

*IMPORTANT NOTICE: The current official version of this document is available via the Sandia National Laboratories WIPP Online Documents web site. A printed copy of this document may not be the version currently in effect.*

## SANDIA NATIONAL LABORATORIES WASTE ISOLATION PILOT PLANT

### AP-171 Revision 0

### Analysis Plan for Derivation of Thermodynamic Properties Including Pitzer Parameters for Solubility Studies of Rare Earth Elements

#### Task 4.4.2.2.1

Effective Date: April 6, 2016

Authored by:	<u>Yongliang Xiong</u> Print Name	<u>Original signed by Yongliang Xiong</u> Signature	<u>April 6, 2016</u> Date
Authored by:	<u>Jonathan Icenhower</u> Print Name	<u>Original signed by Jonathan Icenhower</u> Signature	<u>4/6/16</u> Date
Reviewed by:	<u>Paul Domski</u> Print Name Technical Reviewer	<u>Original signed by Shelly R. Nielsen for</u> Signature	<u>4-6-16</u> Date
Reviewed by:	<u>Shelly R. Nielsen</u> Print Name Quality Assurance Reviewer	<u>Original signed by Shelly R. Nielsen</u> Signature	<u>4-6-16</u> Date
Approved by:	<u>Christi Leigh</u> Print Name Department Manager	<u>Original signed by Shelly R. Nielsen for</u> Signature	<u>4-6-16</u> Date

## Table of Contents

<b>1</b>	<b>Introduction and Objectives .....</b>	<b>3</b>
	1.1 Introduction.....	3
	1.2 Objectives .....	3
<b>2</b>	<b>Approach .....</b>	<b>4</b>
	2.1 Project Resources.....	4
	2.2 Method.....	4
	2.3 Project Tasks and Milestones.....	5
<b>3</b>	<b>Software List .....</b>	<b>5</b>
<b>4</b>	<b>Tasks .....</b>	<b>5</b>
<b>5</b>	<b>Special Considerations .....</b>	<b>8</b>
<b>6</b>	<b>Applicable Procedures.....</b>	<b>8</b>
<b>7</b>	<b>References .....</b>	<b>8</b>

# 1 Introduction and Objectives

## 1.1 Introduction

To model the solution chemistry for brines relevant to the WIPP repository, WIPP PA uses the Pitzer model (Pitzer 1973, 1975) to evaluate the activity coefficients for the various components of the brine. The WIPP brines, both GWB and ERDA-6, contain significant concentrations of borate. As borate could potentially complex with Nd(III) (Borkowski et al., 2010), an analog to Am(III), a comprehensive thermodynamic model for borate is needed to accurately account for the contributions of borate to the solubility of Am(III) in the WIPP brines. To date, the WIPP thermodynamic database does not incorporate adequate thermodynamic descriptions for borate species, especially  $\text{NdHB}_4\text{O}_7^{2+}$  species. To model the contribution of the borate complex with Am(III) to total Am(III) solubility, an accurate description regarding the interactions between  $\text{NdHB}_4\text{O}_7^{2+}$  species and major ions in the WIPP brines is required. As a result, we must obtain the parameters necessary for such a modeling.

This Analysis Plan (AP) is part of an effort to calculate thermodynamic properties including Pitzer parameters for the interactions between  $\text{NdHB}_4\text{O}_7^{2+}$  species and major ions in the WIPP brines. Experimental data being collected under Test Plan TP 12-02, *Experimental Investigation of Borate Interactions with Rare Earth Elements Under the WIPP Relevant Conditions at Sandia National Laboratories Carlsbad Facility*, will be used to provide the inputs for this analysis.

The purpose of the analytical work described in this analysis plan is to utilize the data obtained from the experimental work performed in Test Plan TP 12-02, as well as other solubility data in the open literature, as inputs to derive thermodynamic properties including Pitzer interaction parameters. Using the NONLIN package, and/or the minimization routine written as a Python script coupled with EQ3/6 Version 8.0a, we will derive various parameters for the different sets of species from the relevant experimental data.

The thermodynamic properties obtained will be incorporated into the WIPP EQ3/6 database for the Pitzer model (i.e., DATA0.FM2). The updated WIPP thermodynamic database, in addition to the current modeling capacities, will enable us to model adequately the influence of borate on solution chemistry of WIPP brines. Therefore, this study is considered a compliance decision analysis.

