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Title: STABILITY OF PU (VI) IN SYNTHETIC WIPP BRINE AND
CHLORIDE BRINE SOLUTIONS

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**Los Alamos National Laboratory
EES-12
Test Plan, TP 081501, Rev.0**

**STABILITY OF PU (VI) IN SYNTHETIC WIPP BRINE AND
CHLORIDE BRINE SOLUTIONS**

Rev. 0

Effective Date:

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Test Plan for the Stability of Pu(VI) in synthetic WIPP brine and chloride brine solutions, TP 08-15-01, Rev. 0

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3.0 REVISION HISTORY

This is the first version of this test plan (Revision 0, or Rev. 0). If it becomes necessary to revise this test plan, it will be done in accordance with the Los Alamos National Laboratory (LANL) Actinide chemistry program and it will be re-issued in accordance with LANL-EES-12 "Document Control Process." The history of any and all revisions will be described in this subsection.

4.0 DEFINITION OF ACRONYMS

CBFO: (U.S. DOE) Carlsbad Field Office.

CCA: (WIPP) Compliance Certification Application.

DOE: (U.S.) Department of Energy.

DRC: document review and comment.

E-CO: (LANL) Environmental Science and Waste Technology (Division)-
Carlsbad Operations.

E-ET: (LANL) Environmental Science and Waste Technology (Division)-
Environmental Technology.

ERDA: (U.S.) Energy Research and Development Administration.

ES&H: environment safety and health.

GWB: Groundwater B, synthetic WIPP brine.

I: Ionic Strength.

ILW: Intermediate Level Waste.

LANL: Los Alamos National Laboratory.

LSC: liquid scintillation counting.

m: molal.

M: molar.

MgO: magnesium oxide.

M&TE: measuring and test equipment.

NP: (SNL) Nuclear-Waste-Management-Program procedure.

NWMP: (SNL) Nuclear Waste Management Program.

PA: performance assessment.

PI: principal investigator.

PR: purchase requisition.

Pu: plutonium (oxidation state unspecified).

Pu(III): plutonium in the +III oxidation state.

Pu(IV): plutonium in the +IV oxidation state.

Pu(V): plutonium in the +V oxidation state.

Pu(VI): plutonium in the +VI oxidation state.

Pu(VII): plutonium in the +VII oxidation state.

QA: quality assurance.

QAP: quality assurance procedure.

Rev.: revision.

SCM: (SNL) Software Configuration Manager.

SDR: Sandia-Delegated Representative.

SNL: Sandia National Laboratories.

SP: activity- or project-specific procedures.

STTP: (WIPP) Source-Term Waste Test Program.

TP: test plan.

TRU: transuranic waste.

UV/VIS: ultraviolet/visible (light) spectrophotometry.

WIPP: Waste Isolation Pilot Plant.

WBS: Work Breakdown Structure.

WPO: (SNL) WIPP Project Office.

XRD: X-ray diffraction.

5.0 PURPOSE AND SCOPE

Because geological salt formations are considered possible sites for radioactive waste disposal, the effect of radiolysis on high-saline brine under simulated repository conditions has been the subject of numerous investigations within the last two decades [1-25]. Also of interest is radiation-chemical behavior in brines, because rock salts in geological repositories generally contain a small amount of brine inclusions that are not homogeneously distributed. Over time, these inclusions may migrate towards the waste container, which acts as a heat source. Brines will also form in geological repositories if the groundwater reaches the salt deposits [24].

In the near-field chemistry of a salt repository, the radiolytically-induced redox reactions in concentrated saline solution are of particular importance because the radiolysis of saline solutions results in the creation of oxidizing chlorine species [5, 7-10, 25], which may oxidize actinide species to higher oxidation states [14, 15] but also in reducing species such as hydrogen peroxide which may reduce actinide species to lower oxidation states [26]. Even though the number of publications concerning the influence of radiolysis by-products on the speciation of actinides is limited, when synthetic brine applications are considered, most of the studies report that hypochlorite generated by alpha irradiation [22, 23] of a concentrated NaCl solution oxidizes Am (III) to Am (V), Pu (IV) to Pu (VI), and Np (IV) to Np (V) [14-16, 18-21]. Morgenstern et al. studied the kinetics of the reduction of Pu (V) O_2^+ by hydrogen peroxide in 1.0 m NaCl solution with time and monitored Pu(V) concentration by ultrafiltration combined with solvent extraction using TTA [26]. The reduction of PuO_2^+ was found to be first order with respect to hydrogen peroxide concentration and inverse first order with respect to hydrogen ion concentration.

