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Sandia National Laboratories
Waste Isolation Pilot Plant (WIPP)
Test Plan TP 06-03

Experimental Study of
MgO Reaction Pathways and Kinetics
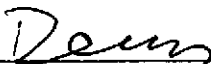# Rev. 1

Task 1.4.2.5

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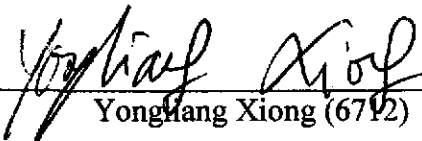
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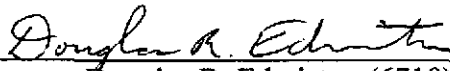
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1 ABBREVIATIONS, ACRONYMS, AND INITIALISMS

Table 1. Abbreviations, Acronyms and Initialisms.

Abbreviation, Acronym or Initialism	Definition
Aq	aqueous
ASTM	American Society for Testing and Materials
BET	Brunauer, Emmett, and Teller
BRAGFLO	Brine and Gas Flow Code
CO_2	carbon dioxide
DAS	data acquisition system
DI water	deionized water
DOE	Department of Energy
DRZ	disturbed rock zone
DSC	differential scanning calorimetry
EBSD	electron backscatter diffraction
EDS	energy dispersive X-ray spectroscopy
ERDA-6	Energy Research and Development Administration (WIPP Well) 6, a synthetic brine representative of fluids in Castile brine reservoirs
ES&H	(SNL) Environmental Safety and Health (procedures)
G	gram(s)
GC-MS	gas chromatography-mass spectrometer
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines
ICP-AES	inductively-coupled plasma atomic emission spectrometer
LOI	loss on ignition
M	molar
M&TE	measuring and test equipment
Martin Marietta	Martin Marietta Magnesia Specialties, LLC
Mg-Cl-OH hydrate	magnesium-chloride-hydroxy-hydrate. A crystalline or amorphous compound with various stoichiometries
Mg	milligram(s)
MgO	magnesium oxide
Mol	mole(s)

Table 1. Abbreviations, Acronyms and Initialisms.

Abbreviation, Acronym or Initialism	Definition
NIST	National Institute of Standards and Technology
NP	(SNL) Nuclear Waste Management Procedure
PA	performance assessment
PABC	Performance Assessment Baseline Calculation
PADF	poly vinyldiene difluoride
P_{CO_2}	partial pressure of CO_2
Premier	Premier Chemicals, LLC
QA	quality assurance
RH	relative humidity
SEM	scanning electron microscope
SNL	Sandia National Laboratories
SP	SNL/WIPP Activity/Project Specific Procedure
STTP	Actinide Source Term Test Program
TDIC	total dissolved inorganic carbon
TGA	thermal gravimetric analysis
TP	test plan
TRU	transuranic
UV	ultraviolet
WIPP	Waste Isolation Pilot Plant
wt %	weight percent
WTS	Westinghouse TRU Solutions
XRD	X-ray diffraction

2 REVISION HISTORY

This is the first revision of this test plan (TP). In this revision, carbonation experiments in environmental chambers have been added to the test plan in Section 6.3 and 6.4. Subsequent versions will be prepared in accordance with the following Sandia National Laboratories (SNL) Waste Isolation Pilot Plant (WIPP) quality assurance (QA) procedures: NP 6-1, NP 6-2, and NP 20-1.

3 PURPOSE AND SCOPE

Magnesium oxide (MgO) is being emplaced in the WIPP as an engineered barrier to mitigate the effect of microbial carbon dioxide (CO_2) generation on actinide mobility in a postclosure repository environment (Bynum, 1997; Krumhansl, 1997; Bynum et al., 1998; Papenguth et al., 1998). MgO will sequester CO_2 and buffer brine pH at a moderately basic level, thus minimizing the solubilities of actinides in WIPP brines. In the past, a series of experiments have been conducted at SNL to verify the efficacy of Premier Chemicals LLC (Premier) MgO as a chemical control agent in the WIPP (Snider et al., 2004). Since September 2004, Premier MgO is no longer available for WIPP emplacement. Westinghouse TRU Solutions (WTS) has chosen Martin Marietta Magnesia Specialties LLC (Martin Marietta) as the new MgO supplier.

The purpose of this work is to gain a fundamental understanding of the kinetics and reaction pathways of MgO carbonation and hydration. This will be accomplished by data collection on the rates of these processes, and by making observations directly relevant to transport and reaction pathways. There remain unanswered questions as to the reaction and transport mechanisms during hydration and carbonation. Does the MgO react as a shrinking core? Does transport occur primarily through fractures in the (MgO) material? A deeper understanding of these processes may aid us in predicting and defending the expected behavior of the MgO over the 10,000-year regulatory time frame. For this purpose, the experimental conditions have been chosen to be directly relevant to WIPP expected conditions, and will therefore directly support upcoming changes to performance assessment (PA).

