Analysis Plan for Analysis Reports documenting Solubility and Complexation of Iron, Lead, Magnesium, Neodymium, and Boron in WIPP-Relevant Brines under Test Plans 00-07, 06-03, 08-02, 10-01, 12-02, 14-03, 14-05, 16-02, 19-01, and 20-01

Effective Date: __July 21, 2021__
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1 Introduction

1.1 Background

This Analysis Plan (AP) aims to provide consistent, streamlined analytical evaluation, parameterization, and uncertainty determination of experimental solubility and complexation data for WIPP-relevant metals and metalloids (iron, lead, magnesium, neodymium, and boron) generated under the following Test Plans (TPs):

1) TP 00-07 Revision 3: Experimental Study of WIPP Engineered Barrier MgO at Sandia National Laboratories Carlsbad Facility (Snider et al., 2004)
2) TP 06-03 Revision 1: Experimental Study of MgO Reaction Pathways and Kinetics (Deng et al., 2007)
3) TP 08-02 Revision 0: Iron, Lead, Sulfide, and EDTA Solubilities Test Plan (Ismail et al., 2008)
4) TP 10-01 Revision 0: Experimental Study of Thermodynamic Parameters of Borate in WIPP Relevant Brines at Sandia National Laboratories Carlsbad Facility (Xiong, 2010)
5) TP 12-02 Revision 2: Experimental Investigation of Borate Interactions with Rare Earth Elements Under the WIPP Relevant Conditions at SNL Carlsbad Facility (Xiong et al., 2015)
6) TP 14-03 Revision 0: Experimental Determination of the Existence of a Mobile Colloidal Fraction of Fe(II) Minerals in Two WIPP-relevant Brines (Jang, 2014)
7) TP 14-05 Revision 0: Test Plan for the Experimental Determination of the Solubilities of Iron and Lead in the Presence of Dissolved Hydrogen Sulfide Species (Brush and Xiong, 2014)
8) TP 16-02 Revision 0: Test Plan for the Measurement of the Concentration of Aqueous Complexes of Iron(II) and Organic Ligands in the Solutions of High Ionic Strength (Jang and Kim, 2016)
9) TP 19-01 Revision 0: Investigation of Neodymium Hydroxide Synthesis and Solubility (Sisk-Scott, 2019)
10) TP 20-01 Revision 0: Solubility and Complexation of Lead in Non-Sulfidic Brines of WIPP-Relevance (Kirkes and Zhang, 2020)

These TPs were developed for collection of experimental solubility and complexation data for WIPP-relevant metals and metalloids (e.g., iron, lead, magnesium, neodymium, and boron) in brines. The goal of this experimental effort has been to evaluate existing, and/or define new, thermodynamic quantities, i.e., base-10 logarithm of equilibrium constants (log Ks) and the relevant Pitzer Interaction Parameters (PIPs), to ultimately build a robust brine geochemical thermodynamic database supported by the Pitzer Activity Coefficient Equation (PACE).

Analysis methods applied in previous APs related to solubility and complexation experimental work (listed at the end of this paragraph) have been implemented to parameterize the experimental data using aqueous thermodynamic models supported by the PACE (Harvie et al., 1984). PACE calculates activity coefficients of aqueous species in solutions over a wide range of ionic strengths using PIPs which account for non-ideal interactions of aqueous species in pairs and/or triplets. Existing APs describing the parameterization of experimental solubility and complexation data include: AP-134 Revision 3 (Xiong, 2012), AP-154 Revision 3 (Kirkes, 2020), AP-155 Revision
3 (Xiong, 2014), AP-171 Revision 0 (Xiong and Icenhower, 2016), AP-176 Revision 0 (Jang, 2016), and AP-182 Revision 0 (Jang, 2019).

This AP will provide the reporting accuracy and precision of experimental data and methods of model fitting. The accuracy and precision of the experimental data should be quantified before model fitting. Otherwise, over-constrained log Ks and/or PIPs might result. Newly derived log Ks and/or PIPs must be checked against general chemical principles, such as mass action, the Debye-Hückel limiting law, cumulative complexation, and double-counting (reaction vs. interaction).