## 1.2 Objectives

The objective of this AP is to derive thermodynamic properties of borate species. The thermodynamic properties to be derived include dimensionless standard chemical potentials ( $\mu^\circ/RT$ )/equilibrium constants and Pitzer interaction parameters, at 25°C and 1 bar, for the majority of tasks.

## 2 Approach

To achieve the objectives of this AP two software programs, either NONLIN or the Python script coupled with EQ3/6 (see following Project Resources), will be used, depending on what data are available. Both of these programs employ inverse fitting methods to obtain the best-fit parameters, and accomplish this by minimizing the difference between the experimental data and the model response.

### 2.1 Project Resources

Sandia National Laboratories has developed a computer program called NONLIN (Babb, 1996; Version 2.01, Ismail, 2008). NONLIN fits parameters for the Pitzer's aqueous electrolyte model based on experimental data for stability constants of aqueous complexes, mineral solubility for a simple system with less than, or equal to,  $\leq$  eight species, osmotic coefficients, electromotive force (e.m.f.), ion exchange data, and solvent extraction. Therefore, this computer program is suitable to achieving the objectives of this AP. In modeling stability constants, osmotic coefficients, e.m.f. data, ion exchange data, and solvent extraction, as a function of ionic strength, the NONLIN code needs to be used. In the user's manual for NONLIN, there are numerous examples of how to model experimental data. Notice that for solubility data, if there are more than one species contributing to the target total solubility, the solubility data have to be speciated before modeling. For example, if one has the total lead solubility data with PbO being a controlling phase in a NaCl medium, the total lead solubility data need to be speciated as  $\text{Pb}^{2+}$ ,  $\text{PbCl}^+$ ,  $\text{PbCl}_2(\text{aq})$ , and  $\text{PbCl}_3^-$  using the relevant conditional stability constants for  $\text{PbCl}^+$ ,  $\text{PbCl}_2(\text{aq})$ , and  $\text{PbCl}_3^-$  before modeling,

In addition, there is a Python minimization script (EQ3CodeModule.py) that can be coupled with EQ3NR calculations in the EQ3/6 Version 8.0a (Kirchner, 2012). In this minimization routine, the target thermodynamic parameter can be adjusted to minimize the difference, or to achieve reasonable difference, between the experimental value and predicted value. This minimization routine also can be used to minimize the saturation index by adjusting the target thermodynamic parameters. In this way, the target thermodynamic parameter can be derived. This minimization script is also suitable for achieving the objectives of this AP. In the user's manual written by Kirchner (2012), there are several examples showing how to obtain the optimized solubility constant by using the script. The Python script coupled with the EQ3/6 Version 8.0a is to be used for evaluation of solubility data to derive Pitzer parameters as well as equilibrium constants.

### 2.2 Method

The strategy in deriving thermodynamic properties is as follows. If the thermodynamic quantities of the experimental system at reference state are well known, the experimental data will be modeled as a function of ionic strength to derive Pitzer parameter(s) only. If one of the thermodynamic quantities of the experimental system at reference state, for instance, the solubility constant, is less well known, the experimental data will be modeled as a function of ionic strength to derive both the Pitzer parameter(s) and dimensionless standard chemical potential/equilibrium constant of the less well known thermodynamic quantity.

The detailed methodology follows that of AP-154, Revision 2 (Xiong, 2013).

The results obtained from running either NONLIN or the Python script will be evaluated and must meet the following acceptance criteria:

- 1) The fitted values of the Pitzer parameters should be of a similar magnitude compared to those in the peer reviewed literature for comparable interaction types. Many of these Pitzer parameters for these interactions may be found in the thermodynamic databases already in the WIPP records center, DATA0.FM2 (Domski, 2015; Xiong and Domski, 2016), DATA0.PIT, and DATA0.YPF. The absolute values of fitted parameters should usually be not larger than the absolute values in the literature by one magnitude. The reference to the literature values should be cited in documents reporting the results.
- 2) The differences between the measured data and the modeled predictions, e.g., the residuals, should form a curve that has a well-defined minimum when plotted versus the parameter values. The selected “best fit” parameters must correspond to the minimum, or are close to the minimum, in agreement with the first criterion.
- 3) Visual inspection of the model response using the best fit parameters in comparison with the experimental data demonstrates that they are in close agreement. Graphs showing such comparisons should be included in documents reporting the results.

