Energy Research and Development Administration Well 6 (ERDA-6): 0.187 mol•kg^{-1} [1]
  - In the low level and intermediate level radioactive sulfate liquid waste (LLW and ILW), they are very rich in Na_2SO_4 with SO_4^{2-} concentrations up to 2.2 mol•kg^{-1} [2].
- However, solubilities of actinides in sulfate solutions are not well studied.



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[1] Y.-L. Xiong, A.C. Lord, Experimental investigations of the reaction path in the $MgO–CO_2–H_2O$ system in solutions with various ionic strengths, and their applications to nuclear waste isolation, Applied Geochemistry, Vol.23, p. 1634, 2008.

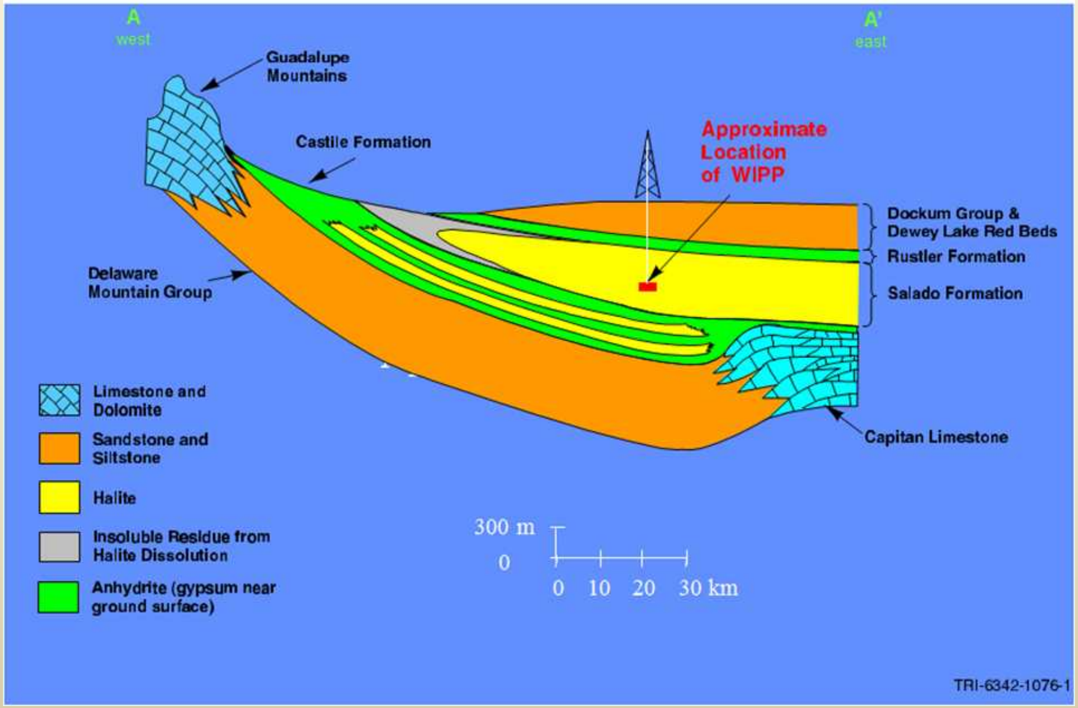
[2] A. Guerrero, S. Goni, M.-S. Hernandez, 2000. Thermodynamic solubility constant of $Ca(OH)_2$ in simulated radioactive sulfate liquid waste. Journal of American Ceramics Society, Vol. 83, p. 882, 2000.

INTRODUCTION (Cont.)

- In deep underground geological repositories, actinides are expected to be speciated as +III and +IV oxidation states [i.e., An(III) and An(IV)] because of the strongly reducing conditions.
- Rare earth elements (REE) in +III oxidation state, such as Nd(III), have been found to be good analogs to An(III).
- In acid mine drainage (AMD), there are high concentrations of sulfate as well as rare earth elements (REE) (e.g., ~70 μmol•kg^{-1})
- In this work, we investigate solubilities of $Nd(OH)_3$(micro cr) in Na_2SO_4 solutions with a wide range of ionic strengths up to 5.4 mol•kg^{-1} under well-constrained conditions.

Table 1. Comparison of effective ionic radii of Nd(III) with those of actinides in +III oxidation state (data taken from [3])

Element	Effective Ionic Radius for 6 Coordination Number in Å	Effective Ionic Radius for 8 Coordination Number in Å
Nd(III)	0.983	1.109
Am(III)	0.975	1.09
Cm(III)	0.97	-----
Pu(III)	1.00	-----



PURPOSE OF THIS STUDY

- To measure solubility of $Nd(OH)_3$(micro cr) in Na_2SO_4 solutions in a wide range of ionic strengths at 298.15 K in the long-term experiments.
- Accurate knowledge of Nd(III) in sulfate solutions is important to understanding the transport of actinides and REE in environment and to recovery of REE from AMD.
- To develop a Pitzer model to describe solubilities applicable to a wide range of ionic strengths:
    - $Nd(OH)_3$(micro cr) from this work, and
    - *$Nd_2(SO_4)_3 \bullet 8H_2O$ from literature*
    - Pitzer Model, using mean activity coefficient for NaCl as an example

$$\ln\gamma_{\pm} = -A_{\phi}\left[\frac{\sqrt{I_m}}{1+1.2\sqrt{I_m}} + \frac{2}{1.2}\ln(1+1.2\sqrt{I_m})\right] + m\left\{2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 \times I_m}\left[1-(1+\alpha\sqrt{I_m}-\frac{\alpha^2 I_m}{2})e^{-\alpha\sqrt{I_m}}\right]\right\} + \frac{3m^2}{2}C^{\phi}$$