The experimental plan described in this document will be used to study the behavior of Martin-Marietta MgO. A minimal set of Premier MgO samples will be also be tested for comparison purpose. Wall (2005) showed that Martin-Marietta MgO behaves differently than that obtained from Premier, hydrating in far less time. We also expect that the carbonation of Martin-Marietta MgO will be faster than Premier; Snider (2002) observed carbonation of only ~20% of Premier MgO within two years. We expect to complete the proposed experiments within three years; however, this timescale is dependant on the rate of carbonation of Martin Marietta MgO.

The following tasks are planned:

- *Characterization of the MgO currently being emplaced in the WIPP.* The purpose of this study is to analyze the Martin Marietta WTS-60 MgO to determine the exact mineral composition, and to describe the morphology and size distribution of this material. Laboratory-sample preparation and storage of the MgO will also be performed in this task.

- *Study of the hydration of Martin Marietta MgO.* Hydration of a significant portion of the emplaced MgO is likely to occur before CO_2 is produced from microbial consumption of organic materials in the waste, owing to the slow rates of microbial gas production (Nemer et al., 2005). The rate of carbonation of magnesium hydroxide (hydrated MgO) is likely to be significantly faster than the carbonation rate of MgO. These experiments will be conducted to evaluate several factors affecting the MgO hydration rates under both inundated and humid conditions. The results will help elucidate hydration rates and pathways, and will help determine whether any solid reaction products (see Subsections 5, 5.8.2, and 6) are important in the kinetics of MgO hydration and carbonation.

- *Study of the carbonation of Martin Marietta MgO.* The reaction of MgO with CO_2 can produce a series of magnesium-carbonate minerals, such as hydromagnesite ($Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$ or $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) and magnesite ($MgCO_3$), with magnesite as the most stable phase (Konigsberger et al., 1999). The different magnesium-carbonate and hydroxy-carbonate minerals that may form (see Subsection 6) can have different buffering capabilities for controlling CO_2 fugacity. The objective of this task is to gain a mechanistic understanding of the reaction pathway(s) and obtain the rates of carbonation.

Throughout this TP, "MgO" refers to the bulk material purchased from the manufacturer, while "periclase" refers to the pure, crystalline mineral whose molecular formula is MgO.

4 TASK #1: CHARACTERIZATION AND STORAGE OF MgO

Martin Marietta WTS-60 is the MgO currently being emplaced in the WIPP. As specified by Martin Marietta, WTS-60 is a hard-burned MgO containing a minimum of 97% weight percent (wt %) MgO. The remaining 3 wt % most likely comprises impurity oxides such as SiO_2, Fe_2O_3, Al_2O_3 and CaO. Typically these impurities don't exist as free compounds but rather are combined mineralogically as calcium-magnesium silicates, aluminates, and ferrites. WTS-60 is a granular powder with 95 to 90 wt % passing through a 6 M mesh sieve, 50 to 80 wt % passing through a 16 M mesh sieve, 15 wt % to 40 wt % passing through 30 M sieve, and 15 to 30 wt % passing through 100 M mesh sieve screen (Wall, 2005).

4.1 Storage of MgO

In order to have a consistent starting material, we will obtain a large batch (ca. 50 kg) of MgO from a single lot of Martin Marietta WTS-60. This material will be carefully split using a sample splitter and inspected visually to ensure the homogeneity of mineral size distribution.

As we will be looking at very small changes in the carbonate concentration of the MgO material due to the slow carbonation rate, it is important to maintain MgO at a fixed initial condition (i.e., preventing small levels of carbonation and hydration during storage). Martin Marietta has recommended a shelf life of one year for the "as-received" MgO if it is stored in sealed glass bottles. For any period of time beyond one year, the manufacturer recommends the material be stored under an inert atmosphere. After splitting, the remaining Martin Marietta MgO will be stored under an inert gas in a suitable container. We will store and pack presplit MgO under an inert gas in clean serum bottles capped and crimped with rubber septa and aluminum caps. All bottles will be labeled with a unique identifier. Before sealing the serum bottles, samples will be collected from a random selection of serum bottles and characterized as described below in Section 4.2. Any inhomogeneity of the characterization tests will be considered as we analyze the reproducibility of the experiment results.

4.2 Characterization of the Material

Impurities, fractures, surface area, and size distribution may all impact the rates of MgO hydration and carbonation. In this task we will perform the following analyses on the prepared-and-stored Martin Marietta MgO:

- mineralogical composition (Subsection 4.2.1),

- phase identification (Subsection 4.2.1),

- particle morphology (Subsection 4.2.2),

- specific surface area analysis (Subsection 4.2.3),

- size distribution by mass (Subsection 4.2.4),

- loss on ignition test (LOI) (Subsection 5.8.1), and

- carbon coulometer test (Subsection 6.2.2.1).

4.2.1 Mineralogical Composition

WTS-60 is a hard-burned MgO containing a minimum of 97 wt % of MgO. The remaining 3 wt % most likely comprises impurity oxides such as SiO_2, Fe_2O_3, Al_2O_3 and CaO. Typically these impurities don't exist as free compounds, but are combined mineralogically as calcium-magnesium silicates, aluminates, and ferrites. The mineralogical composition analyses will determine what impurities might be present in the MgO and in what quantities. Analyses will be done using gravimetric determination of silica followed by inductively coupled plasma atomic emission spectrometer (ICP-AES) using a Perkin Elmer Optima 3000 DV. We will also determine the brucite concentration (described in Subsection 5.8.1) and the carbon content by carbon coulometer analysis (Subsection 6.2.2.1).

