SAND2017-12808C

Am(III)/Nd(III) Interactions with Borate: Experimental Investigations of $Nd(OH)_3$(micro cr) Solubility in NaCl Solutions in Equilibrium with Borax

East Asia Forum on Radioactive Waste Management (EAFORM)

November 27-29, 2017, Osaka, Japan

Yongliang Xiong, Leslie Kirkes, Jandi Knox, Cassie Marrs, Heather Burton

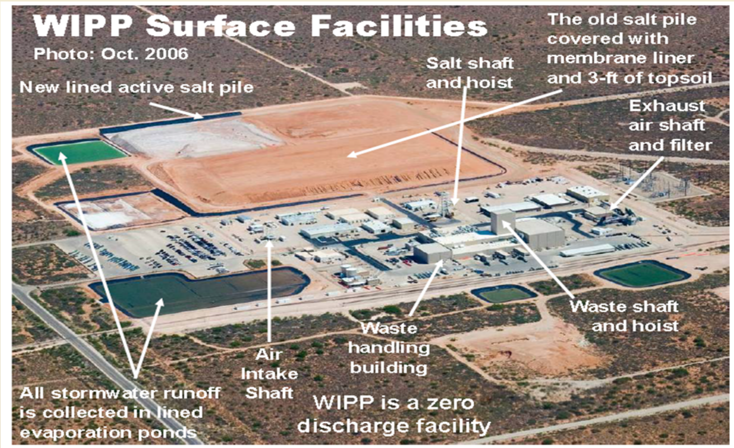
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525..
This research is funded by the WIPP programs administered by the Office of Environmental Management (EM) of the U.S Department of Energy. SAND2017-xxxxxC

OUTLINE OF PRESENTATION

- Introduction
- Objective of This Work
- Experimental Method
- WIPP Borate Model
- Experimental Results and Outline of Thermodynamic Calculations
- Summary

INTRODUCTION

- The accurate knowledge of actinide solubilities that could be dissolved in natural brines is important to safe disposal of nuclear waste.
- Recent experimental work indicates that borate could form a relatively strong complex with Nd(III) ($NdHB_4O_7^{2+}$, $\log \beta_1 = 4.99 \pm 0.30$) at 25°C [1], an analog to Am(III).
- Therefore, the assessment of contributions of borate complexation to solubility of Am(III) is needed.
- Borate is a species with significantly high concentrations in natural brines:
  - The borate concentrations in the Waste Isolation Pilot Plant (WIPP) brines
    - Generic Weep Brine (GWB): 0.180 mol•kg^{-1} and
    - U.S. Energy Research and Development Administration Well 6 (ERDA-6): 0.0692 mol•kg^{-1} [2]

