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SANDIA NATIONAL LABORATORIES  
WASTE ISOLATION PILOT PLANT  

AP-192  
Revision 0  

Analysis Plan for the Analysis Report documenting the Assessment of the Solubility of Lead, EDTA, and other Organic Ligands in Non-Sulfide Systems performed under TP 08-02 Revision 0 and under TP 20-01 Revision 0  

Task 4.4.2.2.1  

Effective Date: July 27, 2021  

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1 Introduction

1.1 Background

Lead (atomic symbol = Pb, atomic weight = 207.2 g/mol) and lead compounds are part of the inventory for transuranic (TRU) waste being emplaced in the WIPP.\(^1\) Metallic lead has been included to construct the shielded containers for the remote-handled TRU waste. Anoxic corrosion products of lead can be a primary source of dissolved lead when brine intrudes the WIPP.

The solubility and complexation of dissolved lead in the WIPP-relevant brines needs to be parameterized to assess the competition of dissolved lead with actinides in solution. The competition could result in the suppression of reactions enhancing the mobility of actinides.

Multiple sets of lead solubility and complexation experiments have been performed by the SNL WIPP Geochemistry Program under the Test Plan (TP) TP 08-02 Revision 0 (Ismail et al., 2008). The experiments were prepared in sealed bottles under well-ventilated ambient laboratory conditions with an estimated atmospheric CO\(_2\) partial pressure of \(~10^{-3.5}\) atm (Stumm and Morgan, 1996). When the experimental data were interpreted to produce Analysis Reports, the interference of CO\(_2\) was considered to be a topic of uncertainty. However, because of the repeated sampling from the same reactors over extended aging times, the following questions were raised by DOE about the experiments conducted under TP 08-02 Revision 0: (1) The results of experiments conducted in acidic pH could have been biased due to the CO\(_2(g)\) intrusion, (2) The formation of secondary lead minerals observed in experiments performed in the presence of organic ligands or carbonate could have been driven by CO\(_2(g)\) intrusion, (3) The reactors may have experienced contamination due to repeated entries into the same reactors for pH measurement and sampling.

Thus, SNL WIPP Geochemistry Program will resolve the DOE-raised questions by conducting a few selected solubility and complexation experiments using methods described in the new Test Plan (TP) TP 20-01 Revision 0 (Kirkes and Zhang, 2020), including the use of CO\(_2\)-minimal gloveboxes in order to eliminate the possibility of CO\(_2\)-intrusion. The experiments to be repeated will be selected from the sets of experiments that had been completed under TP 08-02 Revision 0; or otherwise, a justification will be provided. The experiments selected from the sets conducted under TP 08-02 Revision 0 will be referred to as ‘repetition experiments’ hereafter.

While conducting the experiments under TP 20-01 Revision 0, other sources of uncertainty (Table 1) will be addressed that were not covered when interpreting the data sets produced under TP 08-02 Revision 0.

1.2 Objective and Hypothesis

The objective of this Analysis Plan (AP) is to provide a guideline to assess the quality and validity of lead experimental data obtained under TP 08-02 Revision 0 and TP 20-01 Revision 0. The assessment will be made by comparing the measurement data of the repetition experiments performed under TP 20-01 Revision 0 with the previous data obtained under TP 08-02 Revision 0. In other words, the repetition experiments under TP 20-01 Revision 0 will serve as control

\(^1\)WIPP stands for Waste Isolation Pilot Plant. WIPP is the only actively operational deep geological repository in the world to permanently isolate defense-related transuranic (TRU) radioactive waste.
experiments for the previous experiments conducted under TP 08-02 Revision 0, with the sources of the following two uncertainties removed: (1) CO₂(g) intrusion, and (2) contamination during repeated sampling. The thermodynamic model will not be invoked for the comparison. The comparison made will be solely based on the experimental data, i.e., data-to-data comparison of dissolved component concentrations and solid characterization results. It is hypothesized that a direct comparison of the experimental data generated from the repetition experiments will demonstrate agreement in the identity of lead solids and measured total dissolved concentrations of lead and other relevant components. This agreement would enable the SNL WIPP Geochemistry Program to provide documentation that CO₂(g) intrusion was minimal, if any, and did not affect the identity of lead solids in the solubility experiments. Therefore, minimal CO₂(g) intrusion did not affect the measured total dissolved lead concentrations and that of other relevant solution components within the uncertainty associated with the experimental data. The data comparison results will be used to support compliance decisions per NP 9-1.

