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**Sandia National Laboratories
Waste Isolation Pilot Plant**

Test Plan 14-05

**Test Plan for the Experimental Determination of
The Solubilities of Iron and Lead in the Presence of
Dissolved Hydrogen Sulfide Species**

Task 4.4.2.2.1

Revision 0


Effective Date: October 23, 2014

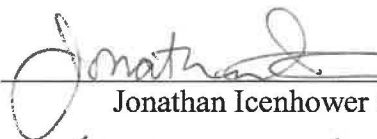
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1 Definitions of Abbreviations, Acronyms, Initialisms, etc.

Am, Am(III)	americium, americium in its +III oxidation state
CRA-2014	(the third WIPP) Compliance Recertification Application (to be submitted to the EPA in March 2014)
DAS	data acquisition system
DB	database
DRC	Document Review and Comment
DOE	Department of Energy
DBR	direct brine release
EDTA	ethylenediaminetetraacetate, $(\text{CH}_2\text{COO})_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2\text{COO})_2^{4-}$ or $(\text{CH}_2\text{CO}_2)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2\text{CO}_2)^{4-}$
ES&H	environmental safety and health
ERDA-6	Energy Research and Development Administration (WIPP Well) 6 (synthetic brine representative of fluids in Castile-Fm. brine reservoirs)
Fm.	Formation
GWB	Generic Weep Brine (synthetic brine representative of intergranular Salado-Fm. brines at or near the stratigraphic horizon of the repository)
Fe, Fe(II)	iron, iron in its +II oxidation state
FeCl ₂	iron chloride
galena	PbS
HS ⁻	bisulfide
IC	ion chromatograph
ICP-AES	inductively coupled plasma-atomic emission spectrometry
mackinawite	Fe _{1+x} S
M&TE	measuring and test equipment
NaHS	sodium bisulfide
NIST	National Institute of Standards and Technology
NP	(SNL/WIPP) Nuclear Waste Management Procedure
PABC	Performance Assessment Baseline Calculation
Pb, Pb(II)	lead, lead in its +II oxidation state
PbCl ₂	lead chloride
pH	the negative, common logarithm of the molar concentration of H ⁺
phase 5	Mg ₃ Cl(OH) ₅ •4H ₂ O
Pu, Pu(III)	plutonium, plutonium in its +III oxidation state
S	sulfur, present in the -II oxidation state in mackinawite and galena
SEM	scanning electron microscopy
SOP	standard operating procedure
SP	(SNL/WIPP) Activity/Project Specific Procedure
TP	test plan
TRU	transuranic
UV-Vis	ultraviolet-visible (spectrophotometry)
WIPP	Waste Isolation Pilot Plant
XRD	X-ray diffraction

2 Revision History

This is revision 0 of this test plan (TP).

3 Purpose and Scope

The objective of this TP is to experimentally determine the solubilities of the Fe(II)- and Pb(II)-bearing sulfides mackinawite (Fe_{1+x}S) and galena (PbS) under the long-term, near-field conditions expected in Waste Isolation Pilot Plant (WIPP) disposal rooms. The WIPP is a U.S. Department of Energy (DOE) repository for the disposal of defense-related transuranic (TRU) waste.

The solubilities measured in the experiments described in this TP will be used, along with experimentally measured Pitzer parameters for dissolved Fe(II) and Pb(II), to predict the effects of Fe(II) and Pb(II) on the solubilities of Pu(III) and Am(III) in geochemical process modeling for the third WIPP Compliance Recertification Application (WIPP CRA-2014) Performance Assessment Baseline Calculations (PABC).

Sandia National Laboratories' (SNL's) WIPP Geochemistry Team is expanding its near-field geochemical modeling capabilities to include dissolved Fe(II), Pb(II), and HS^- species under Test Plan TP 08-02 (Ismail et al., 2008). However, it might not be possible to obtain all of the Pitzer parameters specified by Ismail et al. (2008) for dissolved Fe(II), Pb(II), and HS^- species in time for the CRA-2014 PABC. Specifically, it appears likely that the determination and validation of the Pitzer parameters for dissolved Fe(II) and Pb(II) species, but not for dissolved HS^- species, will be completed in time for the CRA-2014 PABC.

