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ACTIVITY/PROJECT SPECIFIC PROCEDURE

SP 20-4
PREPARING SYNTHETIC BRINES FOR GEOCHEMICAL EXPERIMENTS
Revision 2

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(printed name) (signature) (date)

1.0 Purpose and Scope

This procedure gives recipes for a variety of synthetic brines and tells how to prepare them in both small (≤ 2 L) and large (> 2 L) quantities in geochemical experiments. Synthetic brines are used in various geochemical experiments being done in support of the Waste Isolation Pilot Plant (WIPP) project, and their preparation shall be prepared in accordance with this procedure.

Acronyms and definitions for terms used in this procedure may be found in the Glossary located at the Sandia National Laboratories (SNL) WIPP Online Documents web site.

2.0 Implementation Actions

2.1 Responsibility

2.1.1 The Principal Investigator (PI)

The PI or designee shall determine the requirements for each batch of brine including which recipe to use, and the amount to prepare.

2.1.2 Lab Personnel

Personnel who prepare synthetic brines shall comply with the requirements of this procedure.

2.2 Safety

The activities described in this SP shall conform to SNL Environmental Safety and Health programs (ES&H). There are no unique ES&H issues associated with preparing synthetic brines. General chemical handling and disposal issues are covered in Standard Operating Procedures for the facilities in which the brines will be prepared.

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2.3 Definitions

Charge balance error (ΔC) - groundwaters (including brines) are electrically neutral. That is, the sum of the positive ionic charges equals the sum of the negative ionic charges. However, analytical results of groundwaters may not have the charge balance. The charge balance error is a measure of the apparent deviation from electrical neutrality. The charge balance error may be caused by analytical uncertainty in the analytical results, by important ionic species not being analyzed, or by both. If necessary, charge balance error check will be used to develop recipe(s) for any brine other than GWB and ERDA-6 (see below), which already have recipes.

The charge-balance equation may be written as follows:

$$\Delta C = \frac{\sum cations - \sum anions}{\sum cations + \sum anions} x\,100$$

Where

ΔC = charge balance error in percentage
∑cations = sum of the positive ionic charges
∑anions = sum of the negative ionic charges

2.4 References

- TP 00-07, Experimental Study of WIPP Engineered Barrier MgO at Sandia National Laboratories Carlsbad Facility
- Brush, L.H. 2005. "Results of Calculations of Actinide Solubilities for the WIPP Performance Assessment Baseline Calculations." Analysis report, May 18, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539800.U.S. DOE. 1996.
- Brush, L.H., and Y.-L. Xiong, 2005. "Calculation of Actinide Solubilities for the WIPP Performance-Assessment Baseline Calculations, Analysis Plan AP-120, Rev. 0. April 4, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539255.

2.5 Recipes

Section 2.5.1 discusses recipes for the synthetic Salado (GWB) and Castile brines (ERDA-6) used in geochemical research. Section 2.5.2 describes a method for formulating a recipe from a given bulk composition.

2.5.1 Salado and Castile Brines

GWB is a synthetic brine that represents the bulk composition of the intergranular brines from the Salado Formation at or near the stratigraphical horizon of the WIPP. ERDA-6 is a synthetic brine that has the bulk composition similar to naturally occurring brines from the reservoirs in the Castile Formation. Appendix A gives the recipes for the GWB and ERDA-6. In addition, in order to facilitate experimental work, the recipes of GWB and ERDA-6 equilibrated with halite (NaCl), anhydrite ($CaSO_4$), brucite ($Mg(OH)_2$), and hydromagnesite (5424) ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) are developed in Revision 2 of this SP. The recipes are developed to match as closely as possible the compositions of GWB and ERDA-6 equilibrated with the above solid phases according to the FMT calculations. The chemical compositions of equilibrated GWB and ERDA-6 are listed in Appendix D, and the corresponding recipes on molarity scale are listed in Appendix E.

2.5.2 Formulating a Recipe

As the recipes for GWB and ERDA-6 have been developed, the following is the general guidance for developing any new recipe, if necessary.

In many cases, the measured composition of the brine to be synthesized will not have a charge balance error of zero. In such cases, it will be impossible to generate a recipe that produces that exact composition. If the charge-balance error is not zero, there are several ways to address the problem. The following are two possible ways in addressing the non-zero charge balance problem.

Adjust the concentrations of any or all of the solutes so that the composition has a charge balance error of zero. Then follow steps 2.5.2.1 through 2.5.2.5 below.