### 1.2 Objective

The objective of this AP is to implement specific steps into the Analysis Report (AR) where the uncertainty (accuracy and precision) of experimental solubility and complexation data can be estimated. Resolution of existing, and/or creation of new, thermodynamic quantities will be done within this uncertainty. The model parameterization results to be documented in reports will be used for regulatory compliance decisions.

The AR will evaluate if the experimental solubility and complexation data generated by the SNL WIPP Geochemistry Program can be described by a broader (i.e., non-WIPP-specific, meaning also covering relevant published work) thermodynamic model supported by PACE within the uncertainty, and if such a model can be built on the currently qualified model that consists of Harvie et al. (1984), Choppin et al. (2001), Giambalvo (2002), and Felmy and Weare (1986).

Table 1 is the outline of the output AR that will document thermodynamic interpretations and model parameterizations. This output is a proposed outline for documenting solubility and complexation experimental data for TPs listed in Section 1.1. The order and content of the Introductory Chapters (I, II, and III) are subject to change.
Table 1. Outline of Analysis Reports to be Produced via this AP

<table>
<thead>
<tr>
<th>Analysis Report documenting Solubility and Complexation of Iron, Lead, Magnesium, Neodymium, and Boron in the WIPP-Relevant Brines under TPs 06-03, 08-02, 12-02, 14-03, 14-05, 16-02, 19-01, and 20-01</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
</tr>
<tr>
<td>II. TRANSCRIPTON, TRACEABILITY, AND UNIT CONVERSION OF EXPERIMENTAL DATA</td>
</tr>
<tr>
<td>III. BASIS GEOCHEMICAL BRINE THERMODYNAMIC MODEL</td>
</tr>
<tr>
<td>IV. METAL/METALLOID (Me) (Me = Fe, Pb, Mg, Nd, and B)</td>
</tr>
<tr>
<td>IV.n. An experimental system noted by ingredients: e.g., MeOxalate.2H2O(s) - NaCl - H2O</td>
</tr>
<tr>
<td>IV.n.1. Definition of Chemical System</td>
</tr>
<tr>
<td>IV.n.2. Goals and Hypotheses</td>
</tr>
<tr>
<td>IV.n.3. Description of Reactor Preparation</td>
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<tr>
<td>IV.n.4. Data - Aqueous</td>
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<tr>
<td>IV.n.5. Data - Solids</td>
</tr>
<tr>
<td>IV.n.6. Description of Observations</td>
</tr>
<tr>
<td>IV.n.7. Model Parameterization</td>
</tr>
<tr>
<td>IV.n.8. Summary</td>
</tr>
<tr>
<td>IV.(n+1). Me system of different/additional ingredients: e.g., Me(OH)2(s) - Na2H2EDTA.2H2O - NaCl</td>
</tr>
<tr>
<td>XI. CONCLUSIONS</td>
</tr>
<tr>
<td>XII. REFERENCES</td>
</tr>
</tbody>
</table>

2 **Approach**

In Sections IV.n.3. through IV.n.6. (Table 1), the experimental solubility and complexation data (e.g., measured concentrations) will be statistically processed to produce a plot such as Figure 1 with the uncertainty explicitly noted. Uncertainty will be documented as accuracy and precision. Microsoft Excel will be used to calculate averages and standard deviations of solubility and complexation experimental data.

![Figure 1. Experimental data statistically processed to explicitly present the uncertainty.](image)

(The symbols and the error bars represent, for example, the averages and twice the standard deviations of multiple measurements, respectively, under normal distribution).
In Section IV.n.7., preliminary model calculations will be performed using log K values and PIPs as is from Section “III. BASIS GEOCHEMICAL BRINE THERMODYNAMIC MODEL” and the literature specific to Section IV.n. to determine how well the selected thermodynamic quantities describe the experimental results within their uncertainty (Figure 2). The thermodynamic quantities selected from Section “III. BASIS GEOCHEMICAL BRINE THERMODYNAMIC MODEL” will serve as the basis of the brine model used by the SNL WIPP Geochemistry Program.

