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Sandia National Laboratories
Waste Isolation Pilot Plant

Test Plan TP 18-01

Experimental Investigation of pH Correction in WIPP Relevant Conditions and at Elevated Temperature

Task 4.4.2.2.1

Revision 1

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1 ABBREVIATIONS, ACRONYMS AND INITIALISMS

ACS	American Chemical Society
AR	Analysis Report
ºC	Degree Celsius
DAS	Data Acquisition System
ERDA-6	Energy Research and Development Administration well 6 (Synthetic Castile Formation brine)
F	Faraday constant
GWB	Generic Weep Brine (Synthetic Salado Formation brine)
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometer
ICP-MS	Inductively-Coupled Plasma Mass Spectrometer
L	Liter
M	Molarity
m	Molality
mV	Millivolts
M&TE	Measuring and Test Equipment
NIST	National Institute of Standards & Technology
NP	Nuclear Waste Management Procedure
QA	Quality Assurance
R	Ideal gas constant
SGWB	Simplified Generic Weep Brine
SNL	Sandia National Laboratories
SP	Activity/Project Specific Procedure
T	Temperature
TP	Test Plan
UV-Vis	Ultraviolet-Visible
WIPP	Waste Isolation Pilot Plant

2 REVISION HISTORY

Revision 1 was completed to update the Tasks associated with this Test Plan and align the TP to the NP 20-1 (Test Plans). For all procedures listed in this document, the most current revision of the document will be used.

3 PURPOSE AND SCOPE

The purpose of this Test Plan is to improve pH measurements by probes with liquid junctions by determining correction factors for WIPP relevant high ionic strength solutions (1M and higher), complex WIPP relevant solution matrices, and to determine accurate correction factors of these solutions at elevated temperatures. Accurate pH measurements and high-quality analytical data are required to determine thermodynamic properties and Pitzer parameters used in geochemical modeling. A pH correction may be necessary for high ionic strength solutions (over ~1M), or complex brines in which hydrolysis reactions occur, or for pH probes in which liquid junction potentials occur. A pH correction may also be necessary for solutions at elevated temperatures. The pH of a solution is defined as the negative 10 based logarithms of the hydrogen ion activity:

$$pH = -\log \alpha_{H+} \tag{1}$$

The pH probe measures the hydrogen ion activity of the solution. The activity of the hydrogen ion is defined as:

$$\alpha_{H+} = \gamma_{H+} \cdot b_{H+} \tag{2}$$

where:
α_{H+} is the activity of the hydrogen ion.
γ_{H+} is the activity coefficient of the hydrogen ion and
b_{H+} is the molality or molarity (concentration) of the hydrogen ion.

Therefore, pcH of a solution is defined as:

$$pC_{H+} = -\log\left(\frac{M_{H+}}{M^0_{H+}}\right) \tag{3}$$

Where M_{H+} is the molarity of hydrogen ions in solution, and M^0_{H+} = 1mol/L. pmH is defined as,

$$pmH = -\log\left(\frac{m_{H+}}{m^0_{H+}}\right) \tag{4}$$

Where m_{H+} is the molality of hydrogen ions in solution, and m^0_{H+}= 1mol/kg (standard state for solvent as defined in EQ3/6 (Wolery, T.W. 2003)).

Activity coefficients can be affected by many factors including; temperature, ionic strength, dielectric constant, ion charge, the size of the ions and the density of the medium being measured (Mettler Toledo, pH theory 2007). In many cases, correction factors for these pH interferences are not well defined and need to be measured. Correction factors (A) for the hydrogen ion

concentration (pmH or pC_{H+}) can be determined by completing Gran titrations of the specific solution in question. pC_{H+} can be determined using the following equation (Rai et al 1995):

$$pC_{H+}\ (or\ pmH) = pH_{obs} + A \quad (5)$$

where pH_{obs} is the measured pH reading of the sample, and A is defined as:

$$A = \log \gamma_{H+} + (F/2.303RT)\Delta E_j \quad (6)$$

γ_{H+} is a unitless measurement of the molarity- or molality-scale activity coefficient of H^+, F is the Faraday constant (C/mol, coulombs per mole), R is the ideal gas constant ($8.3144626 \times 10^3 L \cdot Pa \cdot K^{-1} \cdot mol^{-1}$), T is temperature in Kelvin and ΔE_j is the difference in liquid-junction potential between the standard and solutions, measured in Volts (V) (Roselle, G.T. 2011). A is a unitless number that is directly added to the in-situ measured pH. Neither term on the right-hand side of equation 6 can be independently measured and therefore it must be obtained directly using a modified Gran titration (Roselle, G.T. 2011). Once Gran titration data are obtained, the pH correction factor (A) can be determined by plotting the H^+ (M or m) observed vs the H^+ (M or m) added and then calculating the base-10 logarithm of the slope of the line (Roselle, G. T. 2011, Rai et al 1995). SP 12-14 (Use of pH Meters and Electrodes) will be followed for pH measurement procedure and Gran titrations.