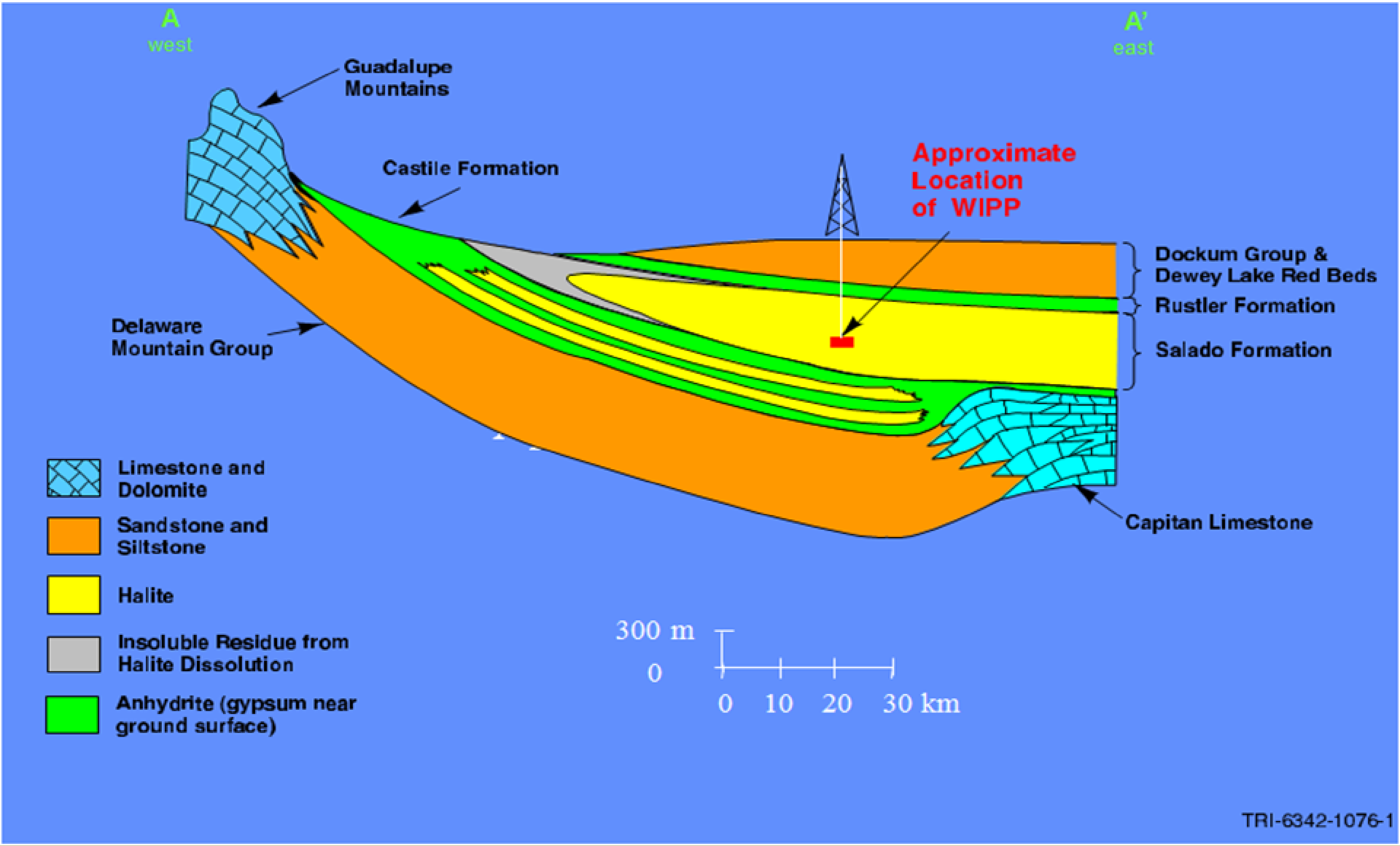


---

[1] Borkowski, M., Richmann, M., Reed, D.T., and Xiong, Y.-L., 2010. Complexation of Nd(III) with tetraborate ion and its effect on actinide(III) solubility in WIPP brine. Radiochimica Acta 98, 577-582.

[2] 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.

WASTE ISOLATION PILOT PLANT (WIPP)



OBJECTIVE OF THIS STUDY

- To measure solubility of $Nd(OH)_3$(micro cr) in NaCl solutions saturated with borax ($Na_2B_4O_7 \bullet 10H_2O$) at 298.15 K in long-term experiments
- The reason for performing experiments at high borate concentrations saturated with borax:
  - It has been observed that tincalconite ($Na_2B_4O_7 \bullet 5H_2O$) can form when borosilicate glasses as waste form for high level nuclear waste (HLW) are corroded under the repository conditions [3].
  - Borax has the same solubility as tincalconite in terms of borate.
  - A previous study [4] was conducted at much lower borate concentrations; therefore the effect of borate on solubility of $Nd(OH)_3$(micro cr) has not been fully assessed.

---

[3] Zhang, Z., Gan, X., Wang, L. and Xing, H., 2012. Alteration Development of the Simulated HLW Glass at High Temperature in Beishan Underground Water. *International Journal of Corrosion*, *2012*.

[4] K. Hinz, M. Altmaier, X. Gaona, T. Rabung, D. Schild, M. Richmann, D.T. Reed, E.V. Alekseev, and H. Geckeis, H., New journal of chemistry 39, 849 (2015).