2 Approach

- Select a set of experiments to repeat from the sets of experiments that had been completed under TP 08-02 Revision 0. If selection is made outside the sets conducted under TP 08-02 Revision 0, provide justification for the selection.
- Present the objective and hypothesis of the selected experiment. Literature review and/or preliminary model calculations can be used to set up the objective and hypothesis. An example is provided in Figure 1.
- Estimate the accuracy and precision associated with the experimental data obtained under TP 08-02 Revision 0 for the repetition experiment by calculating averages and standard deviations. An example is provided in Figure 2.
- Execute the repetition experiment under TP 20-01 Revision 0 by applying the same recipe of the set conducted under TP 08-02 Revision 0.
- If the repetition experiment introduces new sources of uncertainty due to changes in the methods (e.g., Table 1), describe them in detail.
- Estimate the accuracy and precision associated with the data of the repetition experiment by calculating averages and standard deviations. An example is provided in Figure 2.
- Perform comparison of the repetition experiment data set with the previous data set to see if the repetition experiment data set reproduces the previous data set within the estimated accuracy and precision (e.g., within 95% confidence, if the accuracy and precision are estimated as twice the standard deviations assuming a normal distribution).
- If the repetition experiment data set agrees with that of the previous experimental data (including solid characterization results), then it can be stated that the interference of CO₂ on the previous data set is minimal and captured within the experiment uncertainty.
- If the repetition experiment data set is not in agreement with the previous data set (including solid characterization results) and additional explanation cannot be found, then it can be stated that the intrusion of CO₂ affected the previous data set after addressing the sources of uncertainty in Table 1. In such case, the data set of the repetition experiment (including solid characterization results) replaces the previous data set.
- Iterate the above steps for other repetition experiment(s), if necessary.
3 Tasks

3.1 Task 1 – Selection of Experiments

Three sets of experiments were selected according to DOE questions.

1. PbSO\(_4\)(s) - Na\(_2\)SO\(_4\) - NaCl - H\(_2\)O: The solid PbSO\(_4\)(s) is added in excess to the solutions of incremental concentration of Na\(_2\)SO\(_4\) (0.01, 0.10, 0.50, 1.00, 1.50, and 1.80 m) with NaCl concentration fixed at 0.15 m. This set is a repetition experiment.

2. PbCO\(_3\)(s) - NaHCO\(_3\) - NaCl - H\(_2\)O: The solid PbCO\(_3\)(s) is added in excess to the solutions of incremental concentration of NaHCO\(_3\) (0.01, 0.05, 0.50, and 1.00 m) with NaCl concentration fixed at 0.15 m. Experiment using NaHCO\(_3\) = 1.00 m solution is prepared with NaCl = 0.30 m in parallel. This set is a repetition experiment.

3. PbCO\(_3\)(s) - Na\(_2\)CO\(_3\) - H\(_2\)O: The solid PbCO\(_3\)(s) is added in excess to the solutions of incremental concentration of Na\(_2\)CO\(_3\) (0, 0.01, 0.10, 0.50, 1.00, 1.50, 2.00, and 2.50 m). This experiment has not been conducted under TP 08-02 Revision 0.

Justification of the selections are provided below:

Experiments 1 and 2 are selected from the sets of experiments completed under TP 08-02 Revision 0. These two repetition experiments shall be performed using the same recipe as executed under TP 08-02 Revision 0, but under the protocols of TP 20-01 Revision 0, to experimentally resolve the questions raised by DOE on the previous data sets.

