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Experimental Determination of Solubility of $\text{Nd(OH)}_3(\text{s})$ In Na_2SO_4 Solutions to High Ionic Strength: Applications to Nuclear Waste Isolation

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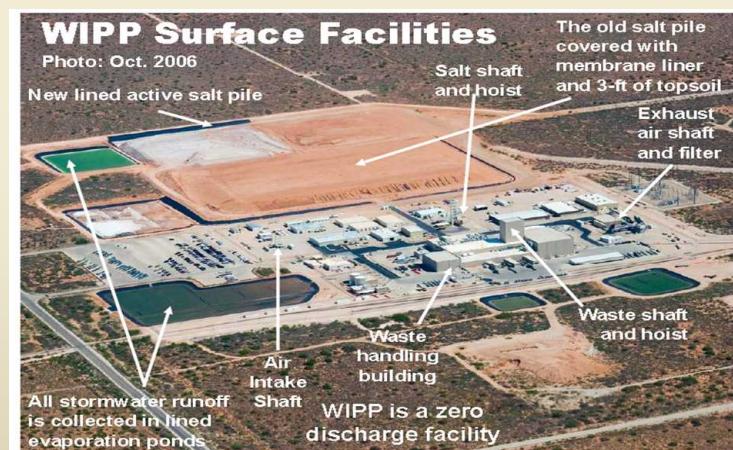
This research is funded by the WIPP programs administered by the Office of Environmental Management (EM) of the U.S. Department of Energy.

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:
 - The sulfate concentrations in the Waste Isolation Pilot Plant (WIPP) brines
 - Generic Weep Brine (GWB): $0.203 \text{ mol}\cdot\text{kg}^{-1}$ and
 - U.S. Energy Research and Development Administration Well 6 (ERDA-6): $0.187 \text{ mol}\cdot\text{kg}^{-1}$ [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 $2.2 \text{ mol}\cdot\text{kg}^{-1}$ [2].
- However, solubilities of actinides in sulfate solutions are not well studied.

[1] Y.-L. Xiong, A.C. Lord, Experimental investigations of the reaction path in the $\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$ 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 $\text{Ca}(\text{OH})_2$ in simulated radioactive sulfate liquid waste. *Journal of American Ceramics Society*, Vol. 83, p. 882, 2000.

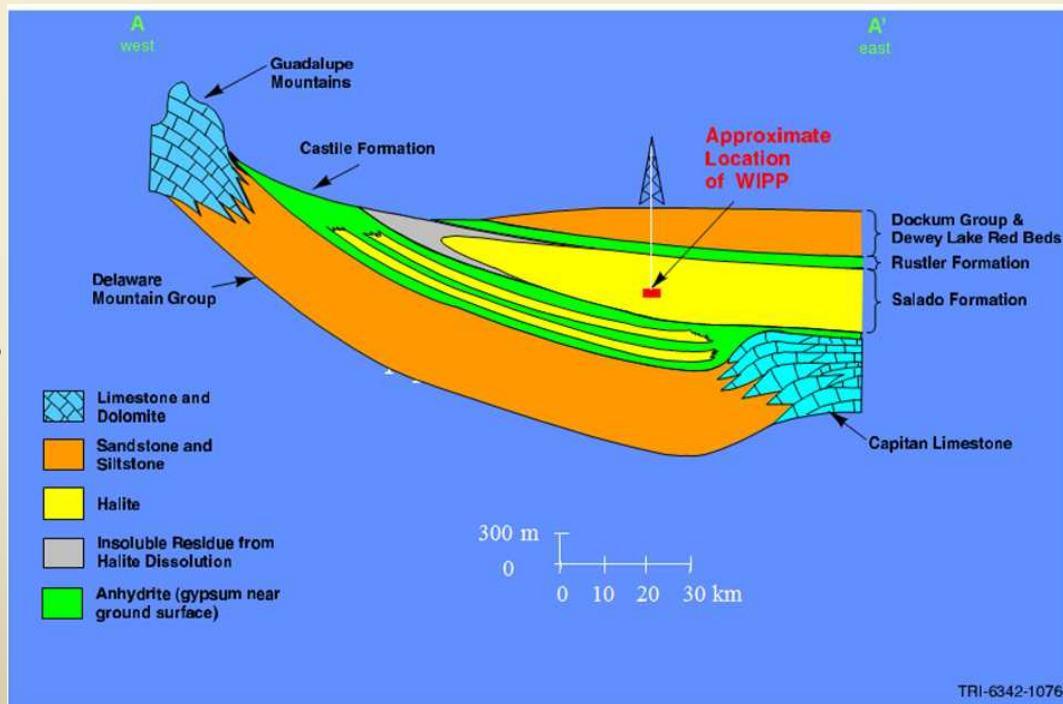


INTRODUCTION (Continued)