The method of gravimetric determination of silica by Kolthoff and Sandell (1961) (or similar procedure) will be used to determine the amount of SiO_2 present in the MgO. In this procedure, MgO is crushed to a size of <200 mesh (75 μm). An approximately 0.5 g MgO sample is weighed and then mixed with ~2.5 g sodium carbonate and ignited. Samples are then leached with HCl, and placed on a hotplate to evaporate overnight. The remaining residue (SiO_2 and various salts) is then leached again with HCl, washed with deionized (DI) water and filtered. At this point, all the soluble salts are removed by filtration. The remaining solid (SiO_2) is reignited with the filter paper, and weighed. The liquid retained from the filtering is saved for analysis by ICP-AES.

ICP-AES will be used to determine the concentrations of Fe, Al, Mg, Ca, and Si in the liquid obtained. The results will also determine whether any silicates were dissolved into the liquid (in the above described method) and if any lime and aluminates constitute a portion of the MgO material.

Phase identification of the crystalline phases present in the MgO will be performed using a Brucker X-ray diffraction (XRD) unit, and a JEOL 5900 LV scanning electron microscope (SEM) associated with a Vantage energy dispersive system (EDS) and electron backscatter diffraction (EBSD). Combing the results from XRD, SEM, and ICP-AES the mineralogical composition of the MgO will be calculated.

4.2.2 Particle Size and Morphology

Particle size, intergranular porosity, and fracture topology of the MgO particles will all affect the mass transport of reactants to the unreacted MgO surface, and thus affect the reaction rate. The particle size, intergranular porosity, and fissure and fracture topology of the MgO particles will be determined using a JEOL 5900LV SEM, and an Olympus optical microscope, followed by image analysis using image analysis software.

The particle-number-size distribution will also be determined using a Malvern Instruments Mastersizer laser-scattering-particle-size analyzer.

4.2.3 Specific Surface Area

We will perform specific-surface-area measurements using a wet chemical sorption method. Iodine sorption methods have been used previously for determining specific-surface-area-type measurements on MgO and brucite (Dunn and Pomeroy, 1947; McBain and Dunn,

1948; Watson and Parkinson, 1955; Kanungo and De, 1970). A modified BET equation or Langmuir equation is usually used to fit the data. Other chemical sorptive analytes may be used if iodine proves unsuccessful.

If sufficient time and resources are available, specific surface area will also be determined by nitrogen sorption (using the Brunauer, Emmett, and Teller (BET) equation) using a BET analyzer. Currently we do not have such an instrument but this analysis is available at several local universities (such as the University of New Mexico, Albuquerque).

4.2.4 Size Distribution by Mass

To determine the size distribution as a function of mass fraction, we will pass the MgO through a series of sieves ranging from 75 μm (200 M) to 4 mm (5 M), then collect and weigh the fractions between each pair of sieves (or above and below the sieve for the largest and smallest). In terms of size characterization, Martin Marietta has only provided the data listed in the beginning of Section 4. We intend to refine these measurements with a greater number of sieves.

5 TASK #2: STUDY OF MGO HYDRATION

After the WIPP is filled and sealed, the periclase in the MgO emplaced in the repository will react with water in the gas phase or in brine to form brucite.

$$MgO(s) + H_2O(aq \text{ or } gas) \rightleftharpoons Mg(OH)_2(s). \tag{1}$$
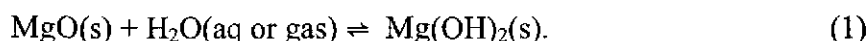
The brucite dissolution reaction,

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \tag{2}$$
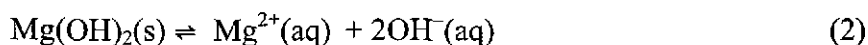
will buffer pH to about 9 (U.S. DOE, 2004), which directly affects actinide speciation and solubility.

The MgO hydration experiment will include two sets of experiments: humid hydration and inundated hydration. The objective of this task is to determine MgO hydration rates and reaction pathways. With Premier MgO, three hydration products were found (Snider, 2003a): brucite, an amorphous magnesium chloride hydroxy hydrate (Mg-Cl-OH hydrate), and a crystalline Mg-Cl-OH hydrate. Brucite was the only hydration product found in humid and inundated experiments (carried out in DI water, 4 molar (M) NaCl solution and a synthetic brine named ERDA-6); ERDA-6 (Energy Research and Development Administration (WIPP Well) 6) is the synthetic Castile brine used in the lab. Mg-Cl-OH hydrate was found in the inundated experiments in Generic Weep Brine (GWB); GWB is a synthetic brine representative of intergranular Salado brines. The compositions of ERDA-6 and GWB can be found in Appendix A. The Mg-Cl-OH hydrate was found initially, and eventually decomposes to brucite. We expect Martin Marietta MgO to have the same reaction products as observed with Premier MgO.