Experiment 1 is selected under the following hypotheses: (1) No carbonate solution was used, thus CO\(_2\)(g) intrusion would have shown in the change of speciation of lead, (2) Lead-sulfate complexation is deemed weaker than that of lead-carbonate at a fixed concentration of NaCl, (3) Thus, intrusion of CO\(_2\)(g) would have been reflected in the total dissolved concentration of Pb (Figure 1), assuming there is no solid precipitation or other process in the uptake of CO\(_2\)(g).

![Figure 1](image-url)  

Figure 1. A preliminary prediction using EQ3/6, Version 8.0a (Wolery and Jarek, 2003)\(^2\) of total dissolved concentration of lead (ΣPb) in solutions of incremental concentration of Na\(_2\)SO\(_4\) with NaCl concentration fixed at 0.15 m with (dashed line) and without (solid line) CO\(_2\)(g) intrusion, where the solubility limiting solid is PbSO\(_4\)(s). This is a preliminary calculation to elaborate the hypotheses in the text to be experimentally tested through this AP. Care must be exercised in interpreting the ΣPb because of the non-ignorable concentration of chloride at 0.15 m. In the presence of 10\(^{-5}\) m dissolved carbonate, the ΣPb is predicted to be higher (dashed line).

\(^2\) This reference is for Version 8.0, and also applicable for Version 8.0a.
The results of the Experiment 1 will be analyzed as described in the Figure 2 caption. If the \( \Sigma \text{Pb} \) of the Experiment 1 performed inside the glovebox (CO\textsubscript{2}-minimal environment) is observed to be lower than the previously measured \( \Sigma \text{Pb} \) under TP 08-02 Revision 0, in other word, if the difference exceeds the precision of the previous set (e.g., error bars in Figure 2), the observation illustrates that the experiment completed under TP 08-02 Revision 0 was affected by CO\textsubscript{2} intrusion. Other solute components than lead will also be compared.

Experiment 2 is selected to evaluate if the formation of abellaite in the TP 08-02 experiments Task 14 was driven by CO\textsubscript{2} (g) intrusion and/or contamination. In the previous experiments, only one out of ten reactors showed the presence of abellaite, while the rest of the experiments have cerussite as the lead-carbonate phase. The results of this repeat experiments will be analyzed to address the DOE question why only one sample out of 10 reactors transformed to abellaite, while the remaining samples in the set remained as cerussite.

Experiment 3 experiment is a control experiment, i.e., without chloride, for a previous data set produced from the PbCO\textsubscript{3(s)} - Na\textsubscript{2}CO\textsubscript{3} - NaCl - H\textsubscript{2}O experiment (Task 15 of TP 08-02). Due to the presence of chloride, the previous data set could not be used to gauge the common ion effect in the lead-carbonate system, with the common ion being carbonate. Additionally, chloride was not measured in the previous experiments. In interpreting the paragenesis of the secondary lead minerals observed from the previous data set, the accuracy of a lead-chloride complexation model in the literature had to be assumed due to the presence of chloride because the dominant aqueous species of lead is one of the lead-chloride complexes in equilibrium with the observed lead carbonate mineral(s). Therefore, by excluding chloride, it is hypothesized that Experiment 3 will address the issue of the common ion effect and solubility products.

### 3.2 Task 2 – Estimation of Uncertainty associated with the Selected Experimental Data Sets

The data produced by the Experiments 1 and 2 under TP 08-02 Revision 0 will be revisited to estimate the accuracy and precision associated with the data sets. An example of such estimation is given in Figure 2 in which pH\textsubscript{r}\textsuperscript{3} and concentration profiles for the PbSO\textsubscript{4(s)} - Na\textsubscript{2}SO\textsubscript{4} - NaCl - H\textsubscript{2}O experiment are presented for the experimental data (Kirkes et al., 2014) obtained under TP 08-02 Revision 0 (Ismail et al., 2008). The plots in Figure 2 can be considered as a template for data analysis of the two repetition experiments.