- In deep 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).
 - The experimental data on Nd(III) as a function of ionic strength → Am(III)
- There have been numerous studies concerning solubilities of Nd(OH)₃(s) in NaCl and NaClO₄ solutions.
- In this work, we investigate solubilities of Nd(OH)₃(micro cr) in Na₂SO₄ 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])

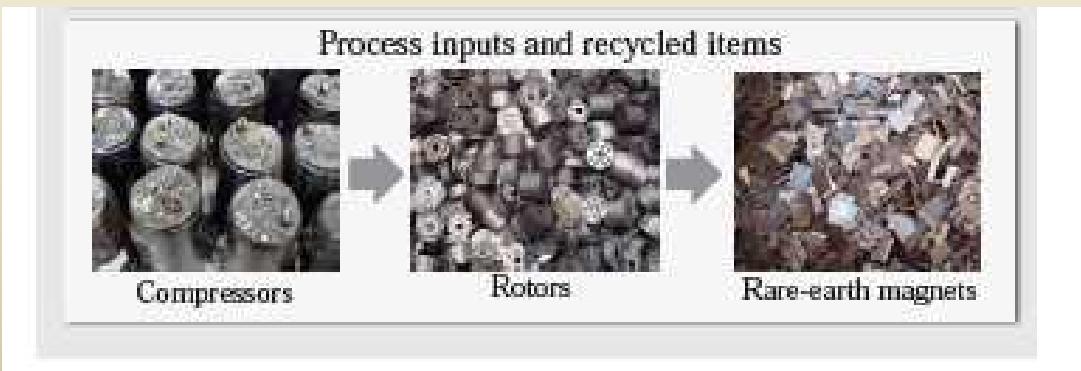
Element	Effective Ionic Radius for 6 Coordination Number in Å	Effective Ionic Radius for 8 Coordination Number in Å
Nd(III)	0.983	1.109
Am(III)	0.975	1.09
Cm(III)	0.97	----
Pu(III)	1.00	----



PURPOSE OF THIS STUDY

- To measure solubility of Nd(OH)_3 (micro cr) in Na_2SO_4 solutions to high ionic strengths at 298.15 K in the long-term experiments.
- To develop a Pitzer model to describe solubilities in solutions with high ionic strengths:
 - Nd(OH)_3 (micro cr) from this work, and
 - $\text{Nd}_2(\text{SO}_4)_3 \bullet 8\text{H}_2\text{O}$ 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