4 EXPERIMENTAL PROCESS DESCRIPTION

4.1 Task List

Tasks for this test plan will include:

1. *pH correction factor determination for $MgCl_2$ brines ranging in concentrations from 1M-3M at temperatures from 25-90°C.*

2. *pH correction factor determination for NaCl brines ranging in concentrations from 1M-5M at temperatures from 25-90°C.*

3. *pH correction factor determination for $NaSO_4$ brines ranging in concentrations from 0 .1M-2M at temperatures from 25-90°C.*

4. *pH correction factor determination for WIPP relevant brines containing organics (Oxalate, Acetate, Citrate, EDTA) at temperatures from 25-90°C.*

5. *pH correction factor determination for WIPP relevant brines containing borate at temperatures from 25-90°C.*

6. *pH correction factor determination for WIPP relevant brines (e.g. GWB, ERDA-6, SGWB) at temperatures from 25-90°C.*

Brine compositions GWB and ERDA-6 are from SP 20-4 (Preparing Synthetic Brines for Geochemical Experiments).

4.2 Overall Strategy and Process

The overall strategy of this test plan is to determine the pH correction factors for liquid junction electrodes in WIPP relevant solutions at temperatures ranging from 25-90°C using a modified gran titration technique. This technique is outlined in SP 12-14 and the Analysis Report, (Determination of pC_{H+} Correction Factors in Brines, Roselle, G.T. 2011). All deviations from these documents will be documented in the associated scientific notebooks as per NP 20-02 (Scientific Notebooks).

- Critical Variables to be Measured:

  pH: measured and controlled utilizing the procedures and acceptance criteria outlined in SP 12-14 (Use of pH meters and Electrodes). A pH electrode that is rated for high temperatures will be used in all titrations.

  Temperature: Temperature will be measured using a calibrated temperature probe. Temperature will be monitored throughout the titration and recorded in the scientific notebook at the initiation and termination of the titration. Temperature cannot fluctuate from initiation to termination of the titration more than 3°C of the target temperature.

  Gran Titration data: For titrations at a minimum, pH after each volume addition and the volume added will be recorded. If the instrumentation allows, mV will also be recorded for each measurement.

  Solution Analysis: All solutions to be titrated will be prepared using solids certified as ACS grade or better. Densities will be measured directly (mass/volume measurement) for each solution after preparation and documented in a scientific notebook or they will be estimated based on established literature values (Sőhnel, O, Novotný, P., 1985). All constituents in the solutions will be verified for expected concentrations using instrumentation such as the ICP-AES, ICP-MS, IC, Refractometer and other means as deemed necessary. Complex brines will be prepared in accordance with SP 20-4 (Preparing synthetic brines for geochemical experiments). All solution preparation and analysis will be documented in a scientific notebook. Criteria documented in the Activity/Project Specific Procedures will be used to determine data acceptance for these analyses. See Table 1 of this document for a detailed list of Activity/Project Specific Procedures to be used for instrument analysis.

- Procedures to be Used: General procedures for solution preparation and analysis, such as weighing, pipetting and use of flasks are standard laboratory analytical procedures. Instrumental analysis will be performed according to the established procedures listed below (Table 1), including further revisions when applicable. Where necessary, new procedures will be implemented as outlined in NP 5-1 (Implementing Procedures).

Table 1. Activity/Project Specific Procedures for use in TP 18-01

Procedure	Title
SP 12-1	Use of Laboratory Balances and Scales
SP 12-9	Calibration, Use, and Maintenance of the Perkin Elmer Optima 8300 Dual View (DV) ICP-AES
SP 12-14	Use of pH meters and Electrodes
SP 12-21	Temperature Measurements
SP 12-22	Calibration, Use, and Maintenance of the Dionex Ion Chromatograph (IC) 6000
SP 12-31	Calibration, Use, and Maintenance of the Perkin Elmer NexIon 300D ICP-MS
SP 12-35	Use of the 300035 Digital Refractometer
SP 20-4	Preparing synthetic brines for geochemical experiments
Note: For all SPs listed, the most current revision of the document will be used.	