Incorporation of Pitzer parameters for dissolved Fe(II) and Pb(II) species in the thermodynamic database (DB) for the WIPP speciation and solubility model, but not for dissolved HS^- species, could result in including the possible positive effect of the expanded DB in the PABC, but not the potentially inefficient or beneficial, yet uncertain effects. The positive effect of expanding the DB to include Fe(II) and Pb(II) species would be to decrease the predicted solubility of Pu(III) and Am(III) due to competition by Fe(II) and Pb(II) with Pu(III) and Am(III) species for the binding sites on EDTA. Other organic ligands (acetate, citrate, and oxalate) are present in the TRU waste to be emplaced in the WIPP, but only EDTA affects the solubility of Pu(III) and Am(III) significantly, and none of the organic ligands affects the solubility of Pu(IV), the other important radioelement/oxidation state in the WIPP. The inefficient effect would be that inclusion of HS^- would significantly decrease the dissolved concentrations of Fe(II) and Pb(II) by precipitating them as mackinawite, galena, or other sulfide-bearing solids that have very low solubilities in brines and other aqueous solutions under reducing conditions, which could result in the insignificant role of the complexation of Fe(II) and Pb(II) with organic ligands in reducing the predicted actinide solubility. The beneficial, yet uncertain effect would be that inclusion of HS^- would form actinide sulfides with much lower solubilities in comparison with the actinide solubility-controlling phases in the current DB. The formation of such actinide sulfides would decrease the predicted actinide solubility. This beneficial, yet uncertain effect will be assessed

when Pitzer parameters for HS^- species are included in the WIPP DB and model after the CRA-2014 PABC.

The possible inefficient effect must be evaluated prior to the CRA-2014 PABC by either: (1) inclusion of Pitzer parameters for HS^- in the WIPP DB and model, or (2) experimental determination of the solubilities of mackinawite and galena and use of these results to specify the total concentrations of dissolved Fe(II) and Pb(II) species in the solubility calculations. Experimental determination of the solubilities of mackinawite and galena will be necessary to defensibly include the Pitzer parameters for dissolved Fe(II) and Pb(II) species in the model, because it appears unlikely that the Pitzer parameters for dissolved HS^- species will be available in time for the CRA-2014 PABC.

4 Experimental Process Description

This section describes the experiments that SNL will use for the determination of the solubilities of Fe(II) and Pb(II) under the long-term, near-field conditions expected in WIPP disposal rooms.

4.1 Overall Strategy and Process

One or more member or members of the SNL/WIPP Geochemistry Team will determine the solubilities of mackinawite and galena simultaneously or separately in GWB and ERDA-6. GWB is a synthetic brine representative of intergranular Salado Fm. brines at or near the stratigraphic horizon of the repository (Krumhansl et al., 1991; Snider, 2003). ERDA-6 (Popielak et al., 1983) is a synthetic brine representative of fluids in brine reservoirs in the Castile Fm., which underlies the Salado Fm.

These brines must include the organic ligands acetate, citrate, EDTA, and oxalate at the concentrations calculated by Brush and Domski (2013a, Table 6) for the current WIPP inventory. At a minimum, experiments will be carried out with these organic ligands present at concentrations calculated for a brine volume of $5 \times$ the minimum volume required for a direct brine release (DBR) from the repository (Brush and Domski, 2013a, Table 6), because: (1) these organic ligands will increase the solubilities of mackinawite and galena, (2) the concentrations of organic ligands are at their lowest in a brine volume of $5 \times$ the minimum required for a DBR; (3) use of organic ligands concentrations calculated for a brine volume of $5 \times$ the minimum required for a DBR is, therefore, “conservative” (i.e., overpredicting the concentrations of Pu(III) and Am(III)) because it will result in the lowest solubilities of Fe(II) and Pb(II).