Allow the most abundant cation and anion (typically Na and Cl) to share the discrepancy. Follow steps 2.5.2.1 through 2.5.2.5 below, and recognize that the amount of NaCl needed to provide the remaining Na and the amount needed to provide the remaining Cl may differ significantly. As instructed in step 2.5.2.5, use the average of the two amounts.

The following steps summarize how to formulate a recipe.

2.5.2.1 Select simple reagents. For example, add potassium as either the chloride or the sulfate salt, rather than some of each. If the reagents are selected carefully, only Na, Cl, and perhaps sulfate will be contributed by more than one reagent, and the calculations will be simpler.

2.5.2.2 Start with an ion that will be contributed by only one reagent (such as B, Br, inorganic carbon, Ca, K, or Mg). Calculate the amount of reagent needed to provide the desired amount of that ion.

2.5.2.3 Repeat step 2.5.2.2 for each ion that will be contributed by only one reagent.

2.5.2.4 If sulfate is being contributed by more than one source, calculate the amount provided for in steps 2.5.2.2 and 2.5.2.3, and then calculate the amount of Na_2SO_4 needed to make up the difference.

2.5.2.5 Calculate the amounts of Na and Cl provided for in steps 2.5.2.2, 2.5.2.3, and 2.5.2.4. Then calculate the amount of NaCl needed to provide the remaining sodium. Calculate separately the amount needed to provide the remaining chloride. Note that even if the composition had a charge balance error of zero, the two numbers may differ slightly because of round-off errors. Use the average of the two numbers.

Be aware that the preceding discussion applies to brines in which sodium and chloride are the dominant solutes (from the vicinity of the WIPP Site).

If a new recipe is developed, the composition of the prepared synthetic brine should be verified by chemical analyses.

For information about how to calculate the concentrations of the various solutes, consult an introductory chemistry textbook or technician's handbook.

2.6 Equipment and Reagents

2.6.1 Equipment

2.6.1.1 Equipment for Drying Reagents

Equipment for drying reagents includes glassware (weighing bottles or beakers), a laboratory oven, desiccators, and desiccant.

2.6.1.2 Equipment for Weighing Reagents

Equipment for weighing reagents includes glass or plasticware (disposable weighing boats, weighing bottles, or beakers), spatulas, an analytical balance (precise to at least 0.01 g), and standard weights (for balance calibration checks).

2.6.1.3 Miscellaneous Labware

Additional equipment includes beakers, watch glasses, stirring equipment (stirring plates, magnetic stir bars, stir bar remover), hot plates, class-A volumetric flasks, plastic bottles or carboys, sieves, filtering equipment (vacuum pump, and filter papers, etc.), adjustable pipettes, and pH measuring equipment (electrodes, meter).

2.6.2 Reagents

2.6.2.1 Solids

Inorganic salts and other solids (such as boric acid) are used to prepare the brine.

- Use ACS reagent grade solids whenever possible.
- Record in the scientific notebook details about the solids used including the manufacturer, the grade, the lot number, and the expiration date (if any).

2.6.2.2 Acid and Base Solutions

Hydrochloric acid and sodium hydroxide are sometimes used to adjust the pH or pcH (hydrogen ion concentration) of the brine. However, such pH or pcH values for the brine are considered to be approximate because accurate measurement of pH or pcH in complex brines is a technically challenging subject, and it is beyond the scope of this SP.

- Use high purity concentrated hydrochloric acid whenever possible.
- Use a commercially prepared NaOH solution, or prepare a solution by dissolving reagent grade NaOH in DI water. In most cases a concentrated solution (≥ 10 N) will be appropriate.
- Record in the scientific notebook details about the hydrochloric acid and sodium hydroxide used including the manufacturer, the grade, the concentration, the lot number, and the expiration date (if any).

2.6.2.3 Water

Unless the Principal Investigator requests something else, use deionized (DI) water.

Record in the scientific notebook details about the water. If it was purified in the lab, include information about the method (such as deionized or distilled), the equipment used, and the purity (specific conductance or resistance). If it was purchased, include information about the manufacturer as well as the method and purity.

2.7 Procedure for Preparing Brine

2.7.1 Summary

Preparing a synthetic brine involves dissolving the appropriate quantities of reagents in water; diluting to the appropriate volume; filtering, and adjusting the pH, if necessary. It is recommended that brines are prepared on molality scale. However, the PI will determine the concentration scale to be used based on convenience, required amounts, or consistency with the concentration scale already adopted in the research. Record all your work in the scientific notebook.