EXPERIMENTAL METHOD

- Experimental Apparatus: All experiments are conducted in a glovebox under Ar + H_2 atmosphere in which O_2 and CO_2 are excluded.
- Experimental conditions: T = 298.15 K
- Starting material: Synthetic $Nd(OH)_3$(micro cr)
- Hydrogen ion concentrations (pH_m, molal scale) of the experimental systems are controlled/buffered by solubility of $Nd(OH)_3$(micro cr).
- pH_m are determined by applying correction factors to pH readings obtained using a pH meter.
  - $pH_m = pH_{ob} + A_m = pH_{ob} + A_M - \log \Theta$
- Nd(III) concentrations are analyzed using Inductively Coupled Plasma Mass Spectrometer (ICP-MS).
- Na concentrations are analyzed using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES).
- Sulfate concentrations are analyzed using Ion Chromatography (IC).
- Approaching equilibrium from undersaturation.
- Supporting solutions: 0.01 to 1.8 mol•kg^{-1} Na_2SO_4

EXPERIMENTAL METHOD: Synthesis of $Nd(OH)_3$(micro cr)

- Having well-defined starting material with high purity is of fundamental importance to the successes in solubility experiments.
  - High purity crystalline $Nd(OH)_3$(micro cr) is synthesized according to the procedure described by Wood et al. [4].
  - High purity Nd_2O_3 is first loaded with deaerated DI water into Paar® reaction vessels, and then the reaction vessels are sealed, in a glovebox under a positive pressure of the inert gas.
  - The reaction vessels are taken out from the glovebox, and are placed into a muffle furnace.
  - $Nd(OH)_3$(micro cr) is synthesized by reacting high purity Nd_2O_3 with deaerated DI water at 473.15 K in Paar® reaction vessels for a period of two weeks.

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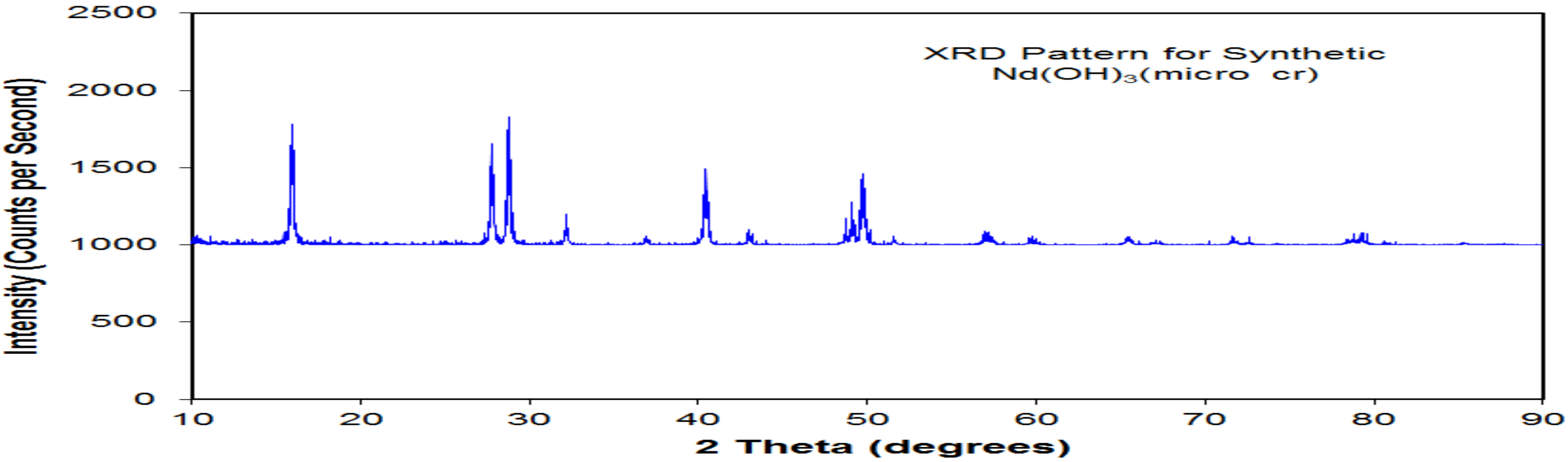
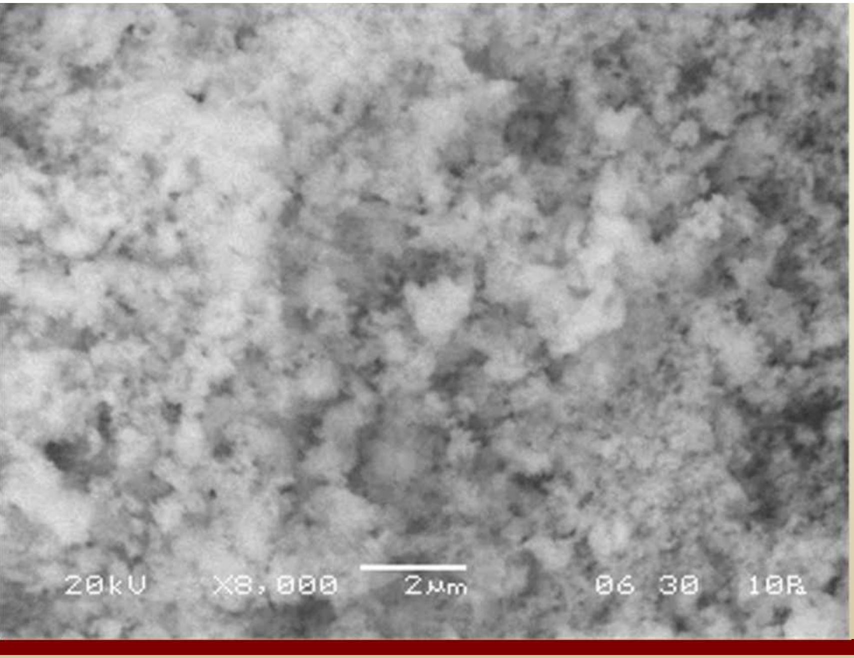
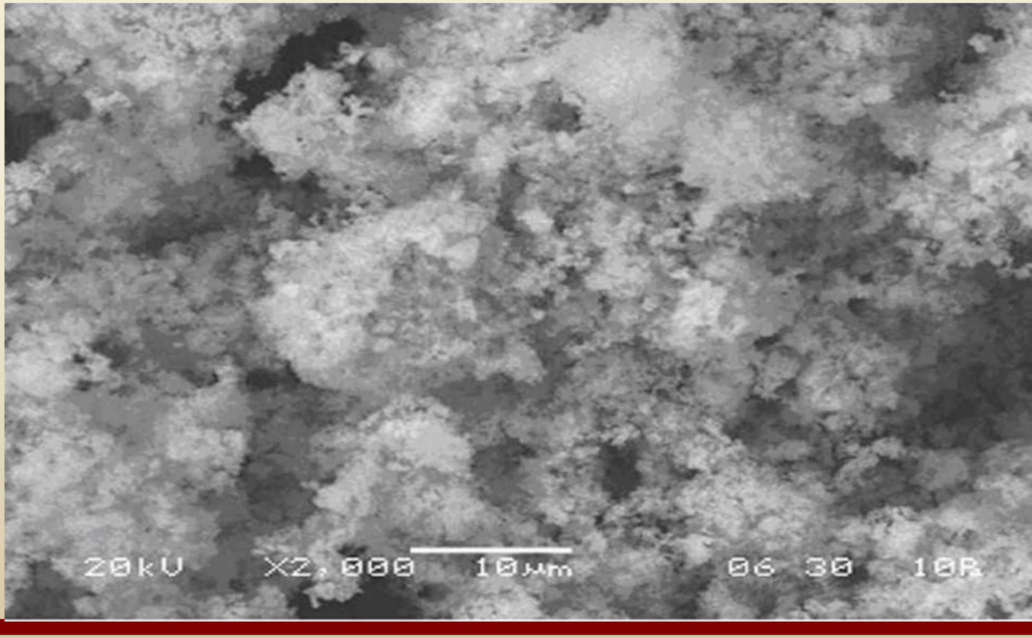
[4] S.A. Wood, D.A. Palmer, D.J. Wesolowski, and P. Bénézeth, In Hellmann, R. and Wood, S.A., ed., Special Publication 7, The Geochemical Society, pp. 229–256, 2002.