The primary objective of these experiments is to clarify the complex chemistry of actual TRU waste in contact with WIPP brines as noted in the LANL Source-Term Waste Test Program (STTP) by examining the sub-effects influencing the overall pH-Eh system. Radiolysis is considered to be the major driving force in oxidation of actinides. Alpha- and gamma-irradiation of chloride solutions (WIPP brine) has the potential to generate secondary oxidizing agents (e.g. hypochlorite, hydrogen peroxide), and further to convert low solubility Pu (III, IV)/Am (III) species to Pu (V, VI)/Am (V) species, which are highly soluble and have a strong tendency for migration in the environment.

The temporary appearance of highly mobile plutonium (VI) and (V) species in the STTP experiments might not prove to be important to the WIPP repository concept. Nevertheless, to fully understand and to predict the long-term behavior of actinides under the complex high-saline repository conditions, additional experimental approaches are necessary. The experiments described in this test plan are necessary to study (1) the stability of Pu (VI)-239 in synthetic WIPP brines as well as chloride brine solutions, (2) the effect of pH on the stability of Pu (VI) in brines, and (3) the effect of H₂O₂ (10⁻² M) on the stability of Pu (VI) in brines at pH 6, 7, 8, and 9.

6.0 EXPERIMENTAL PROCESS DESCRIPTION

6.1 Overall Strategy and Process

LANL personnel will use actinide speciation experiments, and characterization techniques such as UV/Vis spectrophotometry to determine the influence of alpha-radiolysis by-products on the speciation of Pu (VI) in the liquid phase, as well as Diffuse Reflectance, EXAFS and X-Ray diffraction to investigate the speciation of Pu in the solid state. (see Section 5.0, PURPOSE AND SCOPE, above).

LANL personnel will synthesize the brine composition of interest (see Annex A). Two different brines of interest, i.e. ERDA-6 and GWB, will be prepared, as well as a 5m NaCl solution and a 3.7m MgCl₂·6H₂O solution, for comparison. To avoid the formation of CaCO₃ in the ERDA-6 brine solution at pH > 7, we will not add NaHCO₃ in the recipe

of ERDA-6. Since the two synthetic WIPP brines, ERDA-6 and GWB are highly concentrated, it has been decided to use 95% of each constituent present in these brines as the final brine composition. Once the solutions are prepared, pH and Eh are measured, and the final concentration of each constituent is assessed by ICP-MS. In a typical experiment under normal atmosphere, Pu (VI) stock solution is added to a (1) 5 m NaCl solution (2.5 mL), (2) 3.7 m MgCl₂ (2.5 mL), (3) ERDA-6 synthetic brine (2.5 mL), or (4) GWB synthetic brine (2.5 mL), to produce a final activity of $5 \cdot 10^{-4}$ M ²³⁹Pu. Aliquots of 10^{-2} M H₂O₂ will be added to the solution and the pH will be adjusted to its final value by adding NaOH or HCl. Once the sample is prepared, the concentration of Pu species in solution will be monitored by UV/Vis spectrophotometry. The temperature will remain constant at 25°C. The formation of Pu (V) will be monitored by UV/Vis spectrophotometry. Eh and pH will be monitored over time. The experiments described here will be carried out for a period of one year.

The major chemical in the synthetic WIPP groundwater GWB is MgCl₂·6H₂O, but it also contains Na₂SO₄, NaCl, LiCl, KCl, NaBr, and Na₂B₄O₇·10H₂O). Therefore, it is necessary to compare the stability of Pu (VI) in pure MgCl₂·6H₂O solution and synthetic GWB WIPP brine. Another synthetic WIPP groundwater brine called ERDA-6, where the major constituent is NaCl, will be used to compare the stability of Pu (VI) in ERDA-6 and in a pure 5m NaCl solution. The pH values of MgCl₂, NaCl and the two synthetic WIPP brines, ERDA-6 and GWB, are around 7, it is important to know how pH is influencing the stability of Pu (VI) in these solutions. It is also necessary to know the effect of H₂O₂ on the stability of Pu (VI) in these 4 solutions at pH relevant for the WIPP repository (i.e. pH 6, 7, 8 and 9). These experiments will provide some useful and defensible results on Pu (VI) stability under WIPP repository conditions.