2.7.2 Preliminary Steps

Get the requirements for the brine from the Principal Investigator - which recipe is to be used and the amount required.

> **Note:** if the volume of the synthetic brine to be prepared is ≤ 2 L, the volume must correspond to the volume of a Class-A volumetric flask.

Calculate the amounts of the reagents that will be needed. The recipes specify the amounts of reagents needed for one liter of brine. For each reagent, the mass needed is the mass specified in the recipe multiplied by the number of liters of brine to be prepared.

Ensure that adequate amounts of reagents are available.

2.7.3 Drying the Reagents

Dry the anhydrous salts in the laboratory oven at 105 to 110 °C for at least four hours (longer for large quantities). Alternatively, dry the anhydrous salts in the laboratory oven at 90 °C overnight. Do not dry hydrated salts because they will begin to lose their water of hydration when heated above 100 °C. Record the details about the drying in the scientific notebook.

Store the dried salts in a desiccator.

2.7.4 Weighing the Reagents

Comply with the requirements of SP 12-1, *Use of Laboratory Balances and Scales*.

If a reagent is to be used immediately, weigh it into a clean, appropriately sized plastic or glass container (weighing boat or beaker) from which the reagent can be quantitatively transferred.

If a reagent is to be used later, weigh it into a clean, appropriately sized plastic or glass container that can be covered (for example, with parafilm, a watchglass, or a lid) and from which the reagent can be quantitatively transferred. Store it in a desiccator.

2.7.5 Dissolving the Reagents and Adjusting the Volume

The procedure will vary depending on several factors. For example, up to two liters of brine may be prepared in a volumetric flask; larger quantities require some other method for reaching the desired

volume. Brines that are close to saturation with the major constituents are difficult to prepare volumetrically and require special steps and additional time.

Sections 2.7.5.1 and 2.7.5.2 describe methods that are suitable for preparing synthetic brines that are not close to saturation with sodium chloride. It should be mentioned that both GWB and ERDA-6 are close to saturation with salts. Therefore, as long as the following conditions are met, synthetic GWB and ERDA-6 are considered to be successfully prepared:

- Known (weighed) amounts of the appropriate reagents are dissolved in the final brine.
- The requested quantity of brine is prepared.
- If precipitation occurs after certain time of preparation of the brine, it is acceptable if precipitates are re-dissolved by thoroughly stirring the brine before its use in experiments.

2.7.5.1 Synthetic Brines (≤ 2 L)

- If sodium tetraborate (hydrous or anhydrous) is included, quantitatively transfer it to a glass beaker. To ensure that all the sodium tetraborate is transferred, rinse the weighing container with small amounts of DI water at least three times, each time adding the rinsings to the beaker. Add sufficient DI water to dissolve the salt. Add a magnetic stir bar. Cover the beaker. Place the beaker on a stir plate and stir at the lowest speed possible until all the sodium tetraborate has dissolved. It will take several hours or overnight for the sodium tetraborate to dissolve. Remove the stir bar, and rinse it with DI water, each time adding the rinsings to the solution.
- Prepare a second solution using the remaining salts. Quantitatively transfer the first salt to a glass beaker. To ensure that all the salt is transferred, rinse the weighing container with small amounts of DI water at least three times, each time adding the rinsings to the beaker. Add sufficient DI water to dissolve the salts. Add a magnetic stir bar, and cover the beaker. Place the beaker on a stir plate, and stir at the lowest speed possible until all the salt has dissolved.
- Add the next salt, taking care to transfer it quantitatively, and stir until it is dissolved. Continue adding and dissolving the salts one at a time until all of salts have been added and dissolved. Then remove the stir bar, and rinse it with DI water, each time adding the rinsings to the solution.
- Pour the sodium tetraborate solution into an appropriately sized, clean, class-A volumetric flask. Rinse the beaker at least three times with small amounts of DI water to ensure that all the solution is transferred, each time adding the rinsings to the flask.
- Add the solution containing the other salts to the volumetric flask. Rinse the beaker at least three times with small amounts of DI water to ensure that all the solution is transferred, each time adding the rinsings to the flask.
- Adjust the volume with DI water.
- In order to homogenize the solution thoroughly, the volumetric flask with a lid shall be inversed at least 20 times. After that, transfer the solution to a clean, labeled plastic bottle.
- The synthetic brine shall be labeled with a unique batch number, date of preparation, expiration date if applicable, initials of preparer, the scientific notebook name and page

number in which the preparation of the synthetic brine is recorded, per the requirements of NP 13-1, *Control of Samples and Standards*.