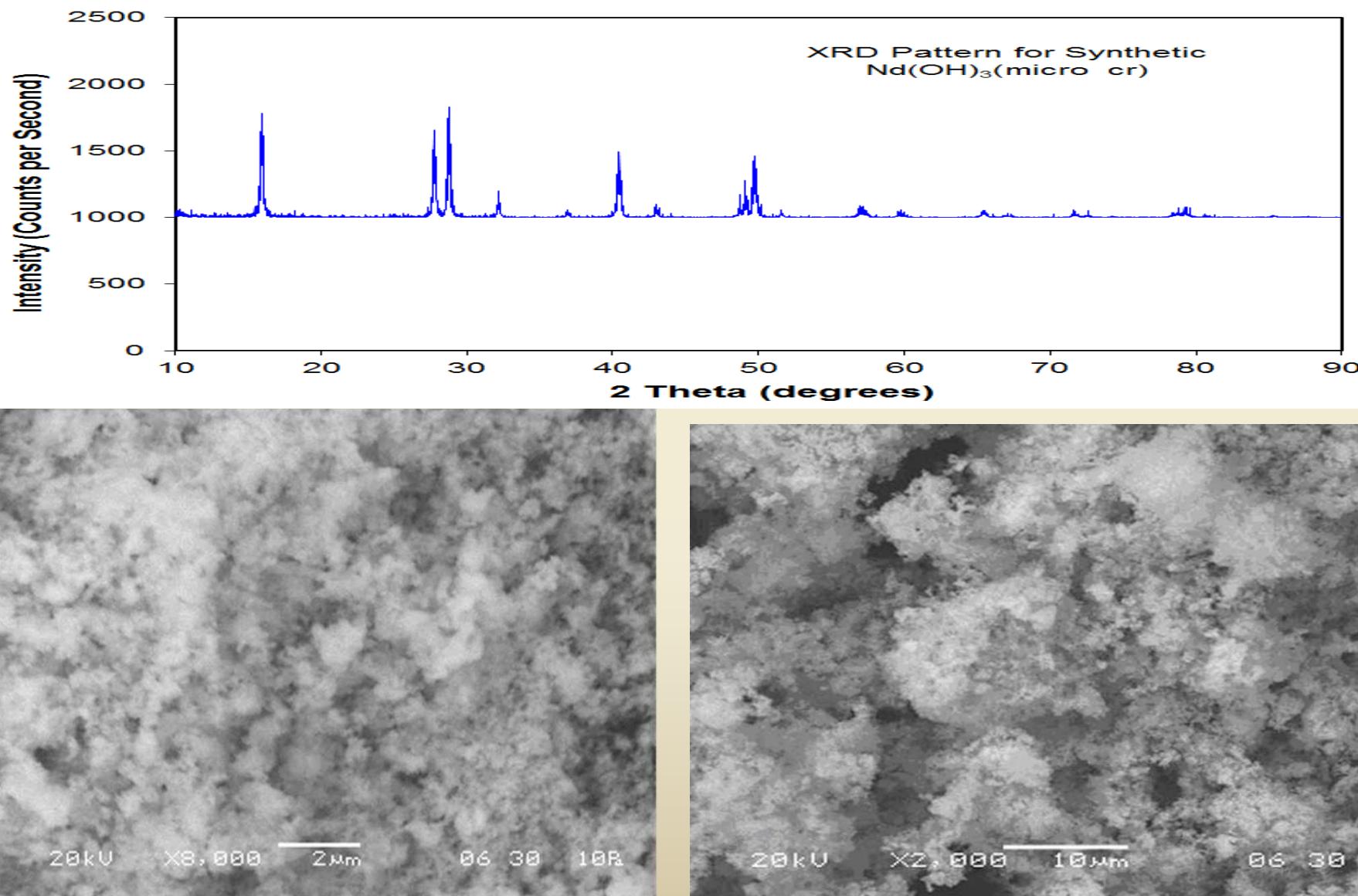
- Experimental Apparatus: All experiments are conducted in a glovebox under Ar + H₂ atmosphere in which O₂ and CO₂ are excluded.
- Experimental conditions: T = 298.15 K
- Starting material: Synthetic Nd(OH)₃(micro cr)
- Hydrogen ion concentrations (pH_m, molal scale) of the experimental systems are controlled/buffered 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 Θ
- Nd(III) concentrations are analyzed using ICP-MS.
- Na concentrations are analyzed using ICP-AES.
- Sulfate concentrations are analyzed using IC.
- Approaching equilibrium from undersaturation.
- Supporting solutions: 0.01 to 1.8 mol•kg⁻¹ Na₂SO₄

EXPERIMENTAL METHOD: Synthesis of Nd(OH)₃(micro cr)