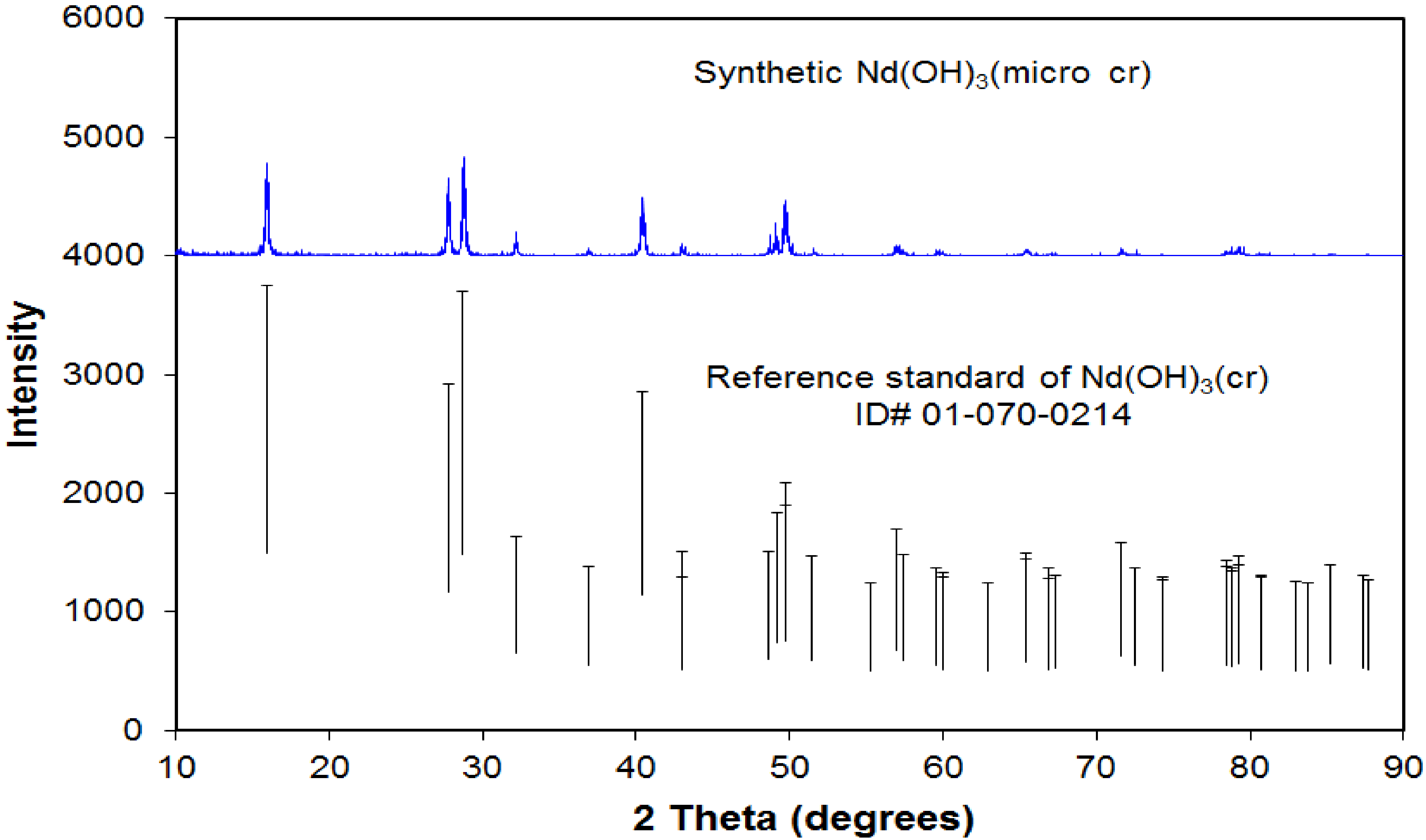
EXPERIMENTAL METHOD

- Experimental Apparatus: All experiments are conducted in a glovebox under N_2 + H_2 atmosphere in which oxygen 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.
- Nd(III) concentrations are analyzed using ICP-MS.
- Na and boron concentrations are analyzed using ICP-AES.
- Chloride concentrations are analyzed using IC.
- Approaching equilibrium from undersaturation
- Supporting solutions:
  - Up to 5.0 $mol \bullet kg^{-1}$ NaCl

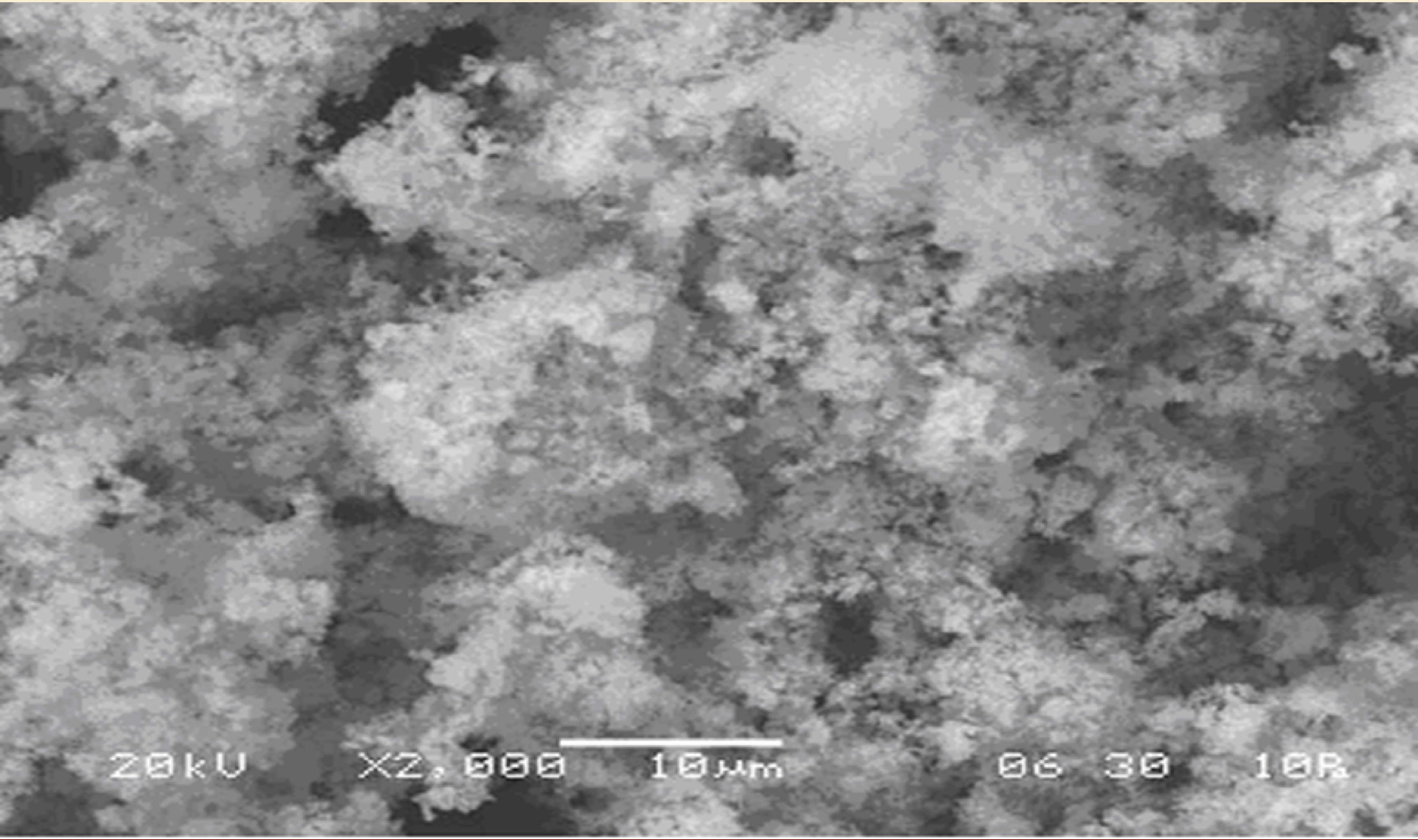
EXPERIMENTAL METHOD: Synthesis of $Nd(OH)_3$(micro cr)

- Having well-defined starting material with high purity is of fundamental importance to the success of solubility experiments.
- 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.
- The reaction vessels are put back into the glovebox, and opened. The synthesized $Nd(OH)_3$(micro cr) is dried in the glovebox.