The quality of model fit is described by the calculated individual and total residuals:

\[
\text{Individual Residual (IR)} = (\log Y_{\text{exp}} - \log Y_{\text{calc}})^2, \quad (1)
\]

\[
\text{Total Residual (TR)} = \sum (\log Y_{\text{exp}} - \log Y_{\text{calc}})^2 \quad (2)
\]

where \( Y_{\text{exp}} \) is the experimentally measured quantity \( Y \) (symbols in Figures 1 and 2), and \( Y_{\text{calc}} \) is the model-calculated quantity \( Y \).

If the preliminary model calculation does not delineate experimental data within their uncertainty (Model 0 in Figure 2), the selected thermodynamic values from the literature specific to Section IV.n will be re-examined and possibly updated. If the updated thermodynamic quantities do not improve the fit to the level of Model 1 in Figure 2, additional fitting is required. The adjusted and/or newly created thermodynamic quantities shall be consistent with general chemical principles prior to being used for additional calculations. Refer to Section 5 Software List for the aqueous speciation code to be used.

If the preliminary model calculation delineates the experimental data within the uncertainty (Model 1 in Figure 2), the preliminary model (Model 1) shall be considered acceptable. If further fitting is performed to produce better agreement (beyond Model 1), such as Model 2 in Figure 2, the model shall be compared against general chemical principles before acceptance. See Section “4 An Example Fitting Procedure” for a proposed/example fitting procedure.

![Image of Figure 2](image-url)
3 Tasks

The sections listed in Table 1 are described in greater detail below. Tasks 1 and 2 are to parameterize the solubility and complexation experimental data collected for the WIPP-relevant metalloid(s), i.e., Fe, Pb, Mg, Nd, and B. The process of the parameterization will be documented in the format outlined in Table 1. The first deliverable via this AP is an AR, GEOC-21-11, which is an FY21 SNL WIPP Geochemistry Program deliverable to the DOE. SNL WIPP Geochemistry PIs are working together to complete the initial deliverable, GEOC-21-11, by 9/30/2021. Successive deliverables, such as milestone reports, memoranda, and/or analysis reports, might result from this AP if and when additional data becomes available.

<table>
<thead>
<tr>
<th>Task Description/Deliverable</th>
<th>Individual to perform Task</th>
<th>Expected Completion Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe - organic system(s)</td>
<td>Jang and co-workers</td>
<td>9/30/2021</td>
</tr>
<tr>
<td>Pb - inorganic system(s)</td>
<td>Kirkes and co-workers</td>
<td>9/30/2021</td>
</tr>
<tr>
<td>Mg - organic system(s)</td>
<td>Hora and co-workers</td>
<td>9/30/2021</td>
</tr>
<tr>
<td>Nd - Borate system(s)</td>
<td>Zhang and co-workers</td>
<td>9/30/2021</td>
</tr>
</tbody>
</table>

3.1 Task 1 – Collation of experimental data and model parameters

ARs to be produced via this AP, such as GEOC-21-11, should include Chapters, “I. INTRODUCTION” and “II. TRANSCRIPTION, TRACEABILITY, AND UNIT CONVERSION OF EXPERIMENTAL DATA” (Table 1). As the ARs evolve, details of these two Chapters may change. However, the following content shall be included:

- Chapter “I. INTRODUCTION”
  - Experimental protocols used in common shall be described in this Chapter. Specifics can be addressed in the level three sections, “IV.n.4. Data - Aqueous” and “IV.n.5. Data - Solids”.
  - Common analytical instruments and their operation shall be described in this Chapter. Specifics can be addressed in the level three sections, “IV.n.4. Data - Aqueous” and “IV.n.5. Data - Solids”.
- Chapter “II. TRANSCRIPTION, TRACEABILITY, AND UNIT CONVERSION OF EXPERIMENTAL DATA”
  - A list of relevant documents, e.g., Milestone Reports, Memoranda, etc., that contain experimental solubility and complexation data relevant to the ARs shall be provided in this Chapter.
  - Specifics can be addressed in the level three sections, “IV.n.4. Data - Aqueous” and “IV.n.5. Data - Solids”.
- Chapter “III. BASIS GEOCHEMICAL BRINE THERMODYNAMIC MODEL”
  - This Chapter shall include (i) log K values of reactions of interest, and (ii) the relevant PIPs. Reactions and their log K values and PIPs for this Chapter shall be collected from: Harvie et al. (1984), Choppin et al. (2001), Giambalvo (2002), and Felmy and Weare (1986). Any exceptions shall be noted with justification(s).
3.2 Task 2 – Data interpretation and parameterization for individual metal(loid)s