If time permits, experiments will be conducted with these organic ligands present at concentrations calculated for brine volumes of the $1 \times$ and $5 \times$ the minimum required for a DBR (Brush and Domski, 2013a, Table 6). The Fe(II) and Pb(II) solubilities will then be interpolated for the intermediate volumes of $2 \times$, $3 \times$, and $4 \times$ the minimum required for a DBR.

The concentrations of the inorganic constituents of GWB and ERDA-6 used for these experiments will be those predicted for these brines after they equilibrate with the important solids in WIPP disposal rooms (Brush and Domski, 2013b, Tables 5 and 6). However,

the inorganic constituents of these brines will be diluted to 90 or 95% of their predicted concentrations, prior to the addition of the organic ligands at the concentrations specified above, to avoid inadvertent coprecipitation of Fe(II) or Pb(II) by evaporite minerals that might precipitate during the experiments if these brines were saturated (i.e., with inorganic constituents present at their predicted concentrations). The Fe and Pb concentrations of initially Fe- and Pb-free GWB and ERDA-6 will be analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after these brines are synthesized and before the addition of any dissolved Fe or Pb, or any mackinawite or galena.

It will be necessary to conduct both undersaturation and oversaturation experiments to demonstrate that the steady-state concentrations of dissolved Fe(II) or Pb(II) species that will (hopefully) be observed by sequential sampling and analysis of the brines from either under- or oversaturation experiment correspond to equilibrium concentrations (solubilities) of these elements. This is consistent with the procedures specified to test for equilibrium by TP 08-02 (Ismail et al., 2008, subsection 2.1.3).

Both undersaturation and oversaturation experiments will be started by placing 100 mL of GWB or ERDA-6 with the organic ligands described above in 125 mL serum bottles. Each of these serum bottles will be sampled several times to demonstrate that steady-state concentrations have been obtained. Each sample will contain ~3 mL of solution analysis for: (1) Fe and Pb by ICP-AES, and (2) HS^- by ultraviolet-visible (UV-Vis) spectrophotometry. The pH of each experiment will be measured before each sampling. Centrifugation and/or filtration will be used to remove suspended solids from the solution samples prior to analysis. All of these experiments, including sampling, will be performed in a glove box using the redox controls specified by Ismail et al. (2008, Subsection 2.2.3).

Specifically, the following four tasks are planned:

Task 1: Undersaturation experiments with mackinawite in ERDA-6 and GWB. In these experiments, the solubility-controlling phase for iron and sulfide, mackinawite, will be placed in initially Fe-free ERDA-6 and GWB. Both ERDA-6 and GWB will have organic concentrations for a brine volume of $5 \times$ the minimum required for a DBR. Brucite in amount of ~1.0 g will be introduced in the experiment with ERDA-6 to control pH. Similarly, synthetic phase 5 ($\text{Mg}_3\text{Cl}(\text{OH})_5 \cdot 4\text{H}_2\text{O}$) in amount of ~2.0 g will be introduced in the experiment with GWB to control pH.

Task 2: Undersaturation experiments with galena in ERDA-6 and GWB. In these experiments, the solubility-controlling phase for lead and sulfide, galena, will be placed in initially Pb-free ERDA-6 and GWB. Both ERDA-6 and GWB will have organic concentrations for a brine volume of $5 \times$ the minimum required for a DBR. Brucite in amount of ~1.0 g will be introduced in the experiment with ERDA-6 to control pH. Similarly, synthetic phase 5 in amount of ~2.0 g will be introduced in the experiment with GWB to control pH.

Task 3: Supersaturation experiments with mackinawite in ERDA-6 and GWB. In these experiments, both ERDA-6 and GWB having organic concentrations for a brine volume of $5 \times$ the minimum required for a DBR will contain a background NaHS concentration of 0.1 M.