XRD Pattern of Starting Material: $Nd(OH)_3$(micro cr)



SEM Image of Starting Material: $Nd(OH)_3$(micro cr)



The WIPP Borate Model

Table 1. The WIPP borate model for the Na–$B(OH)_3$–Cl system (from DATA0.FM2) used for evaluation of formation constant for $AmHB_4O_7^{2+}$

Pitzer Binary Interaction Cofficients					
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Reference
Na^+	$B(OH)_4^-$	–0.0427	0.089	0.0114	[5]
Na^+	$B_3O_3(OH)_4^-$	–0.056	–0.910		[5]
Na^+	$B_4O_5(OH)_4^{2-}$	–0.11	–0.40		[5]
Pitzer Mixing Parameters and Interaction Parameters Involving Neutral Species					Reference
Species, *i*	Species, *j*	Species, *k*	θ_{ij} or λ_{ij}	Ψ_{ijk} or ζ_{ijk}	[5]
$B(OH)_4^-$	Cl^-	Na^+	–0.065	–0.0073	[5]
$B_3O_3(OH)_4^-$	Cl^-	Na^+	0.12	–0.024	[5]
$B_4O_5(OH)_4^{-2}$	Cl^-	Na^+	0.074	0.026	[5]
$B(OH)_3(aq)$	Cl^-		0.091		[5]
$B(OH)_3(aq)$	$B_3O_3(OH)_4^-$		–0.20		[5]
$B(OH)_3(aq)$	Na^+		–0.097		[5]
$NaB(OH)_4(aq)$	Na^+		0.093		[6]
Equilibrium Constant for Complex Formation					
Reaction			log K		Reference
$Na^+ + B(OH)_4^- = NaB(OH)_4(aq)$			0.25		[6]

[5] Felmy, A.R., and Weare, J.H. (1986) The prediction of borate mineral equilibria in natural waters: Applications to Searles Lake, California. Geochimica et Cosmochimica Acta, 50, no. 12, 2771–2783.
[6] Xiong, Y.-L., Kirkes, L., and Westfall, T., 2013. Experimental Determination of Solubilities of Sodium Tetraborate (Borax) in NaCl Solutions, and A Thermodynamic Model for the Na–$B(OH)_3$–Cl–SO_4 System to High Ionic Strengths at 25 °C. American Mineralogist 98, 2030–2036.

Equilibrium Constants Consistent with the WIPP Borate Model (from [7])

Table 2. Equilibrium constant for $AmHB_4O_7^{2+}$ at infinite dilution at 25 °C (298.15 K), and its associated Pitzer interaction parameters

Reaction			log K at 25 °C	
$4B(OH)_4^- + 3H^+ + Am^{3+} \rightleftharpoons AmHB_4O_7^{2+} + 9H_2O(l)$			37.3416	
Pitzer Binary Interaction Cofficients				
Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
$AmHB_4O_7^{2+}$	Cl^-	0.9163	1.74	0

Table 3. Equilibrium constant for $AmB_9O_{13}(OH)_4(cr)$ at infinite dilution at 25 °C (298.15 K)

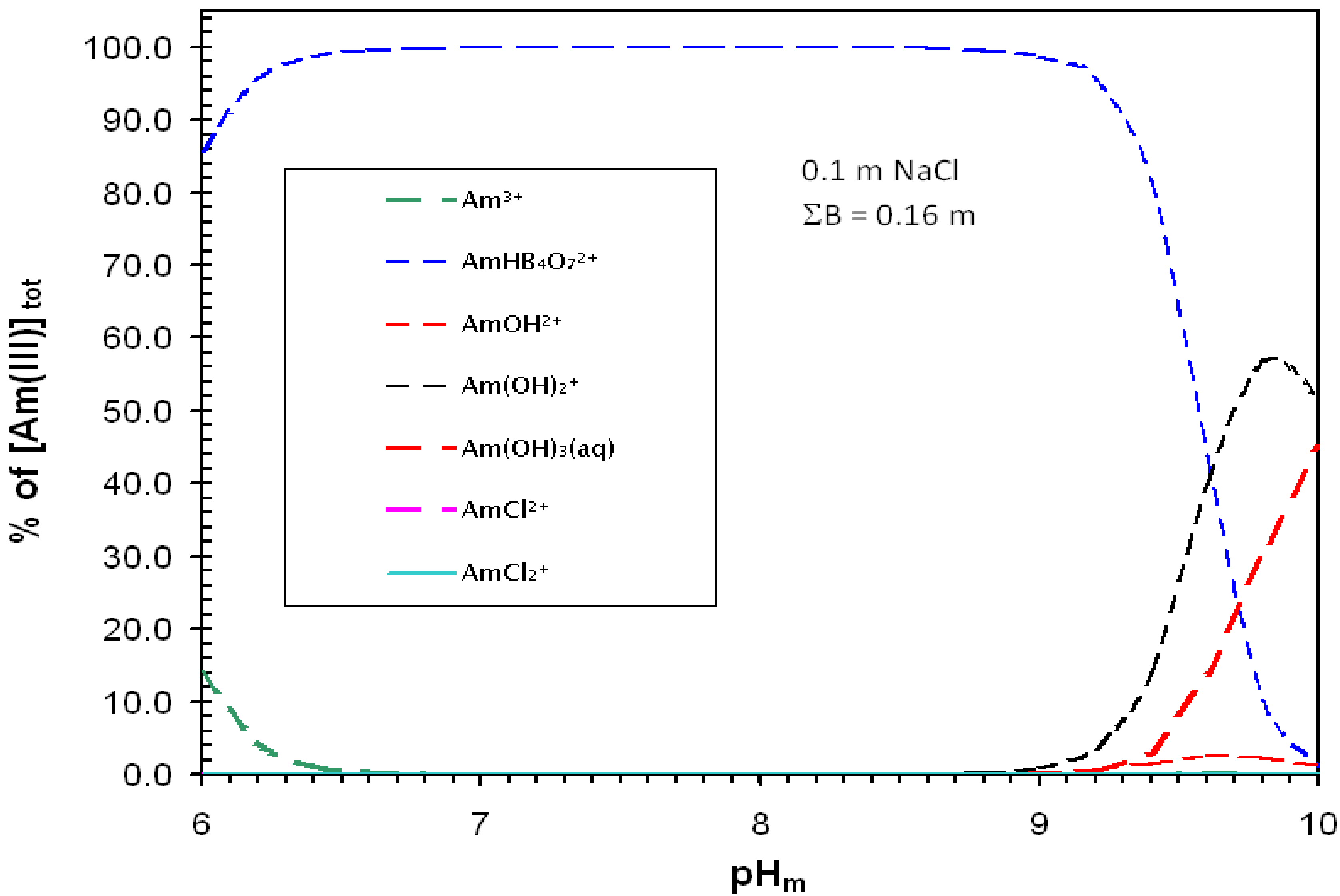
Reaction	log K at 25 °C
$AmB_9O_{13}(OH)_4(cr) + 19H_2O(l) \rightleftharpoons Am^{3+} + 9B(OH)_4^- + 6H^+$	–79.00±0.30