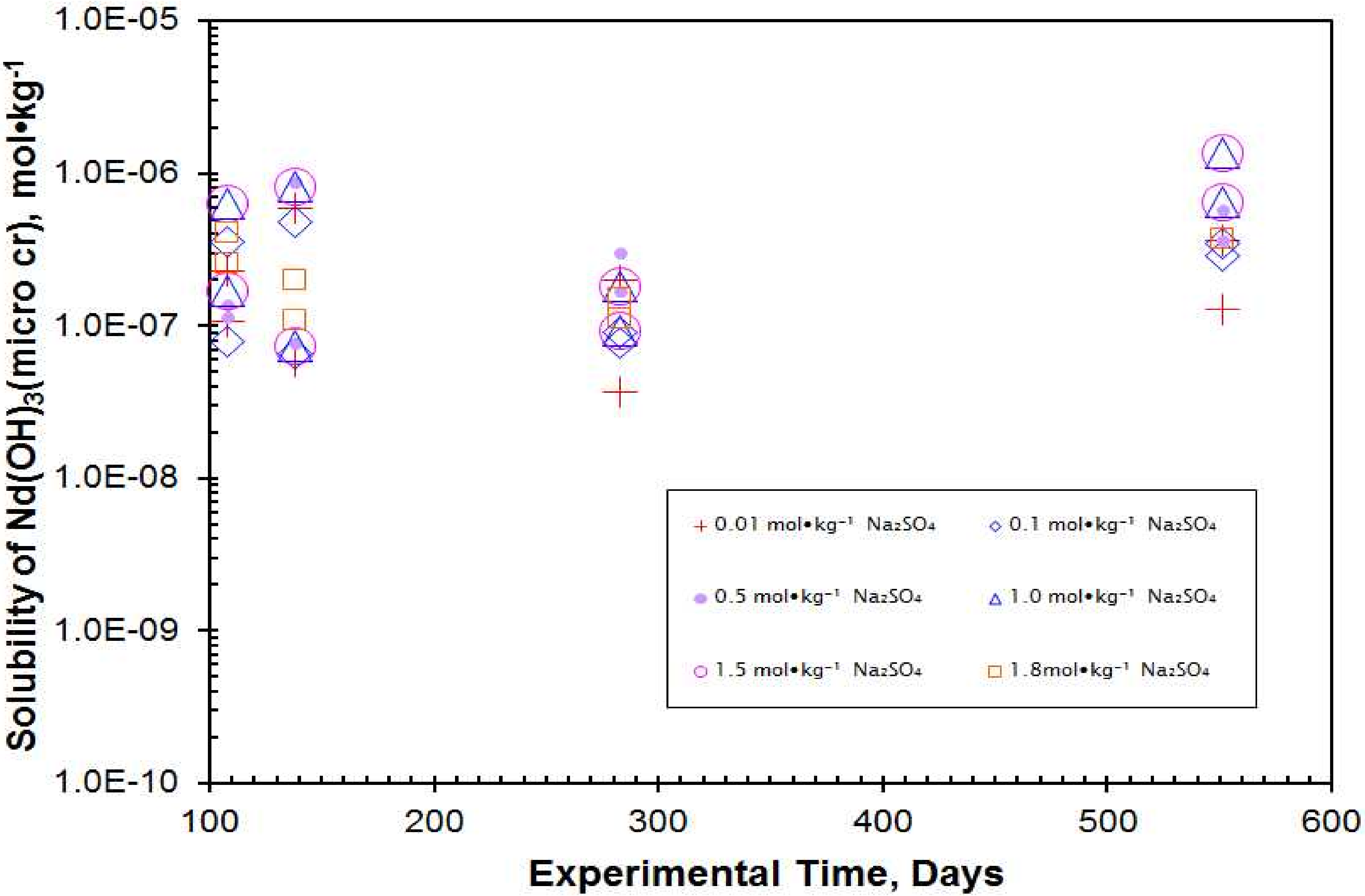
XRD Pattern and SEM Image



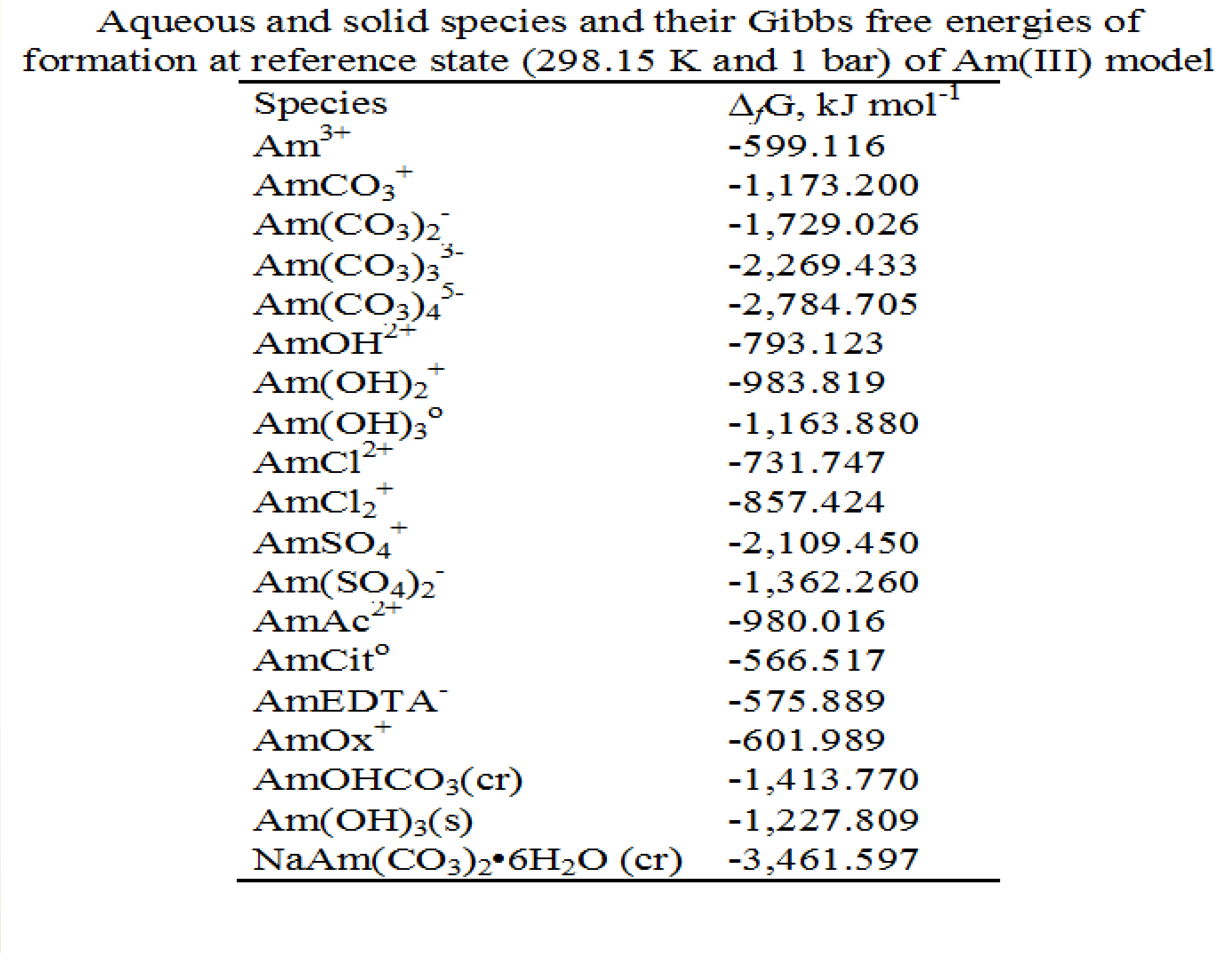




Experimental Results: $m_{Nd(III)}$



WIPP THERMODYNAMIC MODEL: Am(III) MODEL

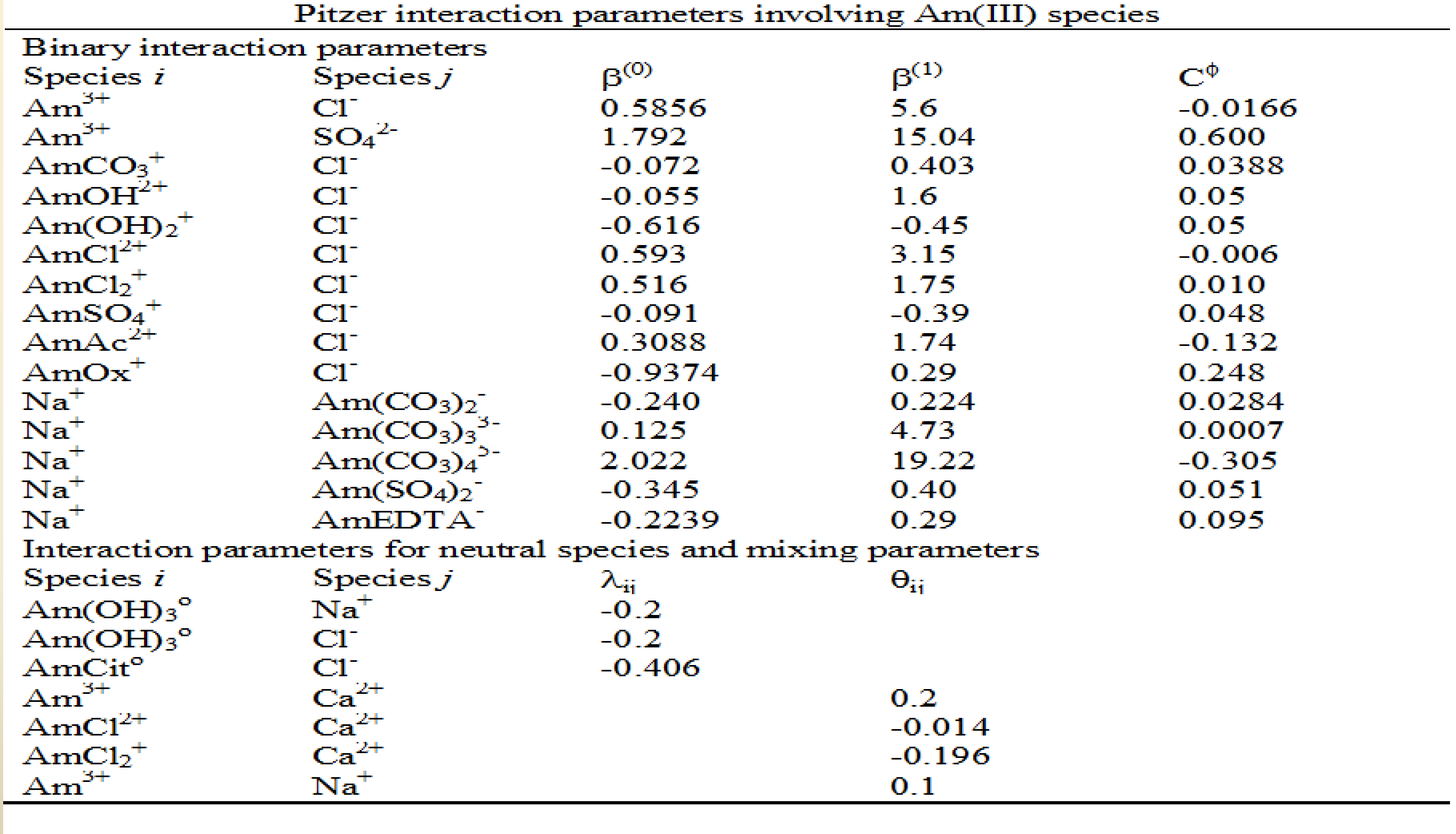


Aqueous and solid species and their Gibbs free energies of formation at reference state (298.15 K and 1 bar) of Am(III) model

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
$NaAm(CO_3)_2 \bullet 6H_2O$ (cr)	-3,461.597

From [5] Xiong, Y.-L., 2013. Extension of The WIPP Actinide Oxidation State Analog Models to Elevated Temperatures under Reducing Conditions. Sandia National Laboratories, Albuquerque, NM, SAND2013-8258c.