The experimental design is described in Table 1.

Table 1. Experimental Design for studying the stability of Pu (VI) in Brines

MgCl ₂ .6H ₂ O	95% GWB synthetic brine	95% ERDA-6, no NaHCO ₃	NaCl
pH 6	pH 7	pH 7	pH 7
pH6 + H ₂ O ₂	pH 7 + H ₂ O ₂	pH7 + H ₂ O ₂	pH7 + H ₂ O ₂
pH 7	pH 8	pH 8	pH 8
pH 7 + H ₂ O ₂	pH 8 + H ₂ O ₂	pH 8 + H ₂ O ₂	pH 8 + H ₂ O ₂
		pH 9	pH 9
		pH 9 + H ₂ O ₂	pH 9 + H ₂ O ₂

The experiments will be conducted in duplicate. A total of 40 samples will be analyzed by UV/Vis spectrophotometry over time (10 minutes, 1 day, 10 days, 30 days, 3 months, 6 months, 1 year). Each sample contains 3 mL of 5×10^{-4} M of Pu (VI) –239, therefore a total of 14.34 mg of Pu-239 will be used.

The ²³⁹Pu (VI) stock solution (14.34 mg) will be made up in a final matrix of dilute HCl acid (pH~2) by Phil Palmer.

In a fume hood, the stock solution of Pu (VI) will be opened. With an Eppendorf pipette, the appropriate volume of stock solution will be transferred from the stock solution container to a UV/Vis cell. The volume of Pu (VI) stock solution transferred will correspond to a final activity of 5×10^{-4} M ²³⁹Pu (VI). Brine solution will be added to Pu (VI) solution to a total volume of 2.5 mL. The pH will be adjusted to 6, 7, 8, or 9 by adding the appropriate amount of NaOH solution, the proper amount of H₂O₂ will be added to the solution. The final volume will be made up to 3mL of Pu (VI) in brine in the UV/Vis cell. The UV/Vis cell will be sealed for an indefinite period of time (~1 year). The cells will be stored in a small controlled-atmosphere box (10 inch * 10 inch). Periodically, an absorbance UV/Vis spectrum will be taken which implies transferring the sealed UV/Vis cell containing the Pu (VI) in brine (5×10^{-4} M) from the fume hood to the spectrophotometer. The lid of the spectrophotometer will be opened, the UV/Vis cell

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will be placed in the spectrophotometer. A spectrum will be taken over the wavelength range between 200 nm to 1100 nm using a time period of approximately 1 minute.

When the operation is finished, the UV/Vis cell containing the Pu (VI) solution will be transferred from the spectrophotometer to its original place in the controlled-atmosphere box in the fume hood.

Notes:

Preliminary tests for adjusting the pH of brine solutions have been performed on non-active brine solutions by adding drops of NaOH of different concentrations, by Dr. Mark Walthall from the Carlsbad Environmental and Monitoring Research Center, Carlsbad. The results obtained are as follows:

3.7M MgCl₂ · 6H₂O - pH 7 no precipitate

3.7M MgCl₂ · 6H₂O - pH 8, and 9 precipitate

95% GW-Brine - pH 7, pH 8 no precipitate

95% GW-Brine - pH 9 precipitate

95% ERDA-6 with NaHCO₃ - pH 7 no precipitate

95% ERDA-6 with NaHCO₃ - pH 8, and 9 precipitate

95% ERDA-6 without NaHCO₃ - pH 7, pH 8, pH 9 no precipitate

5M NaCl - pH 7, pH 8, pH 9 no precipitate

These results were used in the conceptual design of the actual experiments (see Table 1).

6.2 Planning and Quality Assurance

LANL personnel will carry out the work described in this test plan in accordance with SNL/WIPP NPs, formerly known as QAPs or LANL Standard Operating Procedures (SOPs) or project-specific procedures. If project specific procedures are developed, LANL Document Control program will be used to prepare and control them as designated procedures.

Each LANL individual performing work under this test plan is responsible for achieving and maintaining quality. LANL line management is responsible for verifying quality. Independent LANL, SNL, and/or DOE/CBFO assessors are responsible for ensuring that quality is adequate for the intended use and properly documented.