[7] Xiong, Y., 2017. Solution Chemistry for Actinide Borate Species to High Ionic Strengths: Equilibrium Constants for $AmHB_4O_7^{2+}$ And $AmB_9O_{13}(OH)_4(cr)$ and Their Importance to Nuclear Waste Management. *MRS Advances*, *2*(13), pp.741-746.

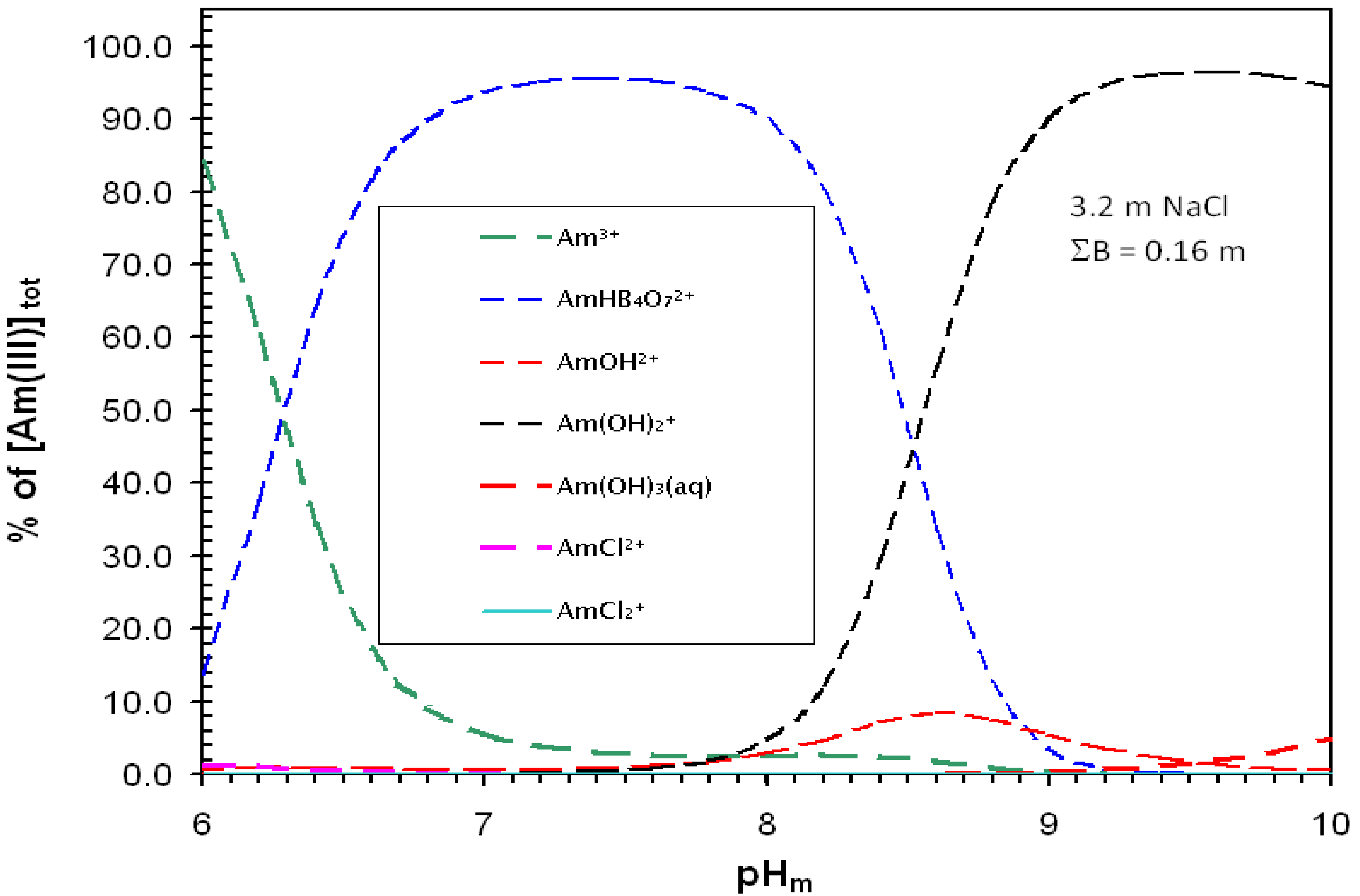
Experimental Results and Outline of Thermodynamic Calculations

- Speciation calculations are performed in NaCl solutions ranging from 0.1 mol•kg^{-1} to 5.6 mol•kg^{-1}.
- Speciation calculations are performed at a constant borate concentration of 0.16 mol•kg^{-1}.
- Am(III) species include Am^{3+}, $AmCl^{2+}$, $AmCl_2^{+}$, $AmOH^{2+}$, $Am(OH)_2^{+}$, $Am(OH)_3$(aq), and $AmHB_4O_7^{2+}$.
- Solubility calculations for $Am(OH)_3$(s) are performed in NaCl solutions ranging from 0.01 mol•kg^{-1} to 5.6 mol•kg^{-1} without borate.
- Solubility calculations for $AmB_9O_{13}(OH)_4$(cr) are performed in NaCl solutions ranging from 0.01 mol•kg^{-1} to 5.6 mol•kg^{-1} at a constant borate concentration of 0.16 mol•kg^{-1}.