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\textsuperscript{3} pH\textsubscript{r} is the pH reading obtained using pH electrode and meter calibrated with commercial buffers of low ionic strengths.
Figure 2. Accuracy and precision of measurements produced from PbSO₄(s) - Na₂SO₄ - NaCl – H₂O experiment (Kirkes et al., 2014) under Test Plan (TP) 08-02 Revision 0 (Ismail et al., 2008). Averages (symbols) and twice the standard deviations (2SDs) (error bars) of more than 14 time-dependent measurements are plotted. A: Data labels indicate average, 2SD, %2SD, and number of measurements used to calculate the statistics of pHr. B: Since Pb is a reactive component, precision is given by the error bars. Note that the solute concentration data are presented in Molarity (M). For the Molarity-to-molality and molality-to-Molarity conversion, see Jang (2020). C, D, and E: Data labels indicate the %deviation of average measured values from the loaded concentrations by gravimetric determination (i.e., accuracy of instrument measurements) and error bars (2SD) indicate the precision of our measurement. E: x axis is inverted to display the data points in the order consistent with A, B, C, and D (i.e., left to right in the order of increasing loading of Na₂SO₄). y axis is inverted to display the line of slope = 1 going up to the right.

4 pHr is the pH reading obtained using pH electrode and meter calibrated with commercial buffers of low ionic strengths.
The data of the repetition experiments will be statistically evaluated and compared to the previous data in the format of Figure 2, and conclusions will be drawn with respect to the uncertainties associated with the CO2 intrusion and sample contamination for the two repetition experiments.

If the data of repetition experiments show statistically meaningful differences (i.e., error bars not overlapping) from the previous data set produced under TP 08-02 Revision 0, a comprehensive review of the sources of non-addressed uncertainty in the following Section 3.3 (Table 1) needs to be performed prior to acknowledging the effect of CO2-intrusion.

Review of the accuracy and precision associated with measurements of other components, such as pHr, also needs to be performed to enhance and/or clarify our conclusion on the CO2 intrusion or contamination.

3.3 Task 3 – Sources of Non-Addressed Uncertainty

Table 1 summarizes the difference in the protocols under the two Test Plans. If results of the repetition experiments do not conform to the previous experimental data set within the accuracy and precision, the following sources of non-addressed uncertainty shall be reviewed and discussed prior to acknowledging the influence of CO2 intrusion or sample contamination.

<table>
<thead>
<tr>
<th>Source of uncertainty</th>
<th>TP 08-02 Revision 0 (Ismail et al., 2008)</th>
<th>TP 20-01 Revision 0 (Kirkes and Zhang, 2020)</th>
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<td>Reactor preparation, storage, and sampling A</td>
<td>Under ambient laboratory conditions</td>
<td>Under minimal CO2 environment (in a glovebox)</td>
</tr>
<tr>
<td>Reactor materials B</td>
<td>Plastic bottle (HDPE)</td>
<td>Glass bottle (Borosilicate)</td>
</tr>
<tr>
<td>Method for timed sampling B</td>
<td>Periodic sampling was performed from the same reactor. This resulted in changes in the solid:solution ratio during sample collections</td>
<td>One reactor will be terminated at each time interval, eliminating the possibility of contamination through resampling</td>
</tr>
<tr>
<td>Aging time B</td>
<td>Multiple years</td>
<td>Three+ months</td>
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A Main Driver of this AP and TP 20-01 Revision 0.

B Possible source of non-addressed uncertainty in both TP 08-02 Revision 0 and TP 20-01 Revision 0.

Following changes were made in TP 20-01 Revision 0.

- **Reactor preparation, storage, and sampling**: This is the main driver of the TP 20-01 Revision 0 and this AP. Previously under TP 08-02 Revision 0, the reactors were prepared and stored under ambient laboratory atmosphere, sealed tight, for example, using a screw cap wrapped with paraffin film. The reactors were open to the ambient laboratory atmosphere only when pH measurements and sampling of the aliquots were performed. This time under TP 20-01 Revision 0, reactor preparation, pHr measurement, and sampling/filtration/preservation will be performed inside CO2-minimal gloveboxes. Solids collected will be dried inside a CO2-minimal glovebox. We hypothesize that this change in the reactor preparation, storage, and sampling will address the major portion of the uncertainty, if any.
- **Reactor materials**: Previously under TP 08-02 Revision 0, the experiments were prepared in plastic bottles (HDPE). This time under TP 20-01 Revision 0, the repetition experiment will be prepared in glass bottles (Borosilicate). The hypothesis is that the uncertainty associated with this change of bottle material would be smaller than uncertainty related to our general laboratory operation.