WIPP THERMODYNAMIC MODEL: Am(III) MODEL, Pitzer Parameters

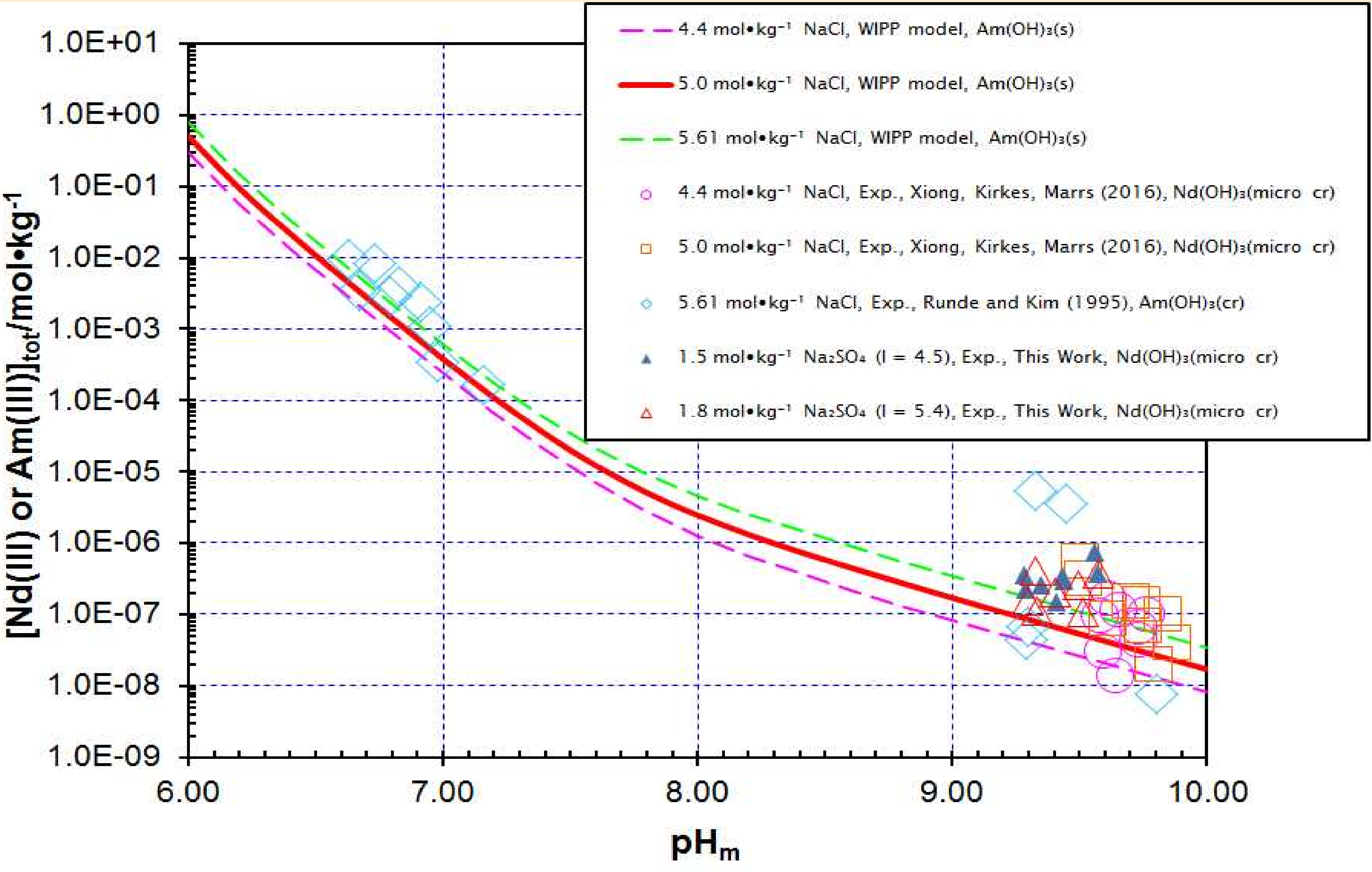


Pitzer interaction parameters involving Am(III) species

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	

From [6] Xiong, Leigh, Domski, 2016. WIPP Thermodynamic Database History and Recent Revisions. Sandia National Laboratories, Albuquerque, NM, SAND2016-1298PE.

Comparison of Nd(OH)$_3$(micro cr) Solubility in NaCl and Na$_2$SO$_4$



Pitzer model of $Nd_2(SO_4)_3 \bullet 8H_2O$ in H_2SO_4

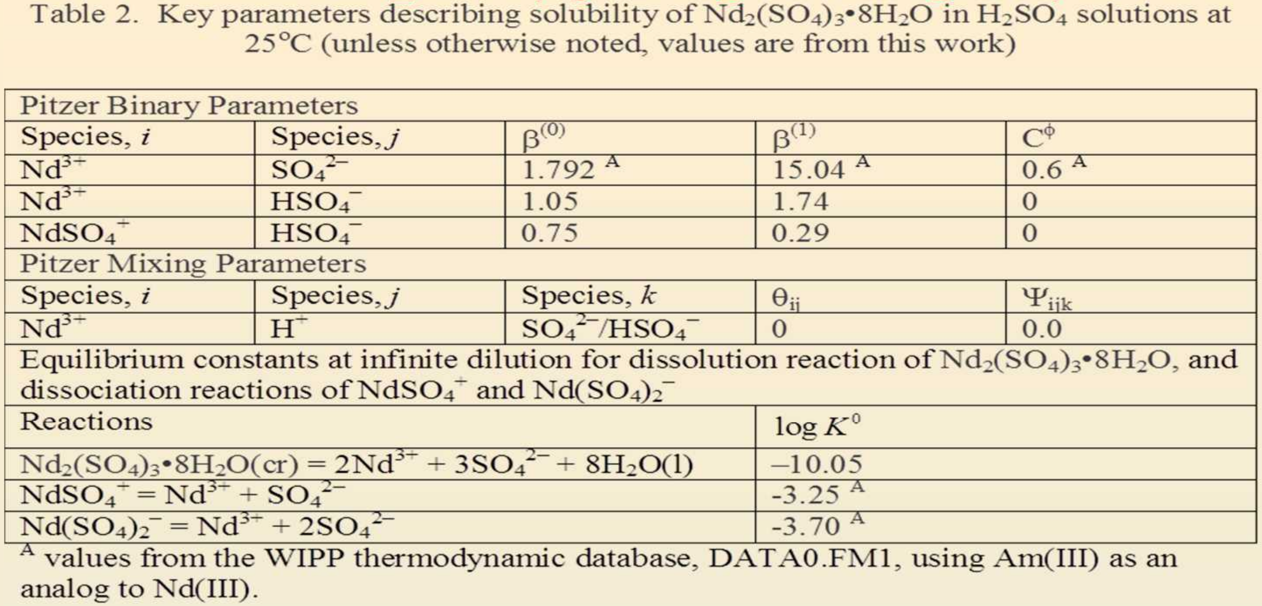


Table 2. Key parameters describing solubility of $Nd_2(SO_4)_3 \bullet 8H_2O$ in H_2SO_4 solutions at 25°C (unless otherwise noted, values are from this work)