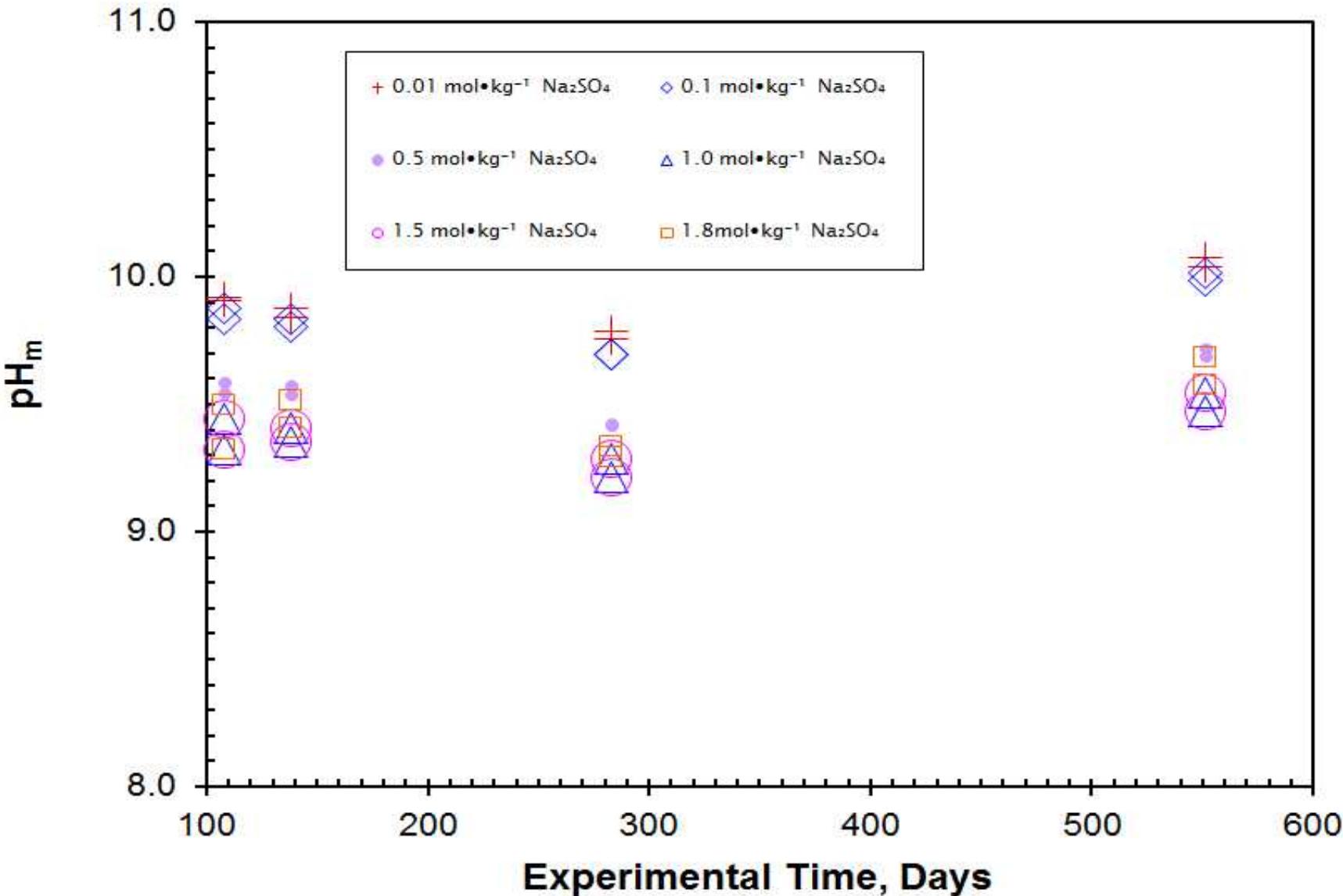
- Having well-defined starting material with high purity is of fundamental importance to the successes in solubility experiments.
 - High purity crystalline Nd(OH)₃(micro cr) is synthesized according to the procedure described by Wood et al. [4].
 - High purity Nd₂O₃ is first loaded with deaerated DI 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 Nd₂O₃ with deaerated DI water at 473.15 K in Paar® reaction vessels for a period of two weeks.

[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.