2.7.5.2 Synthetic Brines (> 2 L)

- If the volume of the synthetic brine required for experiments is more than 2 liters, the synthetic brines can be prepared according to the concentrations on molality scale (see Appendix C). To this end, the concentrations of GWB and ERDA-6 brines in molarity (M) are converted to those in molality (Appendix B). In the conversion, the measured densities of GWB and ERDA-6 are used. The densities of GWB and ERDA-6 are measured to be 1.2368±0.0160 (2σ) g cm^{-3}, and 1.1918±0.0036 (2σ) g cm^{-3}, respectively. Similarly, the recipes for the equilibrated GWB and ERDA-6 on molality scale are listed in Appendix E, and the reference recipes for equilibrated GWB and ERDA-6 on molarity scale is listed in Appendix F, which are calculated from the densities from the FMT runs referenced in the footnotes of Appendix F.

- The weight of DI water can be measured by using a clean, 5L class A glass beaker or a clean, 2L class A volumetric flask, assuming that the density of DI water is 1.0 g cm^{-3}, or by using a balance. The measured value of DI water will be recorded in the scientific notebook. The stated tolerance of such a 5 L glass beaker is ±5%. (The tolerance is stated on the wall of a 5L glass beaker.) As there are uncertainties associated with the measured densities of the brines (see above), the combined tolerance allowed should be within ±10%.

- First dissolve the measured amounts of sodium tetraborate into the desired aliquot of DI water per the specific brine recipe. After sodium tetraborate is dissolved, dissolve the remaining salts. Dissolve each salt, one at a time, until the last salt is dissolved.

- Transfer aliquots of the synthetic brine into the plastic bottle or carboy and mix thoroughly.

- The synthetic brine shall be labeled with a unique batch number, date of preparation, expiration date if applicable, initials of preparer, the scientific notebook name and page number in which the preparation of the synthetic brine is recorded, per the requirements of NP 13-1.

2.7.6 Filtering Brine

2.7.6.1 If filtration is needed, filter the solution through filter paper or a membrane as specified by the Principal Investigator. Record details about the filtering and filter apparatus (including the membrane type and pore size) in the scientific notebook.

2.7.6.2 Store the solution in clean, labeled plastic bottles or carboys.

3.0 Records

The following QA records, generated through implementation of this procedure, shall be prepared and submitted to the WIPP Records Center in accordance with NP 17-1 (Records):

<u>QA Record</u>

- Scientific Notebook

4.0 Appendices

Appendix A: Recipes for Synthetic Salado and Castile Brines on Molarity Scale

Appendix B: Concentration Scales in Molarity (Moles/L Solution) and Molality (Moles/kg H_2O) for Synthetic Salado (GWB) and Castile (ERDA-6) Brines

Appendix C: Recipes for Synthetic Salado and Castile Brines on Molality Scale

Appendix D: Concentration Scale on Molality (Moles/kg H_2O) for Synthetic Salado (GWB) and Castile (ERDA-6) Brines Equilibrated with Halite, Anhydrite, Brucite and Hydromagnesite (5424)

Appendix E: Recipes for Synthetic Salado and Castile Brines Equilibrated with Halite, Anhydrite, Brucite and Hydromagnesite (5424) on Molality Scale

Appendix F: Reference Recipes for Synthetic Salado and Castile Brines Equilibrated with Halite, Anhydrite, Brucite and Hydromagnesite (5424) on Molarity Scale

Appendix A
Recipes for Synthetic Salado and Castile Brines on Molarity Scale

Salt	GWB Grams for 1L	ERDA-6 Grams for 1L
$Na_2B_4O_7 \cdot 10H_2O$	15.06	6.00
NaBr	2.74	1.13
LiCl	0.19	None
NaCl	179.61	261.64
KCl	34.84	7.23
$MgCl_2 \cdot 6H_2O$	207.05	3.86
$CaCl_2 \cdot 2H_2O$	2.03	1.76
Na_2SO_4	25.23	23.70

Appendix B
Concentration Scales in Molarity (Moles/L Solution) and Molality (Moles/kg H_2O) for Synthetic Salado (GWB) and Castile (ERDA-6) Brines