LANL personnel will plan and document the processes used for the experiments described in Subsection 6.1, Overall Strategy and Process (see above), in accordance with the NP 20-2, "Scientific Notebooks." If project-specific procedures are developed, Known sources of error and uncertainty, including any uncertainty about the quality of input data, and the compatibility of data processing with any conceptual/mathematical models used at each applicable stage will also be documented in the scientific notebook. Documents to be maintained as QA records (e.g. scientific notebooks) that are not already specified in this test plan will be specified in the appropriate procedures.

LANL will control documents, as appropriate, in accordance with NP 6-2, "Document Control Process."

LANL will control processes such as performing analyses, checking routine mathematical calculations, or verifying spreadsheet calculations or utility codes to ensure that these processes are accurate, consistent, and reproducible.

LANL will develop, document, review, and approve any software developed or adapted for the WIPP project that performs data reduction or analysis, and/or supports models, and whose results are used in support of the WIPP in accordance with NP 19-1, "Software." (LANL may document simple analyses according to the requirements specified in NP 9-1, "Analyses.") They will list software classified as "off-the-shelf" or "vendor" software, data-acquisition software, and other classifications in their QA records. They will also list software classification, version, and platform and approved

users in their QA records. In addition, they will submit the list to the SNL/WIPP Software Configuration Manager (SCM) for inclusion on the WIPP Software Baseline Inventory List. (They can obtain the name and address of the current SCM from the Sandia-Delegated Representative, or SDR.)

LANL will identify conditions adverse to quality, determine the cause of these conditions, correct them, take actions to prevent recurrence, and document all of these steps.

LANL personnel working in collaboration with CEMRC will identify, label and control all samples in accordance with CEMRC CP-PROC-0003-000 "Logging Research Samples into the SID database". They will transfer all samples in accordance with CEMRC CP-PROC-001-000-100898 "Procedure: Sample Tracking and Chain of Custody" or CEMRC CP-PROC-005-000 "Analytical Request From Procedure".

6.3 Sample Control

The experiments described in Subsection 6.1, Overall Strategy and Process (see above), will require some sampling of solutions and solids for post-test characterization. LANL personnel will identify, label, and control all samples in accordance with NP 13-1, "Sample Control." They will transfer all samples in accordance with SP 13-1, "Chain of Custody."

P. Paviet-Hartmann and N. Lu, the LANL Principal Investigators (PIs) responsible for the work described in this test plan, will determine the disposition of samples after this work is completed.

6.4 Data Quality Control

LANL personnel will implement a calibration program for all of the measuring and test equipment (M&TE) used for the experiments described in Subsection 6.1, Overall Strategy and Process (see above), in accordance with NP 12-1, "Control of Measuring and Test Equipment." This M&TE calibration program will meet the requirements in NP 12-1 for: (1) receiving and testing M&TE; (2) technical operating procedures for M&TE; (3) the traceability of LANL standards to nationally recognized standards such as those from the National Institute of Standards and Technology; and (4) maintaining calibration records.

6.5 Data Identification and Use

LANL personnel will use scientific notebooks to record all of the data and conclusions obtained from the experiments described in Subsection 6.1, Overall Strategy and Process (see above), in accordance with NP 20-2, "Scientific Notebooks." Data transfer and reduction controls, control of erroneous or inadequate data, including identification, segregation and disposition of the data, and data conversion controls will be documented in the scientific notebook or in a project-specific procedure (SP).

LANL will check the results of calculations in accordance with NP 9-1, "Analyses." They will use one of the following methods: (1) separate independent calculations using the same or different analytical methods as the original calculations; (2) a check of each of the calculation steps in the original calculations, or a random (spot) check of the original calculations.

6.6 Records, Reports, and Audits

LANL personnel will consider all records providing evidence of quality, including but not necessarily limited to personnel qualification and training forms, lists of M&TE and software, technical procedures, laboratory notebooks, calibration records, and

reports, to be QA records. All of these records will be accurate, complete, identifiable, and legible.

7.0 TRAINING

P. Paviet-Hartmann and N. Lu, the LANL PIs responsible for the work described in this test plan, will ensure that training of LANL personnel is assigned and completed, and that the certification of personnel qualifications is documented according to the Hazard Control Plan LANL-EES 12 HCP. LANL personnel will complete all personnel qualification and training, and all of the documentation thereof, before beginning work.