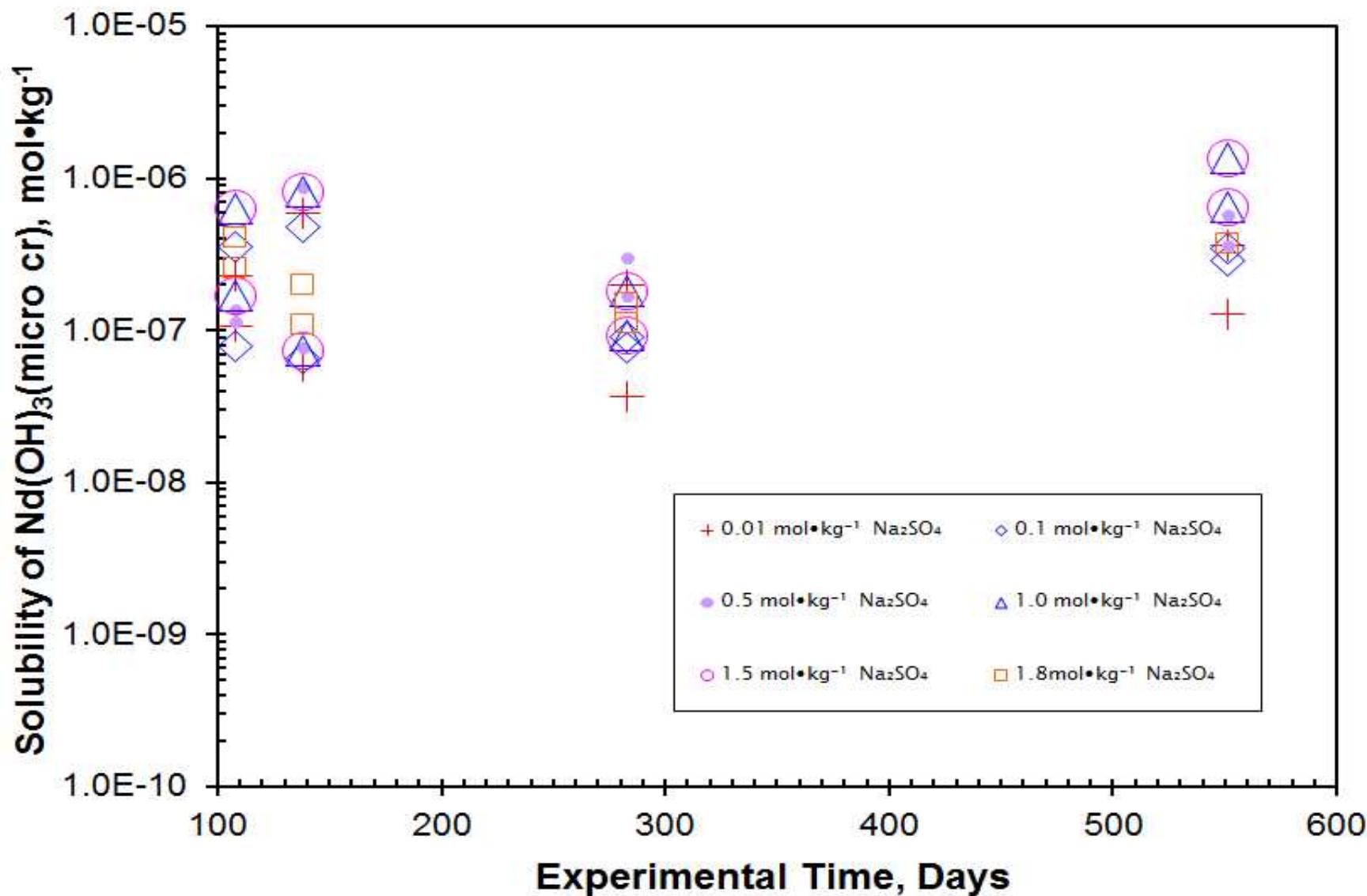
XRD Pattern and SEM Image