Modified Gran Titration Procedure: Basic titration procedure is documented in SP 12-14 and the AR (Roselle, G.T. 2011) any deviations from this procedure will be documented in a scientific notebook as per NP 20-2 (Scientific Notebooks).

- Error and Uncertainty: Potential sources of error in this TP can be contributed by items such as pH measurement, volume measurement, weighing errors, impure reagents, temperature, variation in titration media, variation in acid concentration, and improper set-up or control of experiment during titration.

pH measurements, weight measurements, and the control of the sample during the titration process will be conducted in accordance with SP 12-1 and SP 12-14. The respective acceptance criteria and uncertainties for these measurements are discussed in those documents.

Volume measurement errors will be controlled by utilizing only Class A glassware for all solution preparation and calibrated pipettes if needed (ASTM E288-10(2017), ASTM E1272-02(2019)).

Impure reagent errors will be controlled by using only solids certified as ACS grade or better for solution preparation. In addition, all solutions will be characterized using elemental analysis techniques after preparation to confirm desired purity and concentration. All titrations will be completed using standardized acids.

Variation in titration media between titrations could cause issues with data comparisons between temperatures for a single solution. To account for this a large stock of each solution will be made (i.e. ~2L) and then all of the titrations for that solution will be performed on the same batch stock solution. If a new stock solution needs to be made it will be re-analyzed for solution concentrations of constituents so the proper concentration can be documented.

Temperature error will be controlled by measuring the temperature of the solution being titrated throughout the titration process. The temperature from initiation of the titration to the

termination of the titration is allowed to fluctuate no more than 3°C. The thermometer used for the temperature measurement will be a calibrated or calibration checked thermometer.

Improper set-up or control of the experiment during the titration error will be controlled by completing duplicates or triplicates of each solution at the desired environmental conditions.

- Data Processing: Data processing will be accomplished using the software provided with each instrument, in addition to off-the-shelf software such as Excel. If Excel or other software's are used to complete calculations, the calculations will be reviewed along with the scientific notebooks and milestone reporting per SNL WIPP Quality Assurance (QA) Program.
- Laboratory activities will be recorded in scientific notebooks, and they will be maintained as quality assurance (QA) records per procedure NP 20-2 (Scientific Notebooks).

4.3 Sample Control

The sample control for the work under this Test Plan will follow WIPP Procedure NP 13-1 (Control of Samples and Standards). Each sample will be appropriately labeled with a unique sample ID. Sample preparation and utilization will be documented in scientific notebooks. After titrations are completed on the prepared solutions they can no longer be used and will be disposed according to NP 13-1 and Corporate Procedure GN470110 (Managing Waste at Sandia National Laboratories).. When samples are not in the possession of individuals designated as responsible for their custody, they shall be stored at room temperature and sealed in a secure area with associated documentation when necessary (e.g., Form SP 13-1-1(Chain of Custody)).

4.4 Data Quality Control

4.4.1 Measuring and Test Equipment (M&TE)

A calibration program will be implemented for the work described in this Test Plan in accordance with NP 12-1 (Control of Measuring and Test Equipment). This M&TE calibration program will meet the requirements in procedure NP 12-1 for: (1) receiving and testing M&TE; (2) technical operating procedures for M&TE; (3) the traceability of standards to nationally recognized standards such as those from the National Institute of Standards and Technology; and (4) maintaining calibration records. In addition, NP 13-1 and SNL Activity/Project Specific Procedure (SP) 13-1 (Chain of Custody), identify requirements and appropriate forms for documenting and tracking samples possession. Computer-based data handling will follow NP 9-1 (Analyses).

4.4.2 Data Acquisition System

Data collection procedures are specific to individual instruments. For details of the data acquisition for an instrument, see the 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 Records Center according to procedure NP 17-1 (Records). If

possible, data files may be transferred to portable data storage devices or a CD ROM for submittal to the records center. For instruments that do not have direct data printout, the instrument readings will be recorded directly into the scientific notebook. Current versions of the DAS software will be included in the SNL WIPP Baseline Software List, as appropriate.

Quality control of the scientific notebooks will be established by procedures described in procedure NP 20-2 (Scientific Notebooks). Methods for justification, evaluation, approval, and documentation of deviation from test standards and establishment of special prepared test procedures will be documented in the scientific notebooks. Procedures including use of replicates, spikes, split samples, control charts, blanks, and reagent controls will be determined during the development of experimental techniques.