8.0 HEALTH AND SAFETY

The work described in this test plan will require that LANL personnel use small quantities of Pu. Handling Pu, and other actinide elements in the laboratory, even in small quantities, necessitates specialized requirements for facilities, procedures, training, and oversight. These environment safety and health (ES&H) requirements are even more demanding than those necessary for most other chemical elements.

LANL has extensive experience handling Pu, and other actinide elements, and has developed comprehensive, detailed ES&H requirements and standard operating procedures for such work. Description of these requirements and procedures is beyond the scope of this test plan. All LANL personnel will work under Hazard Control Plans (HCPs) for the appropriate locations where work is performed at LANL sites. All personnel will be qualified and approved to work by the appropriate LANL line manager (Group Leaders of EES-12 and C-INC).

However, it is worth noting that, in the context of LANL's experience with Pu, and other actinide elements, the quantities of Pu LANL personnel will use for this work are small, and the procedures they will use are routine. Consequently, there are no

special licensing or permitting requirements required (see 9.0, LICENSING/PERMITTING, below).

9.0 LICENSING/PERMITTING

There are no licensing or permitting requirements specific to the work described in this test plan (see 8.0, HEALTH AND SAFETY, above).

10.0 DELIVERABLES

The expected deliverables for the investigation on the “ Stability of Pu (VI) in synthetic WIPP brine, and chloride brine solutions” are:

- Quaterly progress reports providing experimental updates
- Final report on “ Stability of Pu (VI) in synthetic WIPP brine, and chloride brine solutions”
- Journal publication if deemed worthwhile

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ANNEX A:-CEMRC Brine Preparation Procedure

1.0 PURPOSE

This procedure describes how synthetic brine solutions are prepared at CEMRC in conjunction with the Actinide Chemistry and Repository Science Program in support of the WIPP.

Two of the synthetic brine solutions are formulated to represent ground water from saline aquifers above and below the WIPP. The ERDA-6 brine solution is representative of brines collected from the Castile formation situated at depth below the WIPP and is dominated by NaCl. The GW brine solution is representative of brines collected from the Salado formation situated above the WIPP and is dominated by MgCl₂. Components at lesser concentrations occur in both of these synthetic brines (Ca, K, Li, B, Br, HCO₃ and SO₄).

Two simplified brine solutions are also utilized in investigations in which the complexity of the ERDA-6 and GW brine solutions can be problematic. A 5 M NaCl solution is used as a simplified ERDA-6 brine. A 3.7 M MgCl₂ solution is used as a simplified GW brine.

The procedures that follow were designed for preparing 1-liter volumes of the individual brines.

2.0 Scope & Limitations

Some exceptions have been taken regarding the synthetic composition of the ERDA-6 and GW brine solutions as originally described (Bryan and Wang, 2000) in order to increase the probability that the composition of the brines can be reproducible and remain stable.

- 2.1. The temperature in the original description of the brine solution is 30°C (Brush, 1990). Trying to prepare these brines at room temperature (21°C) or lower is not realistic, because conditions of super-saturation will force precipitation of the salts. To minimize this problem, the compositions of the ERDA-6 and GW brine solutions have been reduced to 95% of the original solution concentration.
- 2.2. The original composition of the ERDA-6 brine calls for the addition of NaHCO₃, followed by the addition of CaCl₂. The concern in this matter was the precipitation of CaCO₃. The final step in preparing the ERDA-6 solution was the adjustment of the solution pH to 6.17. This solution was initially stable. However, after two to three days a white precipitate was observed as a thin coating on the walls of the glass container. It was decided to omit the addition of NaHCO₃ in the 95% ERDA-6 brine, because the precipitation of CaCO₃ would

limit Pu solubility. It was also decided to omit the pH adjustment to 6.17 as most investigations specify the desired pH of the brine.