Pitzer Binary Parameters				
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Nd^{3+}	SO_4^{2-}	1.792 [A]	15.04 [A]	0.6 [A]
Nd^{3+}	HSO_4^-	1.05	1.74	0
$NdSO_4^+$	HSO_4^-	0.75	0.29	0
Pitzer Mixing Parameters				
Species, *i*	Species, *j*	Species, *k*	θ_{ij}	Ψ_{ijk}
Nd^{3+}	H^+	SO_4^{2-}/HSO_4^-	0	0.0
Equilibrium constants at infinite dilution for dissolution reaction of $Nd_2(SO_4)_3 \bullet 8H_2O$, and dissociation reactions of $NdSO_4^+$ and $Nd(SO_4)_2^-$				
Reactions			$\log K^0$	
$Nd_2(SO_4)_3 \bullet 8H_2O(cr) = 2Nd^{3+} + 3SO_4^{2-} + 8H_2O(l)$			–10.05	
$NdSO_4^+ = Nd^{3+} + SO_4^{2-}$			-3.25 [A]	
$Nd(SO_4)_2^- = Nd^{3+} + 2SO_4^{2-}$			-3.70 [A]	

[A] values from the WIPP thermodynamic database, DATA0.FM1, using Am(III) as an analog to Nd(III).

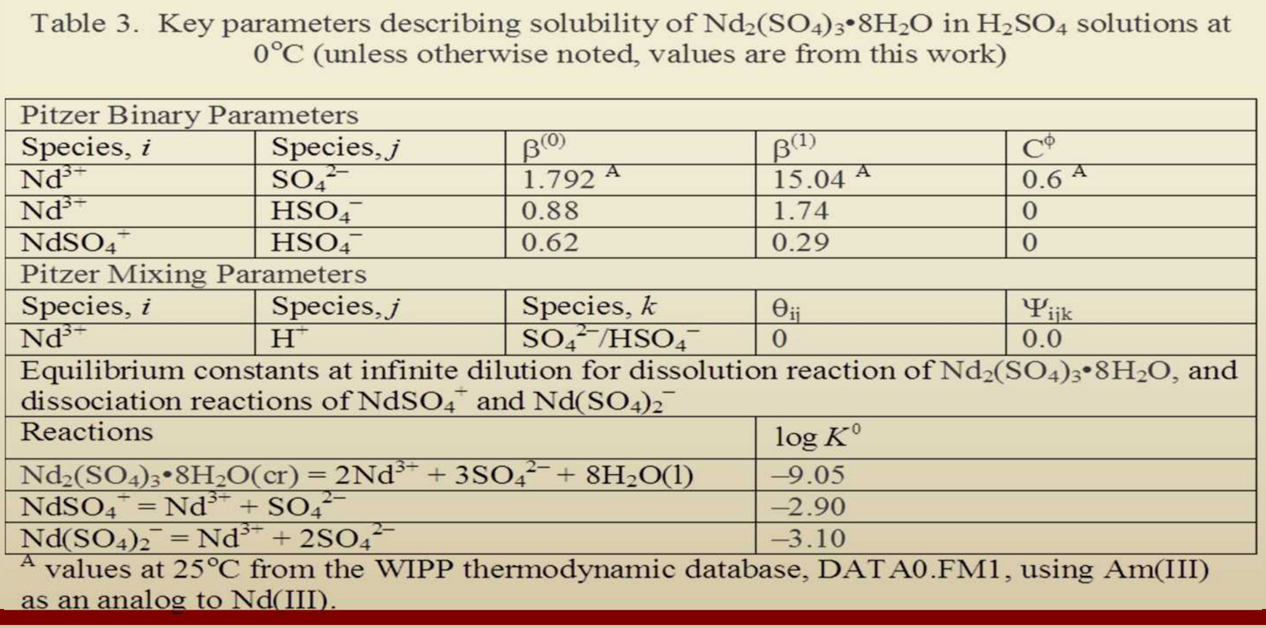
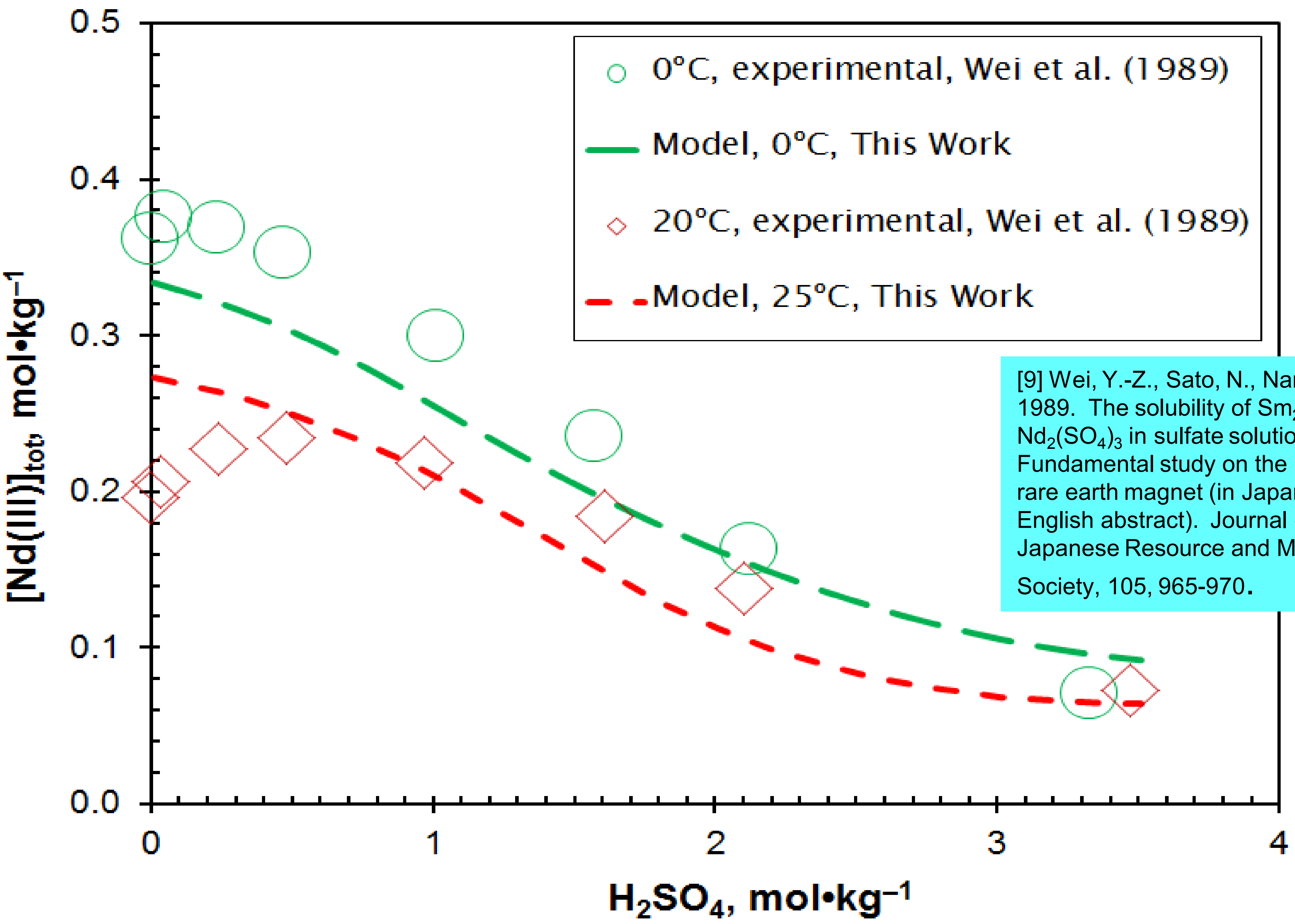


