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 0

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## TABLE OF CONTENTS

1 ABBREVIATIONS, ACRONYMS AND INITIALISMS .............................................. 4
2 REVISION HISTORY ......................................................................................... 5
3 PURPOSE AND SCOPE .................................................................................. 5
4 EXPERIMENTAL PROCESS DESCRIPTION ....................................................... 6
  4.1 Overall Strategy and Process................................................................. 6
  4.2 Sample Control....................................................................................... 7
  4.3 Data Quality Control ............................................................................ 7
    4.3.1 Measuring and Test Equipment (M&TE) ........................................ 7
    4.3.2 Data Acquisition System............................................................... 7
  4.4 Data Identification and Use ................................................................. 8
  4.5 Equipment and Techniques ............................................................... 8
    4.5.1 Weighing Equipment................................................................. 8
    4.5.2 Liquid Measuring Equipment ................................................... 8
    4.5.3 Other Analytical Equipment & Techniques .................................. 8
5 TRAINING ............................................................................................... 9
6 HEALTH AND SAFETY ........................................................................ 9
7 PERMITTING/LICENSEING ................................................................... 9
8 REFERENCES ......................................................................................... 9
1 ABBREVIATIONS, ACRONYMS AND INITIALISMS

DAS Data Acquisition System
ERDA-6 Energy Research and Development Administration well 6 (Synthetic Castile Formation brine)
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
M&TE Measuring and test equipment
NP Nuclear Waste Management Procedure
QA Quality Assurance
SNL Sandia National Laboratories
TP Test Plan
UV-Vis Ultraviolet-Visible
WIPP Waste Isolation Pilot Plant
2 REVISION HISTORY

This is the initial issuance of this Test Plan.

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 corrections can be important to thermodynamic modeling of some mineral solubilities and solute activity coefficients. 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. pH correction may also be necessary for solutions at elevated temperatures. pH can be defined as the negative logarithm of the hydrogen ion concentration (more precisely, it is determined by the activity of the hydrogen ions):

\[
pH = -\log [H_3O^+] \tag{1}
\]

The pH sensor is measuring the activity of the hydronium ion or hydrogen ion within a solution. The activity of the hydrogen ion can be determined by the equation:

\[
\alpha_{H^+} = \gamma_{H^+} \cdot b_{H^+} \tag{2}
\]

where:
- \(\alpha_{H^+}\) is the activity coefficient of the hydrogen ion.
- \(\gamma_{H^+}\) is the activity of the hydrogen ion and
- \(b_{H^+}\) is the molality or molarity (concentration) of the hydrogen ion.

Activity coefficients can be affected by many factors including; temperature, ionic strength, dielectric constant, ion charge, the size of the ions and also 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 (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):

\[
pC_{H^+} = pH_{obs} + A \tag{3}
\]

where pH\(_{obs}\) is the measured pH reading of the sample, and A is defined as:

\[
A = \log \gamma_{H^+} + (F/2.303RT)\Delta E_j \tag{4}
\]

\(\gamma_{H^+}\) is the molarity- or molality-scale activity coefficient of H\(^+\), and \(\Delta E_j\) is the difference in liquid-junction potential between the standard and solutions. Neither term on the right-hand side of equation 4 can be independently measured and therefore must be measured in combination through a modified Gran titration (Roselle 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 LOG of the slope of the line. SP 12-14 (Use of pH Meters and Electrodes) will be followed for pH measurement procedure and Gran titrations. Tasks for this test plan will include:

1. *pH correction factor determination for unequilibrated GWB brine at temperatures from 25-90°C.*

2. *pH correction factor determination for equilibrated GWB brine at temperatures from 25-90°C.*

3. *pH correction factor determination for unequilibrated ERDA-6 brine at temperatures from 25-90°C.*

4. *pH correction factor determination for equilibrated ERDA-6 brine at temperatures from 25-90°C.*

5. *pH correction factor determination for MgCl₂ brines ranging in concentrations from 1M-3M at temperatures from 25-90°C.*

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

7. *pH correction factor determination for NaSO₄ brines ranging in concentrations from 0.1M-2M at temperatures from 25-90°C.*

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

Brine compositions for unequilibrated and equilibrated GWB and ERDA-6 are from SP 20-4 (Preparing Synthetic Brines for Geochemical Experiments). In systems where Pitzer models are available, the acquired data will be compared to these models for consistency and accuracy.

4 EXPERIMENTAL PROCESS DESCRIPTION

4.1 Overall Strategy and Process

The overall strategy is to determine the pH correction factors for WIPP relevant solutions at temperatures ranging from 25-90°C using the Gran titration technique. All pH measurements and titrations will be conducted in accordance with SP 12-14 and all starting solutions will be prepared as per SP 20-4 or described in detail in a scientific notebook. All solutions will be analyzed for elemental composition to determine concentrations. Densities will be measured and reported for all solutions as necessary. All pH measurements and titrations will be conducted using a high-temperature pH probe and temperatures will be monitored during the titrations using a calibrated temperature probe.
Laboratory activities will be recorded in scientific notebooks, and they will be maintained as quality assurance (QA) records.

4.2 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, utilization, and final disposition will be documented in scientific notebooks. 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 (e.g., SNL WIPP Activity/Project Specific Procedure (SP) Form SP 13-1-1, “Chain of Custody”).

4.3 Data Quality Control

4.3.1 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”.

4.3.2 Data Acquisition System

Data collection procedures are specific to individual instruments. For details of the data acquisition for an instrument, see the Specific Procedures (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.
4.4 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.

4.5 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.

4.5.1 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 Calibration Laboratory. Calibration checks will be recorded in a Balance Calibration Records log book.

4.5.2 Liquid Measuring Equipment

Standard Laboratory Class A glassware (pipettes, volumetric flasks, etc.) and adjustable pipettes will be used for all measurements involving of liquids. The calibration of pipettes will be checked periodically against a calibrated balance, and will be recorded in the scientific notebook. The accuracy of pipettes will be within 1%.

4.5.3 Other Analytical Equipment & Techniques

A. 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. Temperature will be maintained using an aluminum bead bath and a hot plate or other heating device.

B. pH Meters and Autotitrators – Solution pH may 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.

C. Equipment for Chemical Analysis – The following instruments may be used for chemical analyses:

- Inductively-Coupled Plasma Mass Spectrometer (ICP-MS)
- Inductively-Coupled Plasma Atomic Emission Spectrometer (ICP-AES)
- UV-Visible (UV-Vis) Spectrophotometer
- CO₂ coulometer
• Ion Chromatograph (IC)
• Refractive Index Analyzer

The usage of these instruments will follow the respective Activity/Project Specific Procedures (SPs).

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: 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”
• SP 13-1 – “Chain of Custody”
• NP 17-1 – “Records”
• NP 20-2 – “Scientific Notebooks”

6 HEALTH AND SAFETY

All the health and safety requirements relevant to the work described in this Test Plan and the procedures that will be used to satisfy these requirements are described in ES&H standard operating procedures (SOP). ES&H SOP describes the non-radiological hazards associated with these experiments and describes the procedures to deal with those hazards, including all the training requirements for personnel involved in conducting the experiments. Additional SOPs may be mandated by SNL ES&H requirements and their issuance will not require revision of this Test Plan.

7 PERMITTING/LICENSING

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

8 REFERENCES


Roselle, G. 2011. Determination of pC\textsubscript{H} Correction Factors in Brines. (Work Carried out under Analysis Plan for Determination of pC\textsubscript{H} Correction Factors in Brines, AP 157 Rev 0). Sandia National Laboratories, Carlsbad, New Mexico. ERMS 556699

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