The crystalline Mg-Cl-OH hydrate was identified as $Mg_3(OH)_5Cl \cdot 4H_2O$ by XRD. The amorphous Mg-Cl-OH hydrate has not been identified. As Mg-Cl-OH hydrate may be an important component of the reaction pathway in GWB, we will study the kinetics of the formation of Mg-Cl-OH hydrate, and the kinetics of its conversion to brucite. This will be accomplished by monitoring the amount of $Mg(OH)_2$ and Mg-Cl-OH hydrate formed during the hydration reaction. We propose an experimental procedure for monitoring these products in Section 5.8.2.

In addition to GWB and ERDA-6, we will perform the long-term inundated hydration experiment in a solution of 4 M NaCl + 1 M $MgCl_2$. The 4 M NaCl+1 M $MgCl_2$ solution has an ionic strength of 7 M, which is similar to GWB (7.2 M). With a concentration of 1 M Mg, we should be able to observe the formation of Mg-Cl-OH-hydrate. If we are not able to obtain the Mg-Cl-OH hydrate with 4 M NaCl + 1 M $MgCl_2$, we will vary these molarities but attempt to maintain the same ionic strength.

According to EQ3/6 calculations Mg-Cl-OH is formed while the Mg concentration is greater than ~0.7 M (Bryan and Snider, 2001). Previous hydration experiments with Premier

MgO in a 4 M NaCl+1 M MgCl$_2$ solution observed the Mg-Cl-OH-hydrate using XRD (Bryan and Snider, 2001). Mg$_2$(OH)$_3$Cl formation has been reported in solutions of brucite + x M MgCl$_2$, for x > 2 (Bodine, 1976; Altmaier et al., 2003).

5.1 Container Selection

The loss of salt and water from the bottles containing brine and MgO is a problem in many long-term geochemical experiments involving brine. The means by which salt creeps out of bottles is unclear, but spray of small droplets and diffusion up a wetted bottle wall are possible mechanisms.

To minimize this problem we will explore various container types and materials to determine which containers and lids minimize the loss of water and salt. In this experiment we will place GWB in various bottles and then periodically measure the weight loss and brine conductivity. Hydrophobic materials such as Teflon should lose less salt compared to more hydrophilic materials. Serum bottles with tightly-fitting septum may prove effective. Borosilicate glass serum bottles may leach silicate into solution in the presence of brucite and/or Mg-Cl-OH-hydrate (Altmaier et al., 2003). Polymer serum bottles may alleviate this problem.

5.2 Solid-to-Liquid Ratio

A WIPP-relevant solid-to-liquid ratio can be approximated by looking at the possible brine volumes in a waste panel, obtained from the Performance Assessment Baseline Calculation (PABC) results (Nemer and Stein, 2005), and the amount of MgO assumed to be emplaced in each panel. This calculation has been performed by Nemer (2006). The results are shown below in Table 2 for scenarios S2, S4 and S6. Scenario S2 corresponds to a repository intruded at 350 years by a drilling intrusion that encounters a Castile brine pocket; Scenario S4 corresponds to a repository intruded at 350 years by a drilling intrusion that does not encounter a Castile brine pocket; Scenario S6 corresponds to a repository intruded at 1000 years by a drilling intrusion that does not encounter a Castile brine pocket, followed by a drilling intrusion at 2000 years that does encounter a Castile brine pocket (Nemer and Stein, 2005).

As shown in Nemer (2006), a more practical solid-to-liquid ratio is found by dividing the amount of MgO assumed to be emplaced in each panel by the minimum brine volume needed for a direct brine release (Stein, 2004) to the surface. This solid-to-liquid ratio is 4 g/ml.

Table 2. Ranked Solid-to-Liquid Ratios in the Waste Area Obtained from the PABC Calculations.

Percentile[1]	Scenario S2 Solid-to-Liquid Ratio (g/ml)	Scenario S4 Solid-to-Liquid Ratio (g/ml)	Scenario S6 Solid-to-Liquid Ratio (g/ml)
0.001	4×10^1	9×10^4	1×10^5
0.01	1×10^1	2×10^4	9×10^3
Mean	9×10^{-1}	3×10^0	2×10^0
0.99	4×10^{-1}	8×10^{-1}	6×10^{-1}
0.999	4×10^{-1}	6×10^{-1}	6×10^{-1}

1. Percentiles were calculated by ranking all values of the solid-to-liquid ratio for each scenario.

5.3 Tracer Dyes

In some samples we will add a tracer dye to characterize hydration-reaction-front morphology at various times using image analysis. Previous models have assumed a spherical reaction rind; however, SEM imaging (Figure 1) shows a fractured reaction front with hydration following the fractures of the underlying material. Two tracer dyes will be used: one that will allow us to view the reaction front in the SEM, and another that will be visible in the optical microscope. For SEM imaging, we will use a compound that is partially soluble in the DI water-MgO slurry (we may also want to add this dye to other solutions such as GWB and ERDA-6). Small amounts of the compound (most likely in the form of a salt) will be added to sample bottles described above. The criteria that we believe are important include: (a) heavy enough nucleus such that the compound (ion) will shine brightly in the SEM when using the backscattered electron detector, (b) an EDS spectrum that does not significantly overlap with the other atoms of interest, and (c) an ion that does not significantly (or in some instances perhaps does) sorb (by adsorption, chemisorption or other phenomena) onto the MgO or brucite. Criterion (c) presents the greatest difficulty as there are limited sorption measurements in the literature for dissolved ions on MgO and brucite. It may be interesting to look at both the case in which the ion does strongly sorb and the case where it does not strongly sorb. For example, in the carbonation experiments, described in Section 6, the sorbed ion may be removed from a site

on brucite when brucite carbonates to form hydromagnesite. This was observed during the carbonation of calcium (Comans and Middelburg, 1987; Davis et al., 1987).