Commercial software list:

Software	Instrument/Hardware
Syngistix Version 3.0.4.3510	ICP-AES
Syngistix Version 2.4	ICP-MS
Excel version 95 or newer	Mettler Toledo G10S Titrator
Chromeleon Version 7.2.8	IC
Excel version 95 or newer	Post processing of titration data

4.5 Data Identification and Use

All calculations performed as part of the activities of TP 18-01 will be documented in a scientific notebook. The notebook will be reviewed periodically to ensure that the technical and QA requirements of procedure NP 20-2 (Scientific Notebooks), are met. If a discrepancy is found, that discrepancy and its resolution will be documented during the review on a Document Review and Comment (DRC) Form NP 6-1-1.

4.6 Equipment and Techniques

A variety of measuring and analytical equipment will be used for the work described in this test plan. A complete equipment list, including serial numbers, will be maintained in the scientific notebook. Scientific notebooks will be used to record all laboratory work activities.

4.6.1 Weighing Equipment

Several balances are present in the facility and may be used for this project. Balance calibration checks will be performed daily or prior to usage, using NIST-traceable weight sets, which, in turn, are calibrated by the SNL Primary Standards Laboratory (PSL). Calibration checks will be recorded in a Balance Calibration Records logbook as per SP 12-1.

4.6.2 Liquid Measuring Equipment

Standard Laboratory Class A glassware (glass pipettes, volumetric flasks, etc.) and adjustable pipettes will be used for all measurements involving liquids. The calibration of pipettes will be

checked prior to use with a calibrated balance and will be recorded in the scientific notebook. The accuracy of the pipettes will be within 1% of the expected value.

4.6.3 Other Analytical Equipment & Techniques

A. Modified Gran Titration Technique- The modified Gran titration technique is a procedure where a solution is slowly titrated with acid or base with known volumes of titrant and the pH or mV is measured throughout the process. The H+ observed can be plotted vs the H+ added to determine the correction factor for the specific solution being tested. The 10 based logarithms of the slope of the line is the correction factor for the measured solution. This technique is described in more detail in SP 12-14 and the Analysis Report (Determination of pC_{H+} Correction Factors in Brines, Roselle, G.T. 2011).

B. Temperature Measuring Equipment- Temperature will be measured at the start and end of each titration to verify that the desired temperature was reached and maintained throughout the titration. A calibrated thermometer will be used for all measurements as per SP 12-21. Temperature will be maintained using an aluminum bead bath and a hot plate or other heating device.

C. pH Meters and Autotitrators – Solution pH shall be measured using pH meters or a pH probe autotitrator assembly. The pH probes and meters used will be recorded in the appropriate scientific notebook at the time of use. The range for all pH meters is 0.00 to 14.00. SP 12-14 will be followed for this procedure.

D. Equipment for Chemical Analysis – The following instruments may be used for chemical analyses if applicable:

- Inductively-Coupled Plasma Mass Spectrometer (ICP-MS)
- Inductively-Coupled Plasma Atomic Emission Spectrometer (ICP-AES)
- Ion Chromatograph (IC)
- Refractometer

The usage of these instruments will follow the respective Activity/Project Specific Procedures (SPs) as listed in section 4.2 of this document.

5 TRAINING

All personnel involved in the experiments described in this Test Plan will be trained and qualified for their assigned work. This requirement will be implemented through procedure NP 2-1 (Qualification and Training). Specifically, the following Nuclear Waste Management Procedures (NPs) and Activity/Project Specific Procedures (SPs) are applicable:

Procedure	Title
NP 2-1	Qualification and Training
NP 6-1	Document Review Process
NP 12-1	Control of Measuring and Test Equipment
NP 13-1	Control of Samples and Standards

Procedure	Title
NP 17-1	Records
NP 20-2	Scientific Notebooks
SP 13-1	Chain of Custody
Note: For all NPs and SP listed, the most current revision of the document will be used.	

6 HEALTH AND SAFETY

All the health and safety requirements relevant to the activity level work described in this Test Plan and the procedures that will be used to satisfy these requirements are described in SNL ES&H Manual (MN471022).

7 PERMITTING/LICENSING

There are no special license or permit requirements for the activities described in this Test Plan.

8 REFERENCES

ASTM E288-10(2017), Standard Specification for Laboratory Glass Volumetric Flasks, ASTM International, West Conshohocken, PA, 2017, www.astm.org

ASTM E1272-02(2019), Standard Specification for Laboratory Glass Graduated Cylinders, ASTM International, West Conshohocken, PA, 2019, www.astm.org

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