- 2.3. The ability to express solution concentrations in units of molarity (M) and molality (m) is needed. The solutions will be prepared volumetrically (M) as described below. However, in addition to knowing the masses of reagents used, it is also necessary to determine the mass of water added for determining the molality. To accomplish this, each volumetric flask used in the final dilution of each brine solution, must be weighed, (1) empty and dry, and (2) after the brine solution has been brought to its final volume.
- 2.4. Each brine solution should be stored under refrigeration (4 °C) for a minimum of two weeks prior to first use and thereafter for periods when not in use to ensure (1) that the solution composition remains stable and (2) that microbial growth is minimized. Before removing an aliquot from the brine solution, the brine shall be allowed to reach room temperature (approximately 24 hours) and agitated. This is to ensure that any precipitates that may have formed due to the reduced temperature are allowed to dissolve. The remaining stock solution should be returned immediately to the refrigerator after the aliquot is removed.
- 2.5. Following initial preparation (and before being used in a task or investigation following refrigeration), the composition of each brine solution should be verified by ICP-MS/IC for the following analytes:
 - 2.5.1. ICP-MS
 - 2.5.1.1. Na, Mg, Ca, K, B, Br, Li (from reagents)
 - 2.5.1.2. Si, Al, Ti, Mn, Ba, Fe, Pb, Sr, U, Th (from impurities or contamination)
 - 2.5.2. IC
 - 2.5.2.1. SO₄, Cl (from reagents)
 - 2.5.2.2. NO₃, PO₄ (from impurities or contamination)

3.0 Definitions

Not applicable

4.0 References

Brush, L.H. 1990. Test Plan for Laboratory and Modeling Studies of Repository and Radionuclide Chemistry for the Waste Isolation Pilot Plant. SAND90-0266. Disposal Room Systems Division. Sandia National Laboratories. Albuquerque, NM.

Bryan, C.R. and Y. Wang. 2000. Test Plan for Cement Borehole Plug Degradation Studies, TP 00-06, Rev. 0. Sandia National Laboratories, Albuquerque, NM.

5.0 Personnel Responsibilities

All brine samples prepared at the CEMRC must be assigned a unique SID using the SID database. These SIDs should be assigned at the earliest opportunity when an aliquot is derived. Aliquots can only be logged into the system if the original sample has been logged in previously. The person logging in a sample is responsible for properly entering appropriate data.

6.0 Procedure

6.1. Materials

6.1.1. Equipment

- 6.1.1.1. top loading balance (12-kg capacity, d = 0.1g)
- 6.1.1.2. analytical balance (>500-g capacity, d = 0.001g)
- 6.1.1.3. pH/mV meter
- 6.1.1.4. pH electrode with automatic temperature compensation
- 6.1.1.5. pH buffers (pH = 4, 7, 10 and 12.5)
- 6.1.1.6. magnetic stirrer and stir-bar
- 6.1.1.7. 2-L graduated beaker
- 6.1.1.8. 1-L volumetric flasks
- 6.1.1.9. 1-L plastic bottles
- 6.1.1.10. vacuum filtration set-up
- 6.1.1.11. 0.2- μ m filter (polypropylene or nylon)
- 6.1.1.12. 20-ml plastic vials with screw caps

6.1.2. Chemicals

All chemical reagents should be reagent grade when possible or certified grade at minimum.

- 6.1.2.1. Concentrated HCl in dropper bottle
- 6.1.2.2. NaCl
- 6.1.2.3. NaBr
- 6.1.2.4. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
- 6.1.2.5. Na_2SO_4
- 6.1.2.6. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- 6.1.2.7. $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
- 6.1.2.8. KCl
- 6.1.2.9. LiCl
- 6.1.2.10. Deionized (DI) H_2O

6.2. Preparation of Brines

All laboratory observations (i.e. sample inventory, final weights, pH values, and comments and observations) should be recorded in the "Laboratory Personnel" and "Brine Preparation" scientific notebooks.

Do not use plasticware for the preparation of the brine solutions as abrasion from the magnetic stir-bar may result in plastic fragments. Do not store the brine solutions in borosilicate glassware. Store all solutions in plastic or Teflon bottles.

Obtain Sample Identification Numbers (SID) from the SID database for the appropriate aliquots. Label brine storage containers with 1) the solution concentration and composition or the name of the brine, 2) date prepared, and 3) the initials of the person preparing the brine solution.

6.2.1. GW Brine (95%)

Reagent	GW Brine - 95% (g / L)
MgCl ₂ •6H ₂ O	196.7
NaCl	170.6
Na ₂ SO ₄	23.97
NaBr	2.602
Na ₂ B ₄ O ₇ •10H ₂ O	14.31
KCl	33.09
LiCl	0.177
CaCl ₂ •2H ₂ O	1.930

- 6.2.1.1. Collect a 20-mL aliquot of DI water in a 20-mL plastic vial with screw cap and reserve for ICP-MS/IC analysis along with final brine solutions.
- 6.2.1.2. Weigh the designated amount of MgCl₂•6H₂O into a large weigh-boat. Quantitatively transfer the salt into a 2-L graduated beaker and dissolve by adding approximately 700 mL of DI H₂O. Add 1 mL of concentrated HCl. Place the solution on a magnetic stirrer, add stir-bar, and stir until salt is completely dissolved.