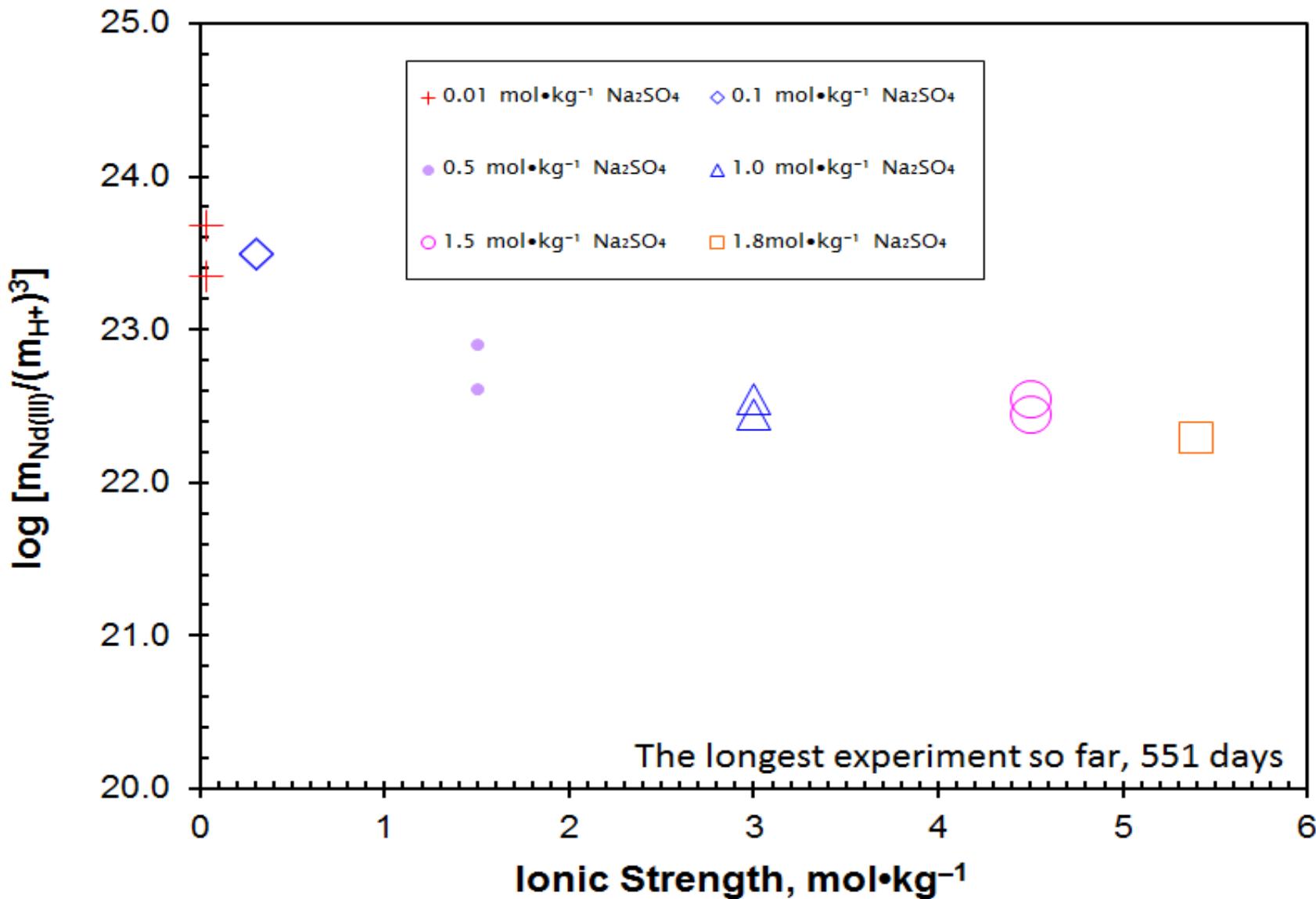
Experimental Results: Hydrogen ion concentrations