## 2.3 Project Tasks and Milestones

There are three major tasks in this AP. The first major task is to compare baseline solubility from the well-constrained experiments without borate with the model predictions to assess the adequacy of the current model. Such a comparison would indicate whether some parameters in the Am(III) model without  $\text{NdHB}_4\text{O}_7^{2+}$  species need to be refitted. The second and third major tasks are to derive Pitzer parameters related to  $\text{NdHB}_4\text{O}_7^{2+}$  species and to compute formation constants and solubility constants from experimental data. The specific project tasks are detailed in Section 4. The majority of the tasks identified in this AP are planned to be completed by the end of calendar year 2017, and the milestones for each individual task are specified in Section 4.

## 3 Software List

The computer programs to be used are NONLIN Version 2.02 (system configuration: Oracle Sunfire); EQ3/6 Version 8.0a with execution platforms with Microsoft Window 7; and the Python minimization script tested under the execution platform of EPD\_Py25V4.3.0, where EPD stands for Enthought Python Distribution.

## 4 Tasks

The tasks of this AP are listed below, and milestones for each task are tabulated in Table 1:

- 1a. Baseline solubility of  $\text{Nd}(\text{OH})_3(\text{cr})$  in  $\text{Na}_2\text{SO}_4$  solutions without borate in comparison with the model predictions.

- 1b. Derivation of Pitzer binary parameters for the interaction between  $\text{NdHB}_4\text{O}_7^{2+}$  and the bulk electrolyte,  $\text{Na}_2\text{SO}_4$ .
- 2a. Baseline solubility of  $\text{Nd}(\text{OH})_3(\text{cr})$  in  $\text{NaCl}$  solutions without borate in comparison with the model predictions.
- 2b. Derivation of Pitzer binary parameters for the interaction between  $\text{NdHB}_4\text{O}_7^{2+}$  and the bulk electrolyte,  $\text{NaCl}$ .
- 2c. Baseline solubility of  $\text{Nd}(\text{OH})_3(\text{cr})$  in  $\text{MgCl}_2$  solutions without borate in comparison with the model predictions.
- 2d. Derivation of Pitzer binary parameters for the interaction between  $\text{NdHB}_4\text{O}_7^{2+}$  and the bulk electrolyte,  $\text{MgCl}_2$ .
3. Derivation of Pitzer binary parameters for the interaction between  $\text{NdHB}_4\text{O}_7^{2+}$  and the bulk electrolyte,  $\text{NaCl}+\text{MgCl}_2$ .
4. Validation of Pitzer parameters related to  $\text{NdHB}_4\text{O}_7^{2+}$  in  $\text{GWB}$  and  $\text{ERDA-6}$ .
- 5a. Determination of speciation of  $\text{Nd}(\text{III})$  in  $\text{NaOH}$  solutions (in combination with the experiments in  $0.01 \text{ m NaCl}$  with high  $\text{pH}$ 's) and derivation of related Pitzer parameters.
- 5b. Determination of solubility constant of  $\text{Nd}(\text{OH})_3(\text{cr})$  in  $\text{NaCl}$  solutions at elevated temperatures and derivation of related Pitzer parameters.