Brucite in amount of ~1.0 g will be introduced in the experiment with ERDA-6 to control pcH. Similarly, synthetic phase 5 in amount of ~2.0 g will be introduced in the experiment with GWB to control pcH. Mackinawite will be precipitated from supersaturation by drop-wise addition of 0.1 M FeCl₂.

Task 4: Supersaturation experiments with respect to galena in ERDA-6 and GWB. In these experiments, both ERDA-6 and GWB having organic concentrations for a brine volume of 5 × the minimum required for a DBR will contain a background NaHS concentration of 0.1 M. Brucite in amount of ~1.0 g will be introduced in the experiment with ERDA-6 to control pcH. Similarly, synthetic phase 5 in amount of ~2.0 g will be introduced in the experiment with GWB to control pcH. Galena will be precipitated from supersaturation by drop-wise addition of 0.1 M PbCl₂.

In addition, if time permits, a parallel set of experiments using one times the minimum brine volume will also be performed for each task.

Posttest scanning electron microscopy (SEM) and X-ray diffraction XRD analysis will be carried out to identify the solids present after the undersaturation experiments, and those that precipitate during the oversaturation experiments.

4.2 Sample Control

Sample control for the experiments carried out under this TP will conform to SNL Nuclear Waste Management Procedure NP 13-1, "Control of Samples and Standards." The reader should check the website for SNL's Nuclear Waste Management Procedures at <https://nwmp.sandia.gov/onlinedocuments> to ensure that the latest version of this and other procedures cited below are used for the work described in this TP.

If and when samples are not in the possession of individuals designated as responsible for their custody, they shall be handled and stored with documentation specified by SNL/WIPP Activity/Project Specific Procedure Form SP 13-1-1, "Chain of Custody."

4.3 Data Quality Control

4.3.1 Measuring and Test Equipment

Calibration of all of the measuring and test equipment (M&TE) used for the experiments conducted under this TP will conform to NP 12-1, "Control of Measuring and Test Equipment."

Any computerized data processing required for this TP will conform to NP 9-1, "Analyses."

4.3.2 Data Acquisition System

Data-collection procedures are specific to individual instruments. For details regarding a specific instrument, see the activity/project specific procedure (SP) or user's manual for that instrument. Any data acquired by a data acquisition system (DAS) will be attached directly to

the scientific notebook or compiled in separate loose-leaf binders with identifying labels to allow cross reference to the appropriate scientific notebook. If the instrument allows data to be recorded electronically, copies of the data disks will be submitted to the SNL/WIPP Records Center according to NP 17-1, "Records."

Scientific notebooks for all of the work performed under this TP will be established and maintained according to NP 20-2, "Scientific Notebooks."

4.4 Data Identification and Use

All calculations conducted under this TP will be documented in a scientific notebook (see Subsection 4.3.2 above), which will be technically and QA reviewed periodically according to NP 6-1, "Document Review Process," and NP 20-2, "Scientific Notebooks." These reviews will be documented on the Document Review and Comment (DRC) Form NP 6-1-1.

4.5 Equipment

A variety of M&TE will be used for the work described in this TP. A complete list of this M&TE, including serial numbers, will be established and maintained in the scientific notebooks.

The user(s) of all of the equipment specified below will follow the appropriate SP and/or user's manual for each instrument.

4.5.1 Weighing Equipment

Several balances are available for use in the work described in this TP. Balance calibration checks will be carried out daily or prior to use, and will be recorded in the balance calibration records. These calibration checks will use National Institute of Standards and Technology-(NIST-) traceable weight sets. These NIST weights are in turn calibrated periodically by the SNL calibration laboratory.

4.5.2 Liquid measurement Equipment

Standard laboratory Class A glassware (pipettes, volumetric flasks, etc.) will be used at all times for the work described in this TP. In addition, several adjustable Eppendorf pipettes are available. The pipettes will be calibrated periodically using a calibrated balance, and will be recorded in a scientific notebook. The accuracy of all pipettes used for this work must be within $\pm 1\%$.