- **Method for timed sampling**: Previously under TP 08-02 Revision 0, reactors were prepared in a larger volume (e.g., 100 mL solution volume with addition of 2.0 gram PbSO₄(s)), and aliquots of supernatant were collected from the same reactor as a function of time over multiple years. As a result, the solid:solution ratio increased as the aliquots of the solution were removed repeatedly from the same reactor. No solid samples were taken when liquid samples were collected from the reactors. Solid characterization was not performed as a function of time. Instead, it was performed at the end of the experiments. This time under TP 20-01 Revision 0, multiplicate reactors of smaller volume (20 mL with addition of 0.4 gram PbSO₄(s)) were prepared to represent one experimental condition for the repetition experiments at the same solid:solution ratio in previous TP 08-02 experiments. Two of the multiplicate reactors will be terminated at a prescribed timed investigation. Termination means that the solution pHr will be obtained prior to the separation of solid and solution, and the entire volume (20 mL) will be filtered to separate the solid and solution. The filtered solution will be diluted and preserved for analytical measurements. For cation analysis using ICP-AES, the sample will be preserved in diluted nitric acid in sealed containers. For anion analysis using IC, the sample will be diluted in DI water and kept in sealed containers. The dried solid will be prepared for characterization. The solid:solution ratio will be kept constant, and characterization results can be obtained for both solid and solution simultaneously at each timed investigation. The hypothesis is that the uncertainty associated with this change of timed sampling method would be smaller than uncertainty related to our general laboratory operation.

- **Aging time**: Previously under TP 08-02 Revision 0, the aging time of the experiments extended over many years, and the experimental data was analyzed at the later stage of the long-term observation. This time under TP 20-01 Revision 0, the data will be initially monitored monthly for up to about three months. If statistically stable measurement results are observed as a function of time for three months, the data processing will begin to estimate the accuracy and precision of the experiments. The processed data will be compared with the previous data set in a format similar to what is depicted in Figure 2. XRD scans and mineral identities will also be compared – between the monthly samples and the terminal samples. The remainder of the replicates will be retained for the case of statistically different measurement results for the first three months. The hypothesis is that the uncertainty associated with a shortened aging time would be smaller than uncertainty related to general laboratory operation.

### 3.4 Task 4 – Prepare Analysis Report

Content of Analysis Report to document the results of the repetition experiments shall include the following:

- Definition of the selected experimental system composition of fluid and solid phases.
- Justification of the selection, that is, hypothesis and objective (e.g., Figure 1).
- Review of the existing data of the repetition experiments obtained under TP 08-02 Revision 0 to estimate the uncertainty associated with the existing data, i.e., accuracy and precision (e.g., Figure 2).
- Review of the new data of the repetition experiments obtained under TP 20-01 Revision 0 to estimate the uncertainty associated with the new data, i.e., accuracy and precision (e.g., Figure 2).
- Address the new source of uncertainty, if any, introduced by the differences of experimental protocols between TP 20-01 Revision 0 and TP 08-02 Revision 0 (e.g., Table 1) through a revision to TP 20-01 outlining additional modeling/experiments to isolate and identify the unknown sources of uncertainty.
- Discussion and conclusion on whether or not the repetition experiments reproduce the results obtained under TP 08-02 Revision 0 within the accuracy and precision.

Tasks 1 to 4 listed in this Section 3 will be performed by Jang and co-workers. Completion of the tasks will be documented in an Analysis Report. The expected completion date of the Analysis Report is 9/30/2021.

4 Software List

Commercial off-the-shelf spreadsheet programs, such as Microsoft Excel, will be used for data processing, reduction, and plotting. XRD-operating software (PDF 4+) and reference peak database will be used to process the XRD data.

5 Special Considerations

No special considerations have been identified.

6 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.

7 References


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