Chemical Species	GWB	GWB	ERDA-6	ERDA-6
	Moles/L sol'n	Moles/kg H_2O	Moles/L sol'n	Moles/kg H_2O
Na^+	3.53	3.98	4.85	5.44
K^+	0.467	0.526	9.70×10^{-2}	0.109
Li^+	4.48×10^{-3}	5.05×10^{-3}	None	None
Ca^{2+}	1.38×10^{-2}	1.56×10^{-2}	1.20×10^{-2}	1.34×10^{-2}
Mg^{2+}	1.02	1.15	1.90×10^{-2}	2.13×10^{-2}
Cl^-	5.61	6.32	4.64	5.20
Br^-	2.66×10^{-2}	3.00×10^{-2}	1.10×10^{-2}	1.23×10^{-2}
SO_4^{2-}	0.178	0.200	0.167	0.187
$B_4O_7^{2-}$	3.95×10^{-2}	4.45×10^{-2}	1.57×10^{-2}	1.76×10^{-2}

Appendix C
Recipes for Synthetic Salado and Castile Brines on Molality Scale

Salt	GWB Grams for 1,000 g H_2O	ERDA-6 Grams for 1,000 g H_2O
$Na_2B_4O_7 \cdot 10H_2O$	16.96	6.73
NaBr	3.09	1.27
LiCl	0.21	None
NaCl	202.32	293.38
KCl	39.25	8.11
$MgCl_2 \cdot 6H_2O$	233.23	4.33
$CaCl_2 \cdot 2H_2O$	2.29	1.97
Na_2SO_4	28.42	26.58

Appendix D
Concentration Scale on Molality (Moles/kg H_2O) for Synthetic Salado (GWB) and Castile (ERDA-6) Brines Equilibrated with Halite, Anhydrite, Brucite and Hydromagnesite (5424)*

Chemical Species	GWB[A]	ERDA-6[B]
	Moles/kg H_2O	Moles/kg H_2O
Na^+	4.98	6.05
K^+	0.559	0.109
Li^+	5.05×10^{-3} [C]	None
Ca^{2+}	1.24×10^{-2}	1.28×10^{-2}
Mg^{2+}	0.634	1.20×10^{-1}
Cl^-	6.24	5.98
Br^-	3.18×10^{-2}	1.24×10^{-2}
SO_4^{2-}	0.209	0.191
ΣB[D]	4.74×10^{-2}	1.78×10^{-2}
ΣC	4.02×10^{-4}	5.35×10^{-4}

[*] From Brush and Xiong (2005) and Brush (2005).
[A] From Run #: FMT_CRA1BC_HMAG_NOORGS_008.
[B] From Run #: FMT_CRA1BC_HMAG_NOORGS_012.
[C] FMT calculations do not have lithium concentrations. Therefore, lithium concentrations on molality scale for GWB are from Appendix B.
[D] Converted to $B_4O_7^{2-}$ based concentration scale in order to be consistent with Appendix B.

Appendix E
Recipes for Synthetic Salado and Castile Brines Equilibrated with Halite, Anhydrite, Brucite and Hydromagnesite (5424) on Molality Scale

Salt	GWB	ERDA-6
	Grams for 922.44 g H_2O[A]	Grams for 983.31 g H_2O[A]
$Na_2B_4O_7 \cdot 10H_2O$	18.06	6.77
NaBr	3.27	1.28
LiCl	0.21	None
NaCl	259.28	328.70
KCl	41.71	8.15
$MgCl_2 \cdot 6H_2O$	129.00	24.50
$CaCl_2 \cdot 2H_2O$	1.82	1.89
Na_2SO_4	29.69	27.11
Na_2CO_3	0.0426	0.0567

[A] Crystalline H_2O in salts is added into solvent of water to make a total of 1,000 g.

Appendix F
Reference Recipes for Synthetic Salado and Castile Brines Equilibrated with Halite, Anhydrite, Brucite and Hydromagnesite (5424) on Molarity Scale

Salt	GWB[A]	ERDA-6[B]
	Grams for 1L	Grams for 1L
$Na_2B_4O_7 \cdot 10H_2O$	15.80	5.96
NaBr	2.86	1.12
LiCl	0.19	None
NaCl	226.79	289.36
KCl	36.49	7.18
$MgCl_2 \cdot 6H_2O$	112.85	21.57
$CaCl_2 \cdot 2H_2O$	1.59	1.66
Na_2SO_4	25.97	23.88
Na_2CO_3	0.0373	0.0500

[A] Based on the density of the density of 1.22960 g/ml from FMT_CRA1BC_HMAG_NOORGS_008.

[B] Based on the density of 1.21679 g/ml from FMT_CRA1BC_HMAG_NOORGS_012.

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