Below we give some, but not an exclusive list, of the possible choices of compounds based on the requirements described above. We have chosen a compound that we expect will not strongly sorb to the MgO or $Mg(OH)_2$ surfaces and a compound that we expect will strongly sorb to the same surfaces. For the least sorbing compound we will select ions that have the greatest aqueous solvated ionic radii compared to that of Mg^{2+}. It has been shown that chemisorption is minimized when the sorbing ion's dry ionic radius is smallest (largest solvated ionic radius) compared to that of the sorption medium (Comans and Middelburg, 1987). Using the above criteria, we find that molybdenium(VI) (ionic radius = 0.55 Å, compared to magnesium(II) with ionic radius = 0.71 Å; Huheey et al., 1993) might be a good choice. For a strongly sorbing metal ion, we believe copper(II) (ionic radius = 0.71 Å) may be a good choice.

For the optical microscopy we will use a fluorescent dye that fluoresces when exposed to ultraviolet (UV) light, or a colored visible dye that can be easily seen without fluorescence. A similar technique was used for looking at fractures in disturbed rock zone (DRZ) halite (Bryan and Hansen, 2000). It was shown that brucite strongly sorbs anionic dyes such as methylene orange and weakly sorbs cationic dyes such as methylene blue (Kul'skii et al., 1986). Dyes will be selected with this criterion in mind, based on the filters and emission spectrum of the microscope that we currently have.

The initial imaging (SEM and optical) of a set of MgO samples containing dye and DI water will be performed within days after the dye has been added. Subsequent images will be taken regularly with a frequency depending on the rate at which the dye front moves through the MgO particles. We may find that the movement of the dye lags behind movement of the water front. Such phenomena need to be accounted for as they will increase the difficulty in interpreting the tracer-dye experiments. With the optical dyes, we may try dye penetration experiments in other solvents (organic solvents). This may add insight as to whether the dye is actually sorbing on to the MgO or just being carried by the brine.
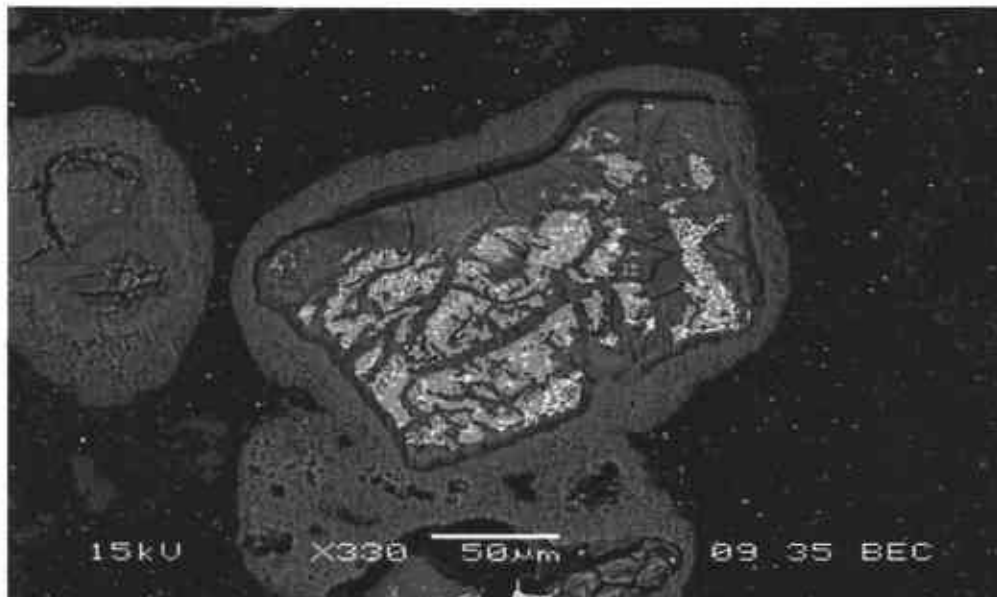
Figure 1. Inundated hydration of Premier MgO in GWB (from Snider, 2002).

5.4 Accelerated Inundated Sensitivity Study

Fernandez et al. (1999) showed that (a) particle size, (b) solid-to-liquid ratio, and (c) stirring speed, all affect the rate of carbonation of MgO slurries. We believe that these factors will also influence MgO hydration kinetics. In order to determine which parameters are most important in determining the MgO hydration and carbonation kinetics, and therefore which should be carefully controlled in long-term experiments, a fractional-factorial (Box et al., 1978) accelerated MgO hydration experiment will be carried out with at least two levels for each of the above factors. We will use the Minitab statistical software package (or other statistical software) to determine our test matrix, in accordance with NP 19-1.