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



Experimental Results: Ionic Strength Dependence



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	$\Delta_f G, \text{ kJ mol}^{-1}$
Am^{3+}	-599.116
AmCO_3^+	-1,173.200
$\text{Am}(\text{CO}_3)_2^-$	-1,729.026
$\text{Am}(\text{CO}_3)_3^{3-}$	-2,269.433
$\text{Am}(\text{CO}_3)_4^{5-}$	-2,784.705
AmOH^{2+}	-793.123
$\text{Am}(\text{OH})_2^+$	-983.819
$\text{Am}(\text{OH})_3^\circ$	-1,163.880
AmCl^{2+}	-731.747
AmCl_2^+	-857.424
AmSO_4^+	-2,109.450
$\text{Am}(\text{SO}_4)_2^-$	-1,362.260
AmAc^{2+}	-980.016
AmCit°	-566.517
AmEDTA^-	-575.889
AmOx^+	-601.989
$\text{AmOHCO}_3(\text{cr})$	-1,413.770
$\text{Am}(\text{OH})_3(\text{s})$	-1,227.809
$\text{NaAm}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O} (\text{cr})$	-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

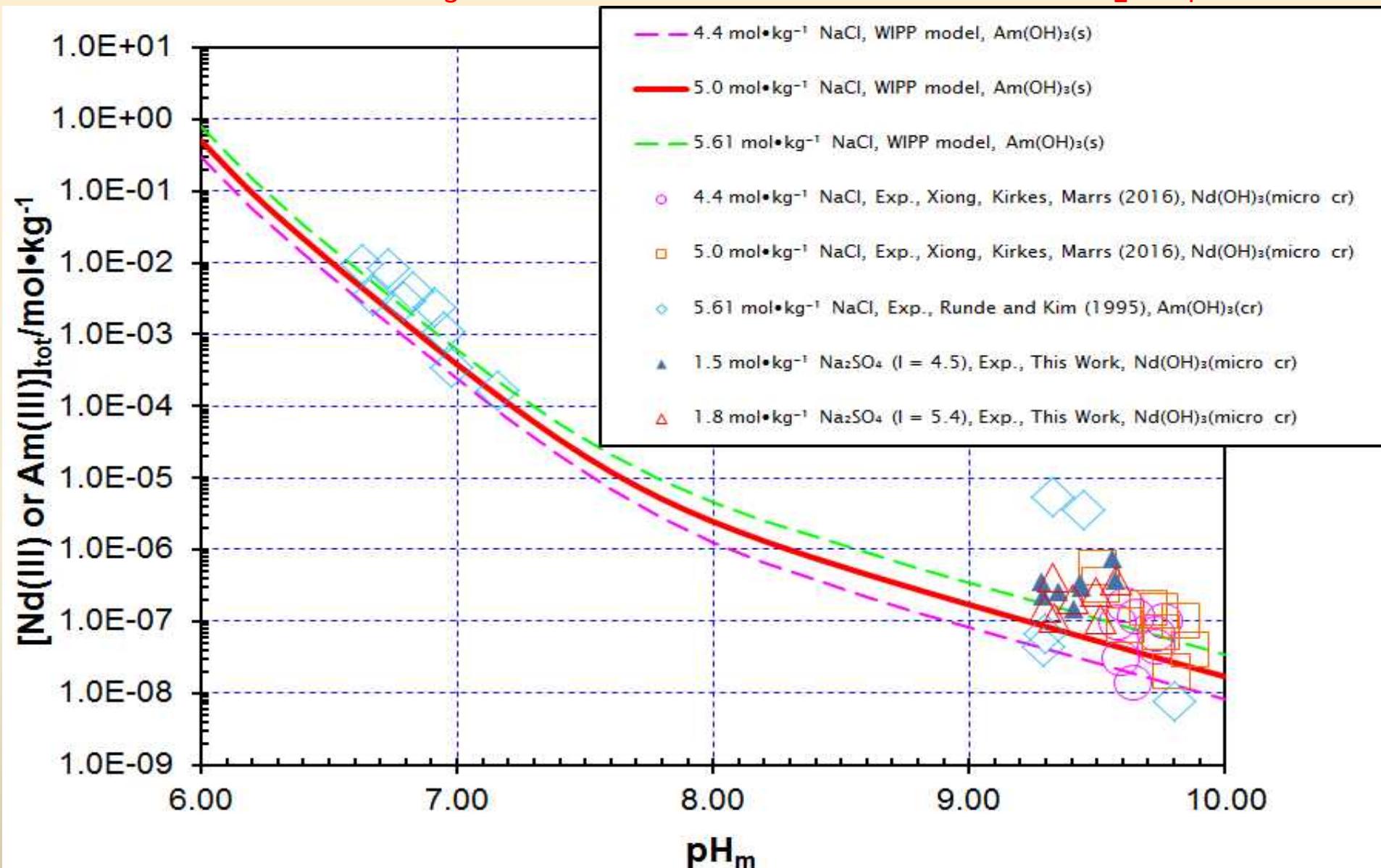
Species i	Species j	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ
Am ³⁺	Cl ⁻	0.5856	5.6	-0.0166
Am ³⁺	SO ₄ ²⁻	1.792	15.04	0.600
AmCO ₃ ⁺	Cl ⁻	-0.072	0.403	0.0388
AmOH ²⁺	Cl ⁻	-0.055	1.6	0.05
Am(OH) ₂ ⁺	Cl ⁻	-0.616	-0.45	0.05
AmCl ²⁺	Cl ⁻	0.593	3.15	-0.006
AmCl ₂ ⁺	Cl ⁻	0.516	1.75	0.010
AmSO ₄ ⁺	Cl ⁻	-0.091	-0.39	0.048
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 ⁰	Na ⁺	-0.2	
Am(OH) ₃ ⁰	Cl ⁻	-0.2	
AmCit ⁰	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.