4.5.3 Other Analytical Equipment

Centrifuge. A floor model Beckman centrifuge will be used for phase separations prior to chemical analyses of solutions. The user will weigh opposing buckets on a balance prior to use of the centrifuge to ensure that the weight is distributed uniformly. Cumulative spinning time will be recorded in a logbook to determine decommissioning time.

Chemical analyses. Five instruments are available for chemical analyses: (1) a Carey model 300 ultraviolet-visible (UV-Vis) spectrophotometer, (2) a DIONEX model 3000 ion chromatograph (IC), (3) a Perkin Elmer NexIon model 300D inductively coupled plasma-mass spectrometer (ICP-MS), (4) a Perkin Elmer Optima model 3300 DV inductively coupled plasma-atomic emission spectrometer (ICP-AES), and (5) a UIC carbon (C) analyzer. The ICP AES and the ICP-MS are the two primary instruments that will be used for this study. The user will calibrate all analytical instruments according to the SP and/or user's manual prior to use.

Mineralogical analyses. A Bruker model AXS D-8 X-ray diffractometer will be used for X-ray diffraction (XRD) analysis. This will be the primary method used for solid-phase characterization. An internal standard will be used periodically to verify the positions of diffraction lines.

An Olympus model BX60 polarizing microscope and a JEOL model JSM 5900LV scanning electron microscope (SEM) may also be used.

Ovens and furnaces. Ovens and furnaces will not be used because they cannot be placed inside the glove box(es) that will be used for redox control. Instead, these experiments will be performed at ambient laboratory temperatures.

pH meters and autotitrator. All pcH measurements carried out for this work will use pH meters and autotitrators. A Mettler model MA235 pH/ion analyzer (or equivalent hand-held models) and a Mettler model DL25 autotitrator will be used. Electrodes will be calibrated daily or before use (whichever is less frequent) with two pH buffers chosen to bracket the expected pcH of the solutions being tested. NIST-traceable pH buffers will be purchased from chemical-supply companies, and the lot numbers and expiration dates of the buffers will be recorded in a scientific notebook. Calibration of electrodes will also be recorded in a scientific notebook.

5 Training

All personnel involved in the experiments described in this TP will be trained to ensure that they are qualified for their assigned work. This requirement will be implemented according to procedure NP 2-1, "Qualification and Training." Specifically, the following NPs and SPs will apply:

- NP 6-1, Document Review Process
- NP 12-1, Control of Measuring and Test Equipment
- NP 13-1, Control of Samples and Standards
- NP 17-1, Records
- NP 20-2, Scientific Notebooks
- SOP CPG-CHEM-TWD-2011-001: ES&H Standard Operating Procedure (ESH SOP) for Activities in the Sandia National Laboratories/Carlsbad Programs Group Laboratory, Building NPHB
- SOP for Oxygen Deficiency Hazard Alarm Response for Carlsbad (Building NPHB)

- SP 13-1, Chain of Custody
- TWD 001: Safety Management of Bruker Analytical X Ray Systems D8 Advanced X-Ray Diffractometer

6 Health and Safety

All of the health and safety requirements that pertain to the experiments described in this TP and the procedures that will be used to implement these requirements are described in SNL/WIPP environmental safety and health (ES&H) standard operating procedures (SOPs). Each of these ES&H SOPs describes the hazards associated with this work and the procedures required to mitigate these hazards, including all of the training requirements for personnel involved in these experiments. Additional SOPs may be implemented to meet SNL's ES&H requirements. However, any additional SOPs that may be required would not necessitate revision(s) of this TP.

7 Permitting and Licensing

There are no permitting or licensing requirements specific to the experiments described in this TP.

8 References

- Brush, L.H., and P.S. Domski. 2013a. "Calculation of Organic-Ligand Concentrations for the WIPP CRA-2014 PA." Analysis report, January 14, 2013. Carlsbad, NM: Sandia National Laboratories. ERMS 559005
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