Previous experiments with Martin Marietta WTS-60 MgO showed that 90 mol % of the MgO hydrated in 3 days at 90 °C in DI water (Wall, 2005), and 80 mol % of Premier MgO hydrated to brucite in 78 days at 70 °C (Snider 2002). The planned accelerated hydration experiment will be carried out in DI water at 70 °C, so as to have adequate time between measurements. If 70 °C proves ineffective (too fast or too slow), we will attempt another temperature.

Characterized MgO (Subsection 4.2) will be placed in sample containers chosen based on the results of container selection described in Subsection 5.1. DI water will be placed in the bottles to achieve a desired solid/liquid ratio.

Based on previous experiments with Premier MgO (Snider, 2001), we know that pH measurements can be performed on samples with solid-to-liquid ratios less than 0.1. We will attempt to capture some of the higher solid-to-liquid ratios in Table 2 (on the order of 10^1) and we will also explore much lower solid-to-liquid ratios (on the order of 10^{-3}). We will most likely not be able to measure pH on samples with solid-to-liquid ratios greater than 0.1 due to the lack of liquid.

Bottles containing DI water and MgO will be closed with caps (lids, perhaps septum) and placed either in an oven or in a temperature-controlled water-bath shaker for stirred samples. Samples will be analyzed according to the procedures described in Subsection 5.8.

In some samples we will add a tracer dye to characterize hydration-reaction-front morphology at various times using image analysis, as described above in Subsection 5.3.

5.4.1 Accelerated-Inundated Test Matrix

Below is the expected test matrix for the accelerated-inundated sensitivity study. At a minimum, duplicate experiments will be set up, and triplicate experiments will be carried out if time and resources allow. Changes to this matrix may be required. We expect this experiment to take no longer than three to four months.

- *Temperature:* 70 °C

  ➢ *Basis:* Wall (2005) showed that Martin Marietta MgO hydrated in 3 days at 90 °C; 80 mol % of Premier MgO hydrated to brucite in 78 days at 70 °C (Snider 2002).

- *Solvent:* DI water

  ➢ *Basis:* For the purpose of the sensitivity study, DI water will hopefully avoid some of the complexities associated with interpreting results in brine (e.g., the formation of Mg-Cl-OH hydrate).

- *Particle Size:* At least two levels that span (most of) the particle-size distribution. Selection of the particle size will depend on the particle-size distribution (Section 4.2.2 of this TP) and thus we cannot be more specific at this moment.

  ➢ *Basis:* Fernandez et al. (1999) showed that particle size affects the carbonation rate of MgO slurries. In his experiment, MgO particles ranging in size from 40 um to 235um was added to distilled water with excess flow of pure CO_2. The MgO conversion rate of 40 um MgO can be twice as much as the 235um MgO conversion rate.

- *Solid-to-Liquid Ratio:* 10^{-3} to 10^1 g/ml, with at least two levels. To begin, we will try 5×10^{-2} g/ml and 10^1 g/ml.

  ➢ *Basis:* Fernandez et al. (1999) showed that the solid-to-liquid ratio affects the carbonation rate of MgO slurries. Nemer (2006) showed that this range brackets the expected range of solid-to-liquid ratios in WIPP. Snider (2001) performed experiments on Premier MgO at 70 °C in DI water for 78 days in which hydration was significant (80 mol %) at a solid-to-liquid ratio above $\sim 10^{-1}$ g/ml.

- *Stirring Speed:* 0 to 300 rpm, with at least two levels. To begin we will try 0 rpm and a nonzero stirring speed that doesn't cause too much splashing in the bottles; we will have

to determine this speed experimentally. A temperature-controlled shaker bath that can shake the bottles from 50-300 rpm will be used.

> *Basis:* Fernandez et al. (1999) showed that stirring speed affects the carbonation rate of MgO slurries. At 6g/l solid/liquid ratio, stirring speed did not affect the precipitation of magnesium carbonate. However, at 20g/l solid/liquid ratio stirring speed affect magnesium carbonate precipitation significantly. 60% MgO is precipitated at the stirring speed of 1100min^{-1}. Only 40% MgO precipitated at 500 min^{-1}. This may yield information on the transport mechanisms of MgO hydration.

5.5 Accelerated Humid Sensitivity Study

Accelerated MgO hydration experiments under humid conditions will be performed similarly to the accelerated inundated hydration experiments described in Subsection 5.4. The outcome of these experiments will guide parameter selection for the long-term humid hydration and carbonation experiments. For these experiments the parameters to be varied are (a) temperature, (b) humidity, and (c) particle size. We don't expect that stirring will be feasible in these experiments.