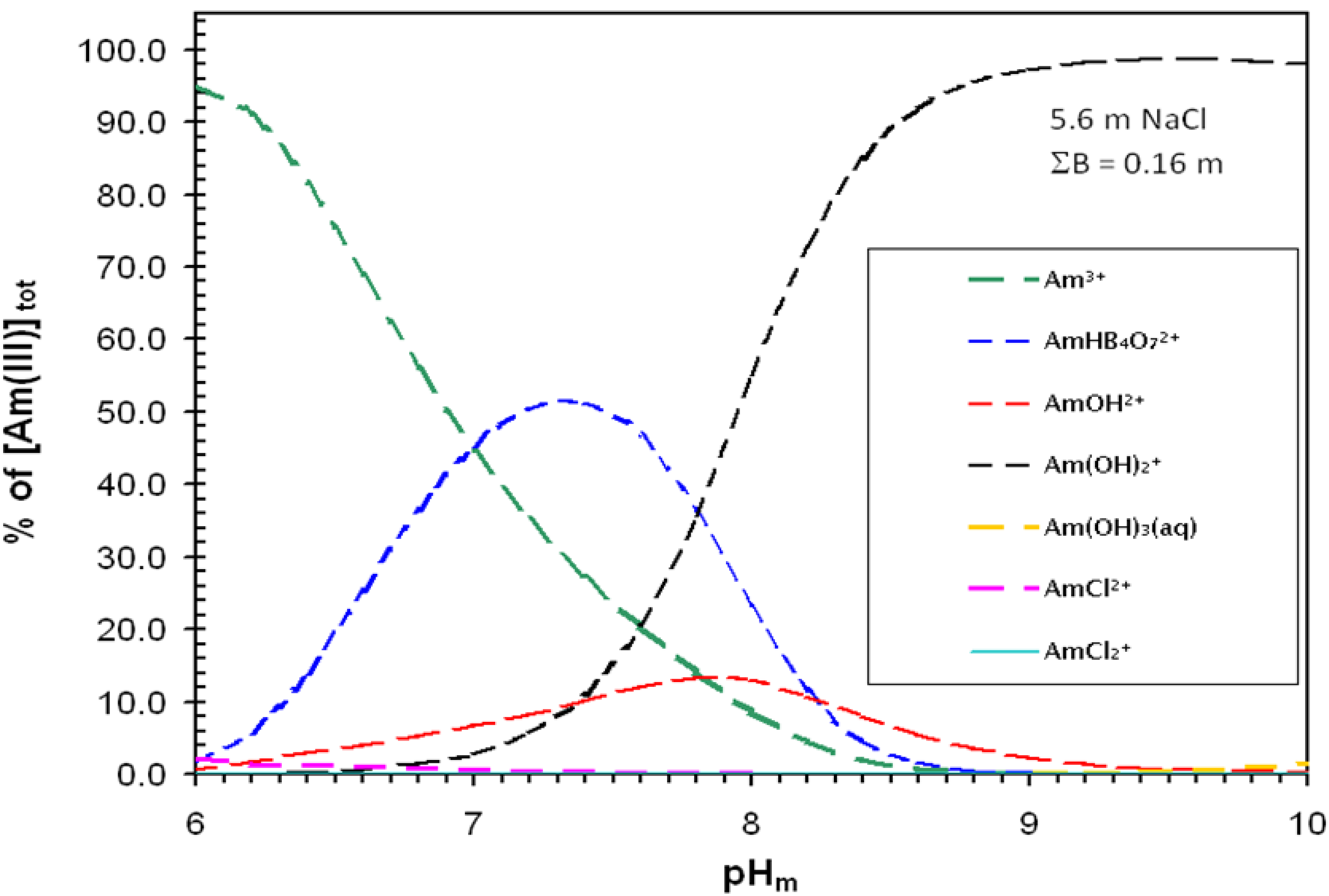
Speciation of Am(III) in NaCl in the Presence of Borate