Table 3. Key parameters describing solubility of $Nd_2(SO_4)_3 \bullet 8H_2O$ in H_2SO_4 solutions at 0°C (unless otherwise noted, values are from this work)

Pitzer Binary Parameters				
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Nd^{3+}	SO_4^{2-}	1.792 [A]	15.04 [A]	0.6 [A]
Nd^{3+}	HSO_4^-	0.88	1.74	0
$NdSO_4^+$	HSO_4^-	0.62	0.29	0
Pitzer Mixing Parameters				
Species, *i*	Species, *j*	Species, *k*	θ_{ij}	Ψ_{ijk}
Nd^{3+}	H^+	SO_4^{2-}/HSO_4^-	0	0.0
Equilibrium constants at infinite dilution for dissolution reaction of $Nd_2(SO_4)_3 \bullet 8H_2O$, and dissociation reactions of $NdSO_4^+$ and $Nd(SO_4)_2^-$				
Reactions			$\log K^0$	
$Nd_2(SO_4)_3 \bullet 8H_2O(cr) = 2Nd^{3+} + 3SO_4^{2-} + 8H_2O(l)$			–9.05	
$NdSO_4^+ = Nd^{3+} + SO_4^{2-}$			–2.90	
$Nd(SO_4)_2^- = Nd^{3+} + 2SO_4^{2-}$			–3.10	

[A] values at 25°C from the WIPP thermodynamic database, DATA0.FM1, using Am(III) as an analog to Nd(III).

Pitzer model of $Nd_2(SO_4)_3 \bullet 8H_2O$ in H_2SO_4



[9] Wei, Y.-Z., Sato, N., Nanjo, M., 1989. The solubility of $Sm_2(SO_4)_3$ and $Nd_2(SO_4)_3$ in sulfate solutions: Fundamental study on the recycling of rare earth magnet (in Japanese with English abstract). Journal of Japanese Resource and Materials Society, 105, 965-970.

Summary

- We have conducted long-term solubility experiments concerning neodymium hydroxide [$Nd(OH)_3$(micro cr)] at Sandia National Laboratories Carlsbad Facility in 0.01 to 1.8 mol•kg^{-1} Na_2SO_4 (ionic strength to 5.4 mol•kg^{-1}) at 25°C.
- $Nd(OH)_3$(micro cr) was synthesized hydrothermally under well-controlled conditions.
- Solubility of $Nd(OH)_3$(micro cr) in Na_2SO_4 solutions is similar to that in NaCl solutions.
- We have developed a Pitzer model to describe solubility of $Nd_2(SO_4)_3•8H_2O$ in H_2SO_4 solutions at 0°C and 25°C.
- The model will have a wide range of applications, including actinide solubility in nuclear waste disposal, recovery of REE from acidic mine drainage, and recycling REE.

References

[1] Xiong, Y.-L., Lord, A.C., 2008. Experimental investigations of the reaction path in the $MgO–CO_2–H_2O$ system in solutions with various ionic strengths, and their applications to nuclear waste isolation, Applied Geochemistry, Vol.23, p. 1634.

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[7] Xiong, Y.-L., Kirkes, L., Marrs, C., 2016. A Pitzer Model for Am(III)/Nd(III) Hydroxide Solubility in $NaCl-H_2O$ at 298.15 K to High Ionic Strengths: Experimental Validation and Model Applications. Sandia National Laboratories, Albuquerque, NM, SAND2016-5527J.

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[9] Wei, Y.-Z., Sato, N., Nanjo, M., 1989. The solubility of $Sm_2(SO_4)_3$ and $Nd_2(SO_4)_3$ in sulfate solutions: Fundamental study on the recycling of rare earth magnet (in Japanese with English abstract). Journal of Japanese Resource and Materials Society, 105, 965-970.