Samples of characterized MgO (see Subsection 4.2) will be placed in sample containers chosen based on the results of Subsection 5.1. Particle size will be varied by using fractions of the MgO obtained during sieving (see Subsection 4.2.4). Humidity will be controlled between 28–96% relative humidity (RH) by placing a saturated salt solution (listed in Table 3) in a separate container or under a beaker that contains MgO. Both the MgO and the saturated salt solution will be placed in a second tightly-sealed container, as shown in Figure 2. If this setup is ineffective at maintaining RH, an alternative setup will be attempted. The exact humidity will be monitored weekly using a hygrometer either attached to the bottle lid (or other part of the bottle) or with a probe that can be inserted into the bottles and documented in a scientific notebook. The acceptance criteria for RH will be ± 12% RH. Bottles will be placed in an oven in which the temperature will be set between 25–70 °C; oven temperature will be monitored using a calibrated thermometer. After the experiment has commenced, MgO will be collected from the sample bottles and analyzed according to the procedures described in Subsection 5.8.
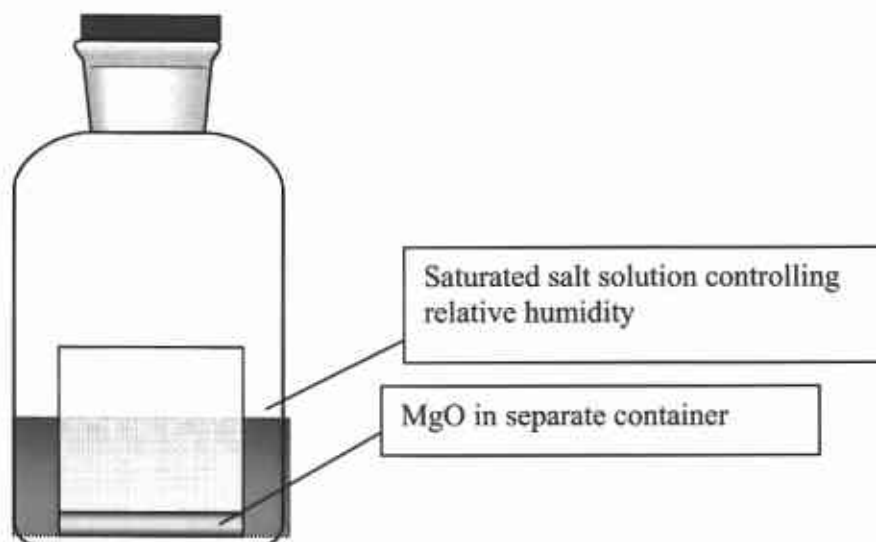
Figure 2. Schematic drawing of humid-hydration apparatus. Alternatively, the MgO may be placed in the main container and the saturated salt solution may be placed in the inner, separate container. Other arrangements may also be used.

A tracer dye, as described in Subsection 5.3, that has a known vapor pressure (as a function of temperature) may be added to either the saturated salt solution bath or in a separate internal container in these experiments. This dye will be a colored-visible dye or a UV fluorescent dye, not a salt. Salts generally have very low vapor pressures, and probably could not be used for this purpose.

Table 3. Saturated Salt Solutions and the RH Values They Maintain.[1]

Temperature (°C)	RH (%)				
	$MgCl_2$	NaBr	NaCl	KBr	K_2SO_4
25	32.8 ± 0.2	57.6 ± 0.4	75.3 ± 0.2	84.2 ± 0.3	97.3 ± 0.5
50	30.5 ± 0.2	50.9 ± 0.6	74.5 ± 0.9	81.2 ± 0.4	95.8 ± 0.5
70	27.8 ± 0.3	49.7 ± 1.1	74.1 ± 0.9	79.5 ± 0.6	NA

1. RH values obtained from ASTM (2005).

5.5.1 Accelerated-Humid Test Matrix

Below is the expected test matrix for the accelerated humid sensitivity study. At a minimum, duplicate experiments will be set up, and triplicate experiments will be conducted if time and resources allow. Changes to this matrix may need to be made. We expect this experiment to take no longer than six months.

- *Temperature:* 25-70 °C, with at least two levels. To begin, we will try 50 and 70 °C.

    ➤ *Basis:* After 6 months at 80 °C and 50% RH, Snider (2003a) found a brucite content of ~50%. After 100 days at 80 °C and 75% RH, Snider (2003a) found a brucite content of ~80 mol %. Since this is an accelerated experiment, we require conditions that will yield results within about 6 months.

- *RH:* 28-97%, with at least two levels. To begin, we will try an RH of ~50 and 80% (see Table 3 for the exact values at 50 and 70 °C).

    ➤ *Basis:* See *Temperature* basis above.

- *Particle Size:* At least two levels that span most of the particle size distribution. We don't yet know the particle size distribution and thus we cannot be more specific here.

    ➤ *Basis:* Fernandez et al. (1999) showed that particle size affects the carbonation rate of MgO slurries. In his experiment, MgO particles ranging in size from 40 um to 235um was added to distilled water with excess flow of pure CO_2. The MgO conversion rate of 40 um MgO can be twice as much as the 235um MgO carbonation rate.

5.6 Long-Term Inundated Experiments

Based on the results of the accelerated sensitivity study in Subsection 5.4, a designed experiment (Box et al., 1978) at laboratory room temperatures (~25 °C) will be performed. Room temperature will be monitored regularly and recorded in the log book. Experiments will be performed similarly to those described in Subsection 5.4, except that various solutions will be used, including: 4 M NaCl + 1 M $MgCl_2$ solution, GWB and ERDA-6 brines, and/or other brines (see Section 5 for a discussion of these solutions). We may also attempt to use a brine(s) that has (have) first been equilibrated with MgO (and other minerals expected under WIPP conditions), in order to investigate the effects of the timescale for the brine to equilibrate with MgO. This brine will be developed through a separate analysis plan and procedure. After the experiment has commenced, samples will be analyzed according to the procedures described in Subsection 5.8.