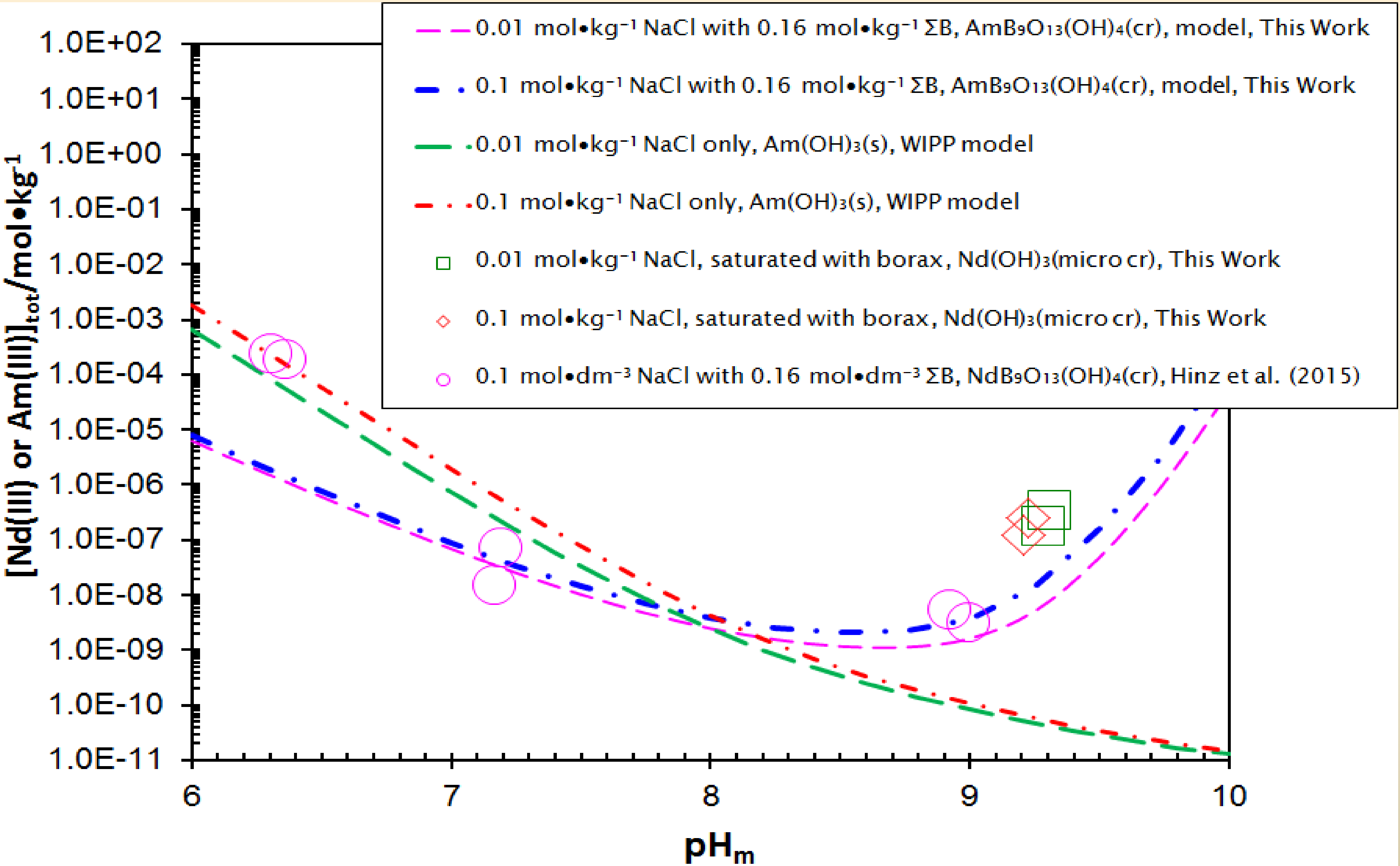
Speciation of Am(III) in NaCl in the Presence of Borate



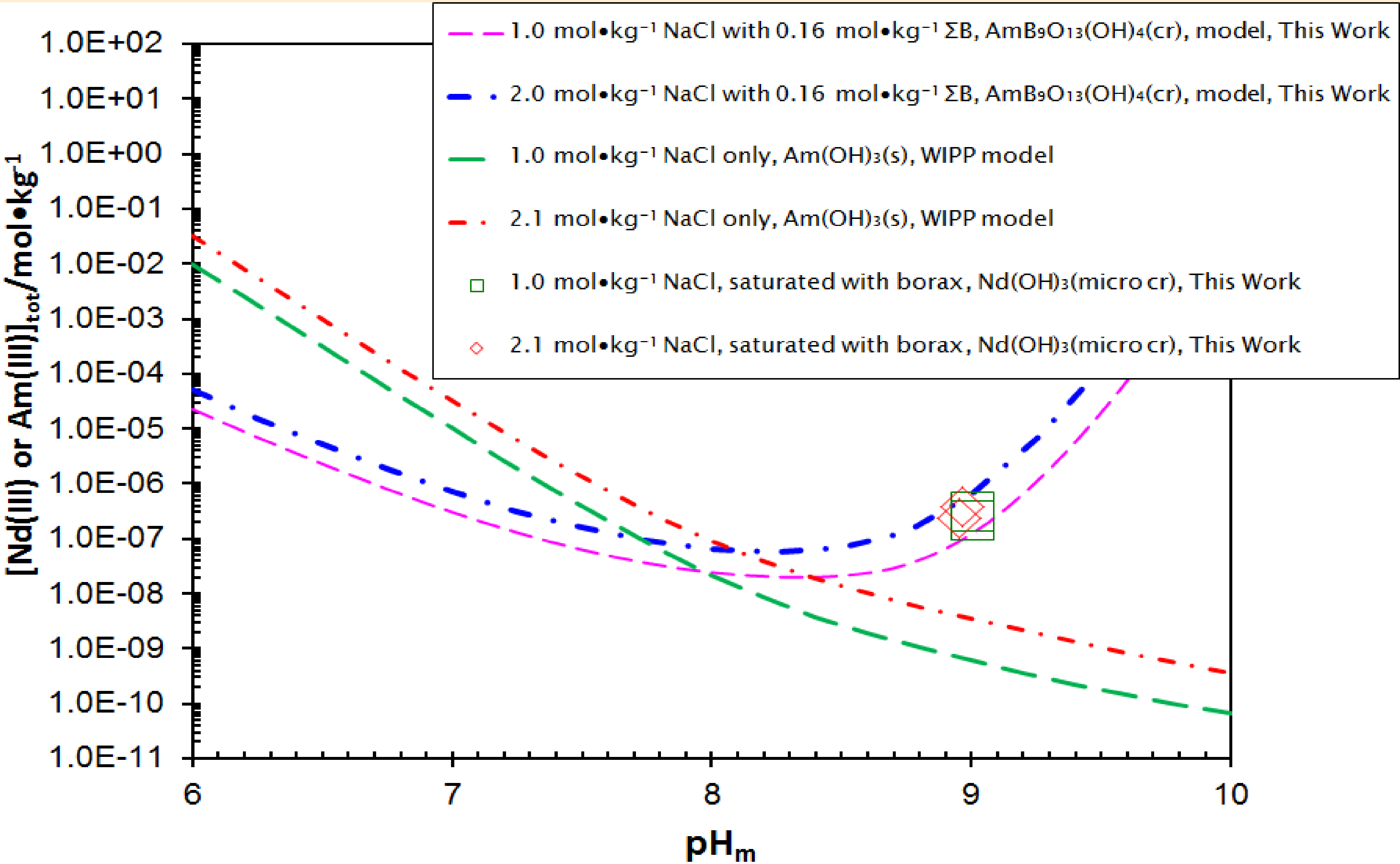
Speciation of Am(III) in NaCl in the Presence of Borate