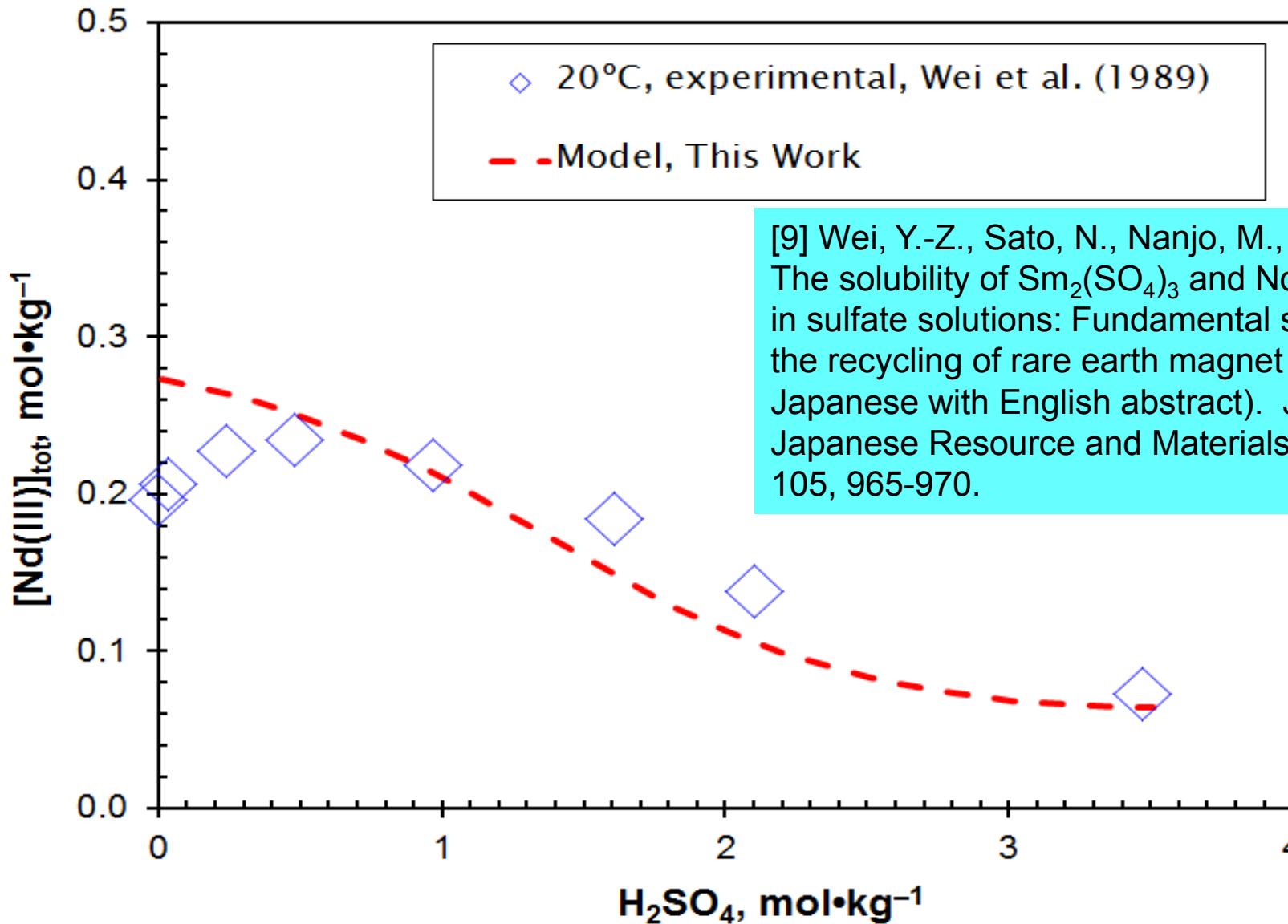
Comparison of Nd(OH)_3 (micro cr) Solubility in NaCl and Na_2SO_4



Work in Progress

- Develop a Pitzer model to describe the solubility behavior of Nd(OH)_3 (micro cr) in Na_2SO_4 solutions, and of $\text{Nd}_2(\text{SO}_4)_3 \bullet 8\text{H}_2\text{O}$ in H_2SO_4 solutions.
- Applications:
 - Nuclear waste management
 - Recycling rare earth elements, including neodymium (Nd)

Pitzer model of $\text{Nd}_2(\text{SO}_4)_3 \bullet 8\text{H}_2\text{O}$ in H_2SO_4 : Preview



Summary

- Long-term solubility experiments concerning neodymium hydroxide Nd(OH)_3 (micro cr) have been conducted at Sandia National Laboratories Carlsbad Facility in 0.01 to $1.8 \text{ mol}\cdot\text{kg}^{-1}$ Na_2SO_4 at 298.15 K.
- Nd(OH)_3 (micro cr) was synthesized hydrothermally under well-controlled conditions.
- The pH_m of the experimental systems are controlled/buffered by the solubility of Nd(OH)_3 (micro cr).
- Solubility of Nd(OH)_3 (micro cr) in Na_2SO_4 solutions is similar to that in NaCl solutions.
- Nd(OH)_3 (micro cr) is a stable phase, even in concentrated Na_2SO_4 solutions.

References

- [1] Xiong, Y.-L., Lord, A.C., 2008. Experimental investigations of the reaction path in the MgO–CO₂–H₂O system in solutions with various ionic strengths, and their applications to nuclear waste isolation, *Applied Geochemistry*, Vol.23, p. 1634.
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- [3] Shannon, S.D., 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallography A*, Vol. 32, p. 751, 1976.
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- [6] Xiong, Y.-L., Leigh, C.D., Domski, P., 2016. WIPP Thermodynamic Database History and Recent Revisions. Sandia National Laboratories, Albuquerque, NM, SAND2016-1298PE.
- [7] Xiong, Y.-L., Kirkes, L., Marrs, C., 2016. A Pitzer Model for Am(III)/Nd(III) Hydroxide Solubility in NaCl-H₂O 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 Sm₂(SO₄)₃ and Nd₂(SO₄)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.