- The title for the level two section in Table 1, such as IV.n., shall be the list of ingredients in the reactors.
- Section “IV.n.1. Definition of Chemical System” shall include the chemical system components defined in a way compatible with the approved speciation codes, e.g., EQ3/6, Version 8.0a (Wolery and Jarek, 2003). The number of components shall be specified.
- Section “IV.n.2. Goals and Hypotheses” can include a literature review and/or preliminary speciation calculations to describe motivations for the work.
- Section “IV.n.3. Description of Reactor Preparation” shall include a unique reactor identifiers, recipe of the reactors, including, for example, composition of solution, volume of solution, mass of solubility-limiting solid, model-calculated or measured properties of the solution, such as solution density (Novotný and Söhnel, 1988; Wolery and Jarek, 2003) and Molarity-to-molality conversion factors (Wolery and Jarek, 2003; Jang, 2020). Starting solids characterization should also be described. If the solids are custom-made, the syntheses and subsequent characterization shall be described. Links to Section “IV.n.5. Data - Solids” and to the Scientific Notebooks (SN’s) should be provided if necessary.
- Section “IV.n.4. Data - Aqueous” shall include presentation of measurements of the components in both tabulated and graphical formats, as well as statistical parameters, such as average, twice the standard deviation, and count of measurements used to calculate the statistics.
- Section “IV.n.5. Data - Solids” shall include characterization results of the solids collected at the end and/or during the experiment.
- Section “IV.n.6. Description of Observations” shall include assumptions and justification made to (i) statistically process the experimental data, and (ii) assure the attainment of equilibrium. If the given data set does not support the attainment of equilibrium, additional time-dependent measurements will be collected. Discussion of the data quality relative to that of non-reactive and/or conservative components can be included in this section. This section shall conclude by showing plots similar to Figure 1, where uncertainties of the measured quantities X and Y are illustrated, and tables listing the statistical values used in Figure 1.
- Section “IV.n.7. Model Parameterization” shall include tables of the thermodynamic quantities, i.e., log K values of reactions and the related PIPs, taken from literature specific to the experimental system of Section IV.n. They will be used in the model calculation in combination with the thermodynamic quantities selected from Chapter “III. BASIS GEOCHEMICAL BRINE THERMODYNAMIC MODEL”. A model calculation for the aqueous only system shall be done to assess if the selected thermodynamic quantities indicates that the solubility-limiting solid (identified in Section “IV.n.5. Data - Solids”) has a saturation index, SI, close to zero. The “closeness to zero” shall be addressed and discussed in this section.
  - Upon positive identification of the solubility-limiting solid(s), model calculation and parameterization for the solid-aqueous system will be done as per Section “2 Approach” of this AP.
  - Selecting the thermodynamic quantities to be adjusted/created shall be justified and discussed case-by-case based on general chemical principles.
Section “IV.n.8. Summary” shall contain a plot of the finalized model calculation results (e.g., Figure 2), and a table of the thermodynamic quantities selected for and tested/adjusted to produce the final model.

Chapter “XI. CONCLUSIONS” shall include a tabulated presentation of log K values and PIPs finalized in all the level three sections, i.e. “RN.n.8. Summary”, where RN stands for the Roman Numeral Chapter identifiers for individual metal(loid)s (RN = IV, V, VI, ...). The log Ks and PIPs in Chapter “III. BASIS GEOCHEMICAL BRINE THERMODYNAMIC MODEL” and Chapter “XI. CONCLUSION” will be the content of the new database, “data0.fmx (x > 5)”.

Chapter “XII. REFERENCES” shall include the following references: Harvie et al. (1984), Choppin et al. (2001), Giambalvo (2002), and Felmy and Weare (1986). References specific to elements, i.e., Fe, Pb, Mg, Nd, and B, shall be included in this chapter.