Note: To speed the dissolution of the large quantities of salt, it is acceptable to heat the solution at a temperature between 50-70° C.

Note: MgCl₂•6H₂O is very hygroscopic and will adsorb water from the air. It is important that the reagent storage container be tightly sealed immediately after use. This salt is also difficult to work with, as the crystals are long thin blades that do not pack well and tend to “jump”. Do not try to dry this reagent in a drying oven, as crystalline water will be lost.

- 6.2.1.3. Add the specified amount of NaCl to the beaker. Bring the solution volume to approximately 900 mL (including the stir bar) with DI H₂O. This volume is needed to dissolve the NaCl. Do not exceed this amount at this time.
- 6.2.1.4. Weigh and quantitatively transfer the remaining salts into the 2-L beaker (1) in the order listed, (2) after the preceding salt has been completely dissolved, and (3) without exceeding approximately 950 mL.
- 6.2.1.5. Quantitatively transfer the brine solution into a 1-L volumetric that has been weighed empty. (If the brine was heated to complete dissolution of the salts, it is critical that you allow the solution to adjust to room temperature before transferring.) Bring the solution to volume. Weigh the volumetric with contents and record weight.
- 6.2.1.6. Transfer the brine solution into a 1-L plastic storage bottle after vacuum filtering through a 0.2- μ m filter (polypropylene or nylon). Collect a 20-mL aliquot for ICP-MS/IC analysis in a 20-mL plastic vial with screw cap. Measure and record the solution pH.
- 6.2.1.7. Store the solution under refrigeration for a minimum of two weeks before using.
- 6.2.1.8. Before using the stored solution, remove it from the refrigerator approximately 24 hours before its intended use and allow it to reach room temperature. Remove a 30-mL aliquot from the plastic storage bottle and transfer into a small beaker; measure and record the pH (see QA comments at end of procedure).
- 6.2.1.9. Collect a 20-mL aliquot of the brine for ICP-MS/IC analysis in a 20-mL plastic vial with screw cap.

6.2.2. ERDA-6 (95%)

Reagent	ERDA-6 - 95% (g / L)
NaCl	248.6
Na ₂ SO ₄	22.52
Na ₂ B ₄ O ₇ •10 H ₂ O	5.700
NaBr	1.074
KCl	6.869
MgCl ₂ •6H ₂ O	3.667
CaCl ₂ •2H ₂ O	1.672

- 6.2.2.1. Collect a 20-mL aliquot of DI water in a 20-mL plastic vial with screw cap and reserve for ICP-MS/IC analysis along with final brine solutions.
- 6.2.2.2. Add the specified amount of NaCl to a 2-L beaker. Bring the solution volume to approximately 850 mL with DI H₂O. This volume is needed to dissolve the NaCl. Do not exceed this amount at this time.

Note: To speed the dissolution of the large quantities of salt, it is acceptable to

heat the solution at a temperature between 50-70° C.

- 6.2.2.3. Place the solution on a magnetic stirrer, add stir-bar, and stir. If this volume of water is not enough to dissolve the NaCl after one hour of stirring, increase the volume to 900 mL (including stir bar).
- 6.2.2.4. Weigh and quantitatively transfer the remaining salts into the 2-L beaker (1) in the order listed, (2) after the preceding salt has been completely dissolved, and (3) without exceeding approximately 950 mL.
- 6.2.2.5. Quantitatively transfer the brine solution into a 1-L volumetric that has been weighed empty. (If the brine was heated to complete dissolution of the salts, it is critical that you allow the solution to adjust to room temperature before proceeding.) Bring the solution to volume. Weigh the volumetric with contents and record the weight.
- 6.2.2.6. Transfer the brine solution into a 1-L plastic storage bottle after vacuum filtering through a 0.2- μ m filter (polypropylene or nylon). Collect a 20-mL aliquot for ICP-MS/IC analysis in a 20-mL plastic vial with screw cap. Measure and record the solution pH (see QA comments at end of procedure).
- 6.2.2.7. Store the solution under refrigeration for a minimum of two weeks before using.
- 6.2.2.8. Before using the stored solution, remove it from the refrigerator approximately 24 hours before its intended use and allow it to reach room temperature. Remove a 30-mL aliquot from the plastic storage bottle and transfer into a small beaker; measure and record the pH (see QA comments at end of procedure).
- 6.2.2.9. Reserve a 20-mL aliquot of the brine for ICP-MS/IC analysis in a 20-mL plastic vial with screw cap.