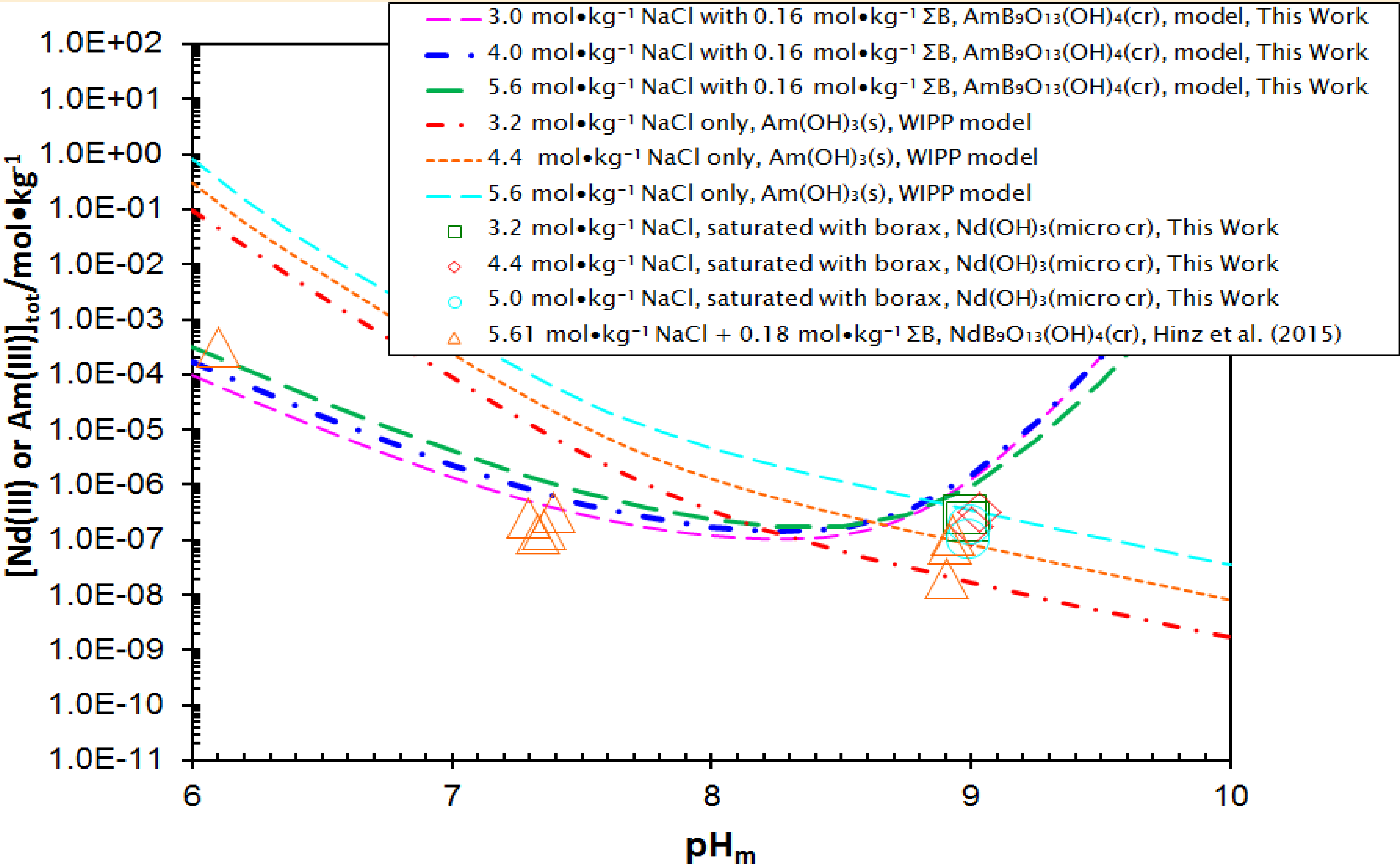
Solubility of Am(III) in NaCl in the Presence of Borate



Solubility of Am(III) in NaCl in the Presence of Borate



Solubility of Am(III) in NaCl in the Presence of Borate



Summary

- In this work, we have conducted solubility measurements regarding $Nd(OH)_3$(micro cr) in NaCl solutions saturated with borax at 25^{o}C.
- Our results indicate that high borate concentrations (~0.5 mol•kg^{-1}) in 0.01 and 0.1 mol•kg^{-1} NaCl solutions have an obvious effect on Nd(III) and Am(III).
- At such a high concentration of borate, borate can
  - Significantly enhance the solubility of $Nd(OH)_3$(micro cr).
  - or $NdB_9O_{13}(OH)_4$(cr) may control the solubility.