4 An Example Fitting Procedure

Steps 1-6 below constitute an example approach to model parameterization for this AP (Section “IV.n.7. Model Parameterization” in Table 1), as distinct from previous APs.

1. Scan saturation indices by performing the EQ3NR calculation without assuming solid-aqueous equilibrium. Compare the model-predicted solid(s) that show SI \( \approx 0 \) with the solid(s) identified in Section “IV.n.5. Data - Solids”.
   1.1. NOTE: Before performing the EQ3NR calculation, ensure the thermodynamic quantities retrieved from the literature specific to Section “IV.n.” include the solubility constant(s) of the solid(s) identified in Section “IV.n.5. Data - Solids”

2. After positively identifying the solubility limiting phase(s) in step 1, re-run the calculation assuming solid-aqueous equilibrium and calculate the residuals.
   2.1. If the model calculation delineates the experimental data (e.g., Model 1 in Figure 2) within the experimental uncertainty, record the residuals, and the Principal Investigator(s) shall then decide whether:
       2.1.1. To finalize the interim model by stating, for example, “We validated the thermodynamic quantities contained in Sections “III. BASIS GEOCHEMICAL BRINE THERMODYNAMIC MODEL” and “IV.n.7. Model Parameterization” using SNL WIPP-specific experimental data. Justifications are provided in the following section(s).” OR
       2.1.2. Go to step 3.
   2.2. If the model calculation does not predict the experimental data within the uncertainty, go to step 3.

3. Provide a discussion of the basis thermodynamic quantities listed in Section “III. BASIS GEOCHEMICAL BRINE THERMODYNAMIC MODEL” and Section “IV.n.7. Model Parameterization”, if any. For example, “The thermodynamic quantities in Section ‘III. BASIS GEOCHEMICAL BRINE THERMODYNAMIC MODEL’ remain the basis. Changing them puts at risk the internal consistency of the basis database, i.e., data0.fm1, and the final database.”

4. The Principal Investigator(s) will decide whether one or more of the thermodynamic quantities selected from the literature in Section “IV.n.7. Model Parameterization” will be fitted further. A few preliminary calculations would be helpful.

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1 EQ3NR is one of the two codes packaged in EQ3/6, Version 8.0a (Wolery and Jarek, 2003). The other is EQ6.
4.1. If decided to fit one or more of the thermodynamic quantities, provide justification and record the changes of residuals as model fitting proceeds.

5. If the Principal Investigator(s) finds the need to create new log K values and/or new PIPs, a technical justification based on general chemical principles will be provided. Changes of residuals shall be recorded as the model fitting proceeds.

6. Address the need for cross-fitting of the thermodynamic quantities common, and relevant, to other experimental systems.

5 Software List


- Supporting softwares
  - Python script (EQ3CodeModule.py in Kirchner (2012))
  - Python Installation Package (epd-7.2-2-win-x86.msi)
  - Excel macro to extract calculation results from EQ3/6 output files, i.e., *.3o and *.6o (GetEQData_v101f.xls).
  - Commercial off-the-shelf spreadsheet programs, such as Microsoft Excel, will be used for data processing, reduction, and plotting.

6 Special Considerations

No special considerations have been identified.

7 Applicable Procedures

All applicable WIPP quality-assurance procedures will be followed when conducting these analyses. Training of personnel will be done in accordance with the requirements of NP 2-1, Qualification and Training. Analyses will be performed and documented in accordance with the requirements of NP 9-1, Analyses and NP 20-2, Scientific Notebooks. All software used will meet the requirements of 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.

8 References


Xiong, Y., 2010. Experimental Study of Thermodynamic Parameters of Borate in WIPP Relevant Brines at Sandia National Laboratories Carlsbad Facility. Test Plan TP 10-01, Revision 0. Sandia National Laboratories, Carlsbad, New Mexico, U.S.A. ERMS 553558.


Xiong, Y., J. Jang, and J. Icenhower, 2015. Experimental Investigation of Borate Interactions with Rare Earth Elements under the WIPP Relevant Conditions at Sandia National Laboratories Carlsbad Facility, Test Plan TP 12-02, Revision 2. Sandia National Laboratories, Carlsbad, New Mexico, U.S.A. ERMS 563597.


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