6.2.3. NaCl 5M

Reagent	5 M NaCl (g / L)
NaCl	292.2

- 6.2.3.1. Collect a 20-mL aliquot of DI water in a 20-mL plastic vial with screw cap and reserve for ICP-MS/IC analysis along with final brine solutions.
- 6.2.3.2. Add the specified amount of NaCl to a 2-L beaker. Bring the solution volume to approximately 900 ml with DI H₂O. This volume is needed to dissolve the NaCl. Do not exceed this amount at this time.
- 6.2.3.3. Place the solution on a magnetic stirrer, add stir-bar, and stir. If this volume of water is not enough to dissolve the NaCl after one hour of stirring, increase the volume to 950 mL (including stir bar).

Note: To speed the dissolution of the large quantity of salt, it is acceptable to heat the solution at a temperature between 50-70° C.

- 6.2.3.4. Quantitatively transfer the brine solution into a 1-L volumetric that has been weighed empty. (If the brine was heated to complete dissolution of the salts, it is critical that you allow the solution to adjust to room temperature.) Bring the solution to volume. Weigh the volumetric with contents and record the weight.
- 6.2.3.5. Transfer the brine solution into a 1-L plastic storage bottle after vacuum filtering through a 0.2- μ m filter (polypropylene or nylon).
- 6.2.3.6. Remove a 30-mL aliquot from the plastic storage bottle and transfer into a small beaker; measure and record the pH (see QA comments at end of procedure).
- 6.2.3.7. Reserve a 20-mL aliquot of the brine for ICP-MS/IC analysis in a 20-mL plastic vial with screw cap.

6.2.4. MgCl₂•6H₂O 3.7 M

Reagent	3.7 M MgCl ₂ •6H ₂ O (g / L)
MgCl ₂ •6H ₂ O	751.9

- 6.2.4.1. Collect a 20-mL aliquot of DI water in a 20-mL plastic vial with screw cap and reserve for ICP-MS/IC analysis along with final brine solutions.
- 6.2.4.2. Add the specified amount of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to a 2-L beaker. Bring the solution volume to approximately 900 mL with DI H_2O .

Note: Heating is not necessary to dissolve this salt.

- 6.2.4.3. Quantitatively transfer the brine solution into a 1-L volumetric that has been weighed empty. Bring the solution to volume. Weigh the volumetric with contents and record the weight.
- 6.2.4.4. Transfer the brine solution into a 1-L plastic storage bottle after vacuum filtering through a 0.2- μm filter (polypropylene or nylon).
- 6.2.4.5. Remove a 30-mL aliquot from the plastic storage bottle and transfer into a small beaker; measure and record the pH (see QA comments at end of procedure).
- 6.2.4.6. Reserve a 20-mL aliquot of the brine for ICP-MS/IC analysis in a 20-mL plastic vial with screw cap.

7.0 Records

“Laboratory Personnel” scientific notebooks
“Brine Preparation” scientific notebook
“Gravimetric Balance” logbook
“Sample Identification Number” SID Database

8.0 Quality Assurance

Gravimetrics – Check “Gravimetric Balance” logbook to verify that balance has been tested for compliance with check weights for the day of use.

pH Measurements – Verify that all pH calibration standards do not exceed their expiration date. Perform a three-point calibration of the electrode in use that includes buffers above and below the pH of the brine solution. If calibration slope is less than 90%, repeat calibration. If calibration slope fails after a second attempt at calibration, notify laboratory supervisor before proceeding. Before proceeding with the first unknown sample, repeat measurement of the pH 7 standard. If the pH reading is not within ± 0.05 pH units of the expected value, repeat the calibration procedure. If the calibration check fails after two calibration attempts, notify the laboratory supervisor before proceeding. After determining the pH of five samples, or if 30 minutes has elapsed from the time of calibration (which ever comes first), measure the pH of the pH 7 buffer

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solution. If the pH reading does not fall within ± 0.05 pH units of the expected value, repeat the calibration procedure.

9.0 Appendices

Not applicable