**Table 1. Milestones for each individual task**

<b>Task</b>	<b>Description</b>	<b>Responsible Individuals</b>	<b>Estimated Completion Date</b>
1a	Baseline solubility of Nd(OH) <sub>3</sub> (cr) in Na <sub>2</sub> SO <sub>4</sub> solutions without borate in comparison with the model predictions.	Xiong	12/31/2017
1b	Derivation of Pitzer binary parameters for the interaction between NdHB <sub>4</sub> O <sub>7</sub> <sup>2+</sup> and the bulk electrolyte, Na <sub>2</sub> SO <sub>4</sub> .	Xiong	12/31/2017
2a	Baseline solubility of Nd(OH) <sub>3</sub> (cr) in NaCl solutions without borate in comparison with the model predictions.	Xiong	12/31/2017
2b	Derivation of Pitzer binary parameters for the interaction between NdHB <sub>4</sub> O <sub>7</sub> <sup>2+</sup> and the bulk electrolyte, NaCl.	Xiong	12/31/2017
2c	Baseline solubility of Nd(OH) <sub>3</sub> (cr) in MgCl <sub>2</sub> solutions without borate in comparison with the model predictions.	Xiong	12/31/2017
2d	Derivation of Pitzer binary parameters for the interaction between NdHB <sub>4</sub> O <sub>7</sub> <sup>2+</sup> and the bulk electrolyte, MgCl <sub>2</sub> .	Xiong	12/31/2017
3	Derivation of Pitzer binary parameters for the interaction between NdHB <sub>4</sub> O <sub>7</sub> <sup>2+</sup> and the bulk electrolyte, NaCl+MgCl <sub>2</sub> .	Xiong	12/31/2017
4	Validation of Pitzer parameters related to NdHB <sub>4</sub> O <sub>7</sub> <sup>2+</sup> in GWB and ERDA-6.	Xiong	12/31/2017
5a	Determination of speciation of Nd(III) in NaOH solutions (in combination of the experiments in 0.01 m NaCl with high pH's) and derivation of related Pitzer parameters.	Xiong	12/31/2017
5b	Determination of speciation of Nd(III) in NaCl solutions at elevated temperatures and derivation of related Pitzer parameters.	Xiong/Icenhower	12/31/2017

## 5 Special Considerations

The thermodynamic properties including Pitzer interaction parameters derived in this AP will be summarized in memos/analysis report that will be submitted to the WIPP Records Center.

## 6 Applicable Procedures

All applicable WIPP QA procedures will be followed when conducting this AP.

- Training of personnel will be conducted in accordance with the requirements of NP 2-1, *Qualification and Training*.
- Analyses will be conducted and documented in accordance with the requirements of NP 9-1, *Analyses*.
- All software used will meet the requirements laid out in NP 19-1, *Software Requirements* and NP 9-1, as applicable.
- The analyses will be reviewed following NP 6-1, *Document Review Process*.
- All required records will be submitted to the WIPP Records Center in accordance with NP 17-1, *Records*.

## 7 References

- Babb, S.C. 1996. "NONLIN, Ver. 2.00, User's Manual." Unpublished report, January 31, 1996. Albuquerque, NM: Sandia National Laboratories. WPO 30740.
- 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.
- Domski, P.S. 2015. "Memo AP-173, EQ3/6 Database Update: DATA0.FM2" Memorandum to WIPP Records, October 27, 2015. Carlsbad, NM: Sandia National Laboratories. ERMS 564914.
- Ismail, A.E., 2008. "WIPP PA User's Manual for NONLIN, Version 2.01." Carlsbad, NM: Sandia National Laboratories, ERMS #54617.
- Kirchner, T.B., 2012. User's Manual for The EQ3CodeModule Version 1.00. Carlsbad, NM: Sandia National Laboratories. ERMS 557360.
- Pitzer, K. S. 1973. "Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations." *Journal of Physical Chemistry*, Vol. 77, no. 2, 268.
- Pitzer, K. S. 1975. "Thermodynamics of Electrolytes. V. Effects of Higher-Order Electrostatic Terms." *Journal of Solution Chemistry*, Vol. 4, no. 3, 249.
- Xiong, Y.-L., 2013. Sandia National Laboratories Waste Isolation Pilot Plant (WIPP) Analysis AP-154, Revision 2, Analysis Plan for Derivation of Thermodynamic Properties

Including Pitzer Parameters for Solubility Studies of Iron, Lead and EDTA. Carlsbad, NM: Sandia National Laboratories. ERMS 561114.

Xiong, Y-L., and P.S. Domski 2016. Updating the WIPP Thermodynamic Database. Analysis Report for AP-173, Revision 1. ERMS 565730. Sandia National Laboratories, Carlsbad, NM.

This work of authorship was prepared as an account of work sponsored by an agency of the United States Government. Accordingly, the United States Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so for United States Government purposes. Neither Sandia Corporation, the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately-owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by Sandia Corporation, the United States Government, or any agency thereof. The views and opinions expressed herein do not necessarily state or reflect those of Sandia Corporation, the United States Government or any agency thereof.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Parties are allowed to download copies at no cost for internal use within your organization only provided that any copies made are true and accurate. Copies must include a statement acknowledging Sandia Corporation's authorship of the subject matter.