If the tracer-dye experiments in the accelerated sensitivity study (section 5.4) are successful, tracer dye may be added to some long-term inundated samples to monitor the hydration-reaction front as a function of time.

5.6.1 Long-Term Inundated Test Matrix

Below is the expected test matrix for the long-term inundated sensitivity study. Duplicate experiments (at a minimum) and triplicate experiments (if time and resources allow) will be set up. Changes to this matrix may be required. We expect this experiment will take three years.

- *Temperature:* Laboratory room temperatures (~25 °C). We may try higher temperatures to reach a high degree of hydration within the experiment timeframe.

  ➤ *Basis:* This is the ambient laboratory temperature, which is about 3 °C below the expected in-situ WIPP temperature. Higher temperatures may yield higher reaction rates but will also decrease the carbonate concentration in the brine.

- *Solvents:* 4 M NaCl + 1 M $MgCl_2$ solution, GWB, ERDA-6, GWB and ERDA-6 that has first been equilibrated with WIPP-relevant minerals (see Subsection 5.6).

  ➤ *Basis:* GWB, ERDA-6, and brines that are first equilibrated with WIPP-relevant minerals represent brines under expected WIPP conditions. The 4 M NaCl + 1 M $MgCl_2$ brine will be used to study the kinetics of Mg-Cl-OH hydrate formation. Bryan and Snider (2001) observed significant differences in the hydration rate in different brines, particularly in GWB.

- *Particle Size:* If the accelerated-inundated sensitivity study (Subsection 5.4) shows this to be an important parameter, then at least two levels will be chosen. The two levels will be chosen based on the results of the sensitivity study (i.e., some fractions may be too slow to obtain data with within the experimental window).

  ➤ *Basis:* Fernandez et al. (1999) showed that particle size affects the carbonation rate of MgO slurries.

- *Solid-to-Liquid Ratio:* If the accelerated-inundated sensitivity study (Subsection 5.4) shows this to be an important parameter, then at least two levels within the range of 10^{-3} to 10^1 g/ml will be used The two levels will be chosen based on the results of the sensitivity study.

  ➤ *Basis:* Fernandez et al. (1999) showed that the solid-to-liquid ratio affects the carbonation rate of MgO slurries. Nemer (2006) showed that this range brackets the expected range of solid-to-liquid ratios in the WIPP. Bryan and Snider (2001) performed experiments on Premier MgO at 70 °C for 28 days in which hydration was a strong function of the solid-to-liquid ratio.

- *Stir Speed:* If the accelerated-inundated sensitivity study (Subsection 5.4) shows this to be an important parameter, then at least two levels within the range of 0 to 300 rpm will be used.

▷ *Basis:* Fernandez et al. (1999) showed that stir speed affects the carbonation rate of MgO slurries. This may yield information on the transport mechanisms of MgO hydration.

5.7 Long-Term Humid Experiments

The results of the accelerated humidity sensitivity study (Subsection 5.5) will guide us as to what parameters can be used to achieve humid hydration in a reasonable amount of time (3 years or less). Experiments will then proceed, varying only the most sensitive parameters, and using the lowest temperature (at or above ambient laboratory temperature) that yields hydration in 3 years or less. Samples will be collected from the sample bottles and analyzed according to the procedures in Subsection 5.8.

Tracer dye may be added to some long-term humid hydration experiments if this is successful in the accelerated humid hydration experiments of Subsection 5.5.

5.7.1 Long-Term Humid Test Matrix

Below is the expected test matrix for the long-term humid sensitivity study. Duplicate or triplicate experiments will be set up (see Subsection 5.4.1 above). Changes to this matrix may be required. We expect that this experiment may take as long as three years; however, little work will be required to maintain these samples during this time.

- *Temperature:* Room temperature (~25 °C) and the lowest temperature (<70 °C) that yields a high degree of hydration within the experimental timeframe. This will be determined by the results of the accelerated humid-hydration experiment described in Subsection 5.5.

  ▷ *Basis:* Room temperature and 75% RH are close to the expected WIPP conditions. While the chosen higher temperature may not be the WIPP in-situ temperature, it's important to observe the entire hydration process. Snider (2003a) found that that at 80 °C, it took about 1 year to hydrate 75 mol % of Premier MgO at an RH of 75%.

- *RH:* Room temperature and an RH of 75% and at least two levels within the range 28-97% will be used (with the constraint that we wish to achieve a significant mole fraction of brucite by the end of three years) *if* the accelerated-humid sensitivity study (Subsection 5.5) shows this to be an important parameter.

  ▷ *Basis:* Snider (2003a) found that that at 80 °C it took about a year to hydrate 75 mol % of Premier MgO at an RH of 75%.

- *Particle Size:* At least two levels will be chosen *if* the accelerated-inundated sensitivity study (Subsection 5.5) shows this to be an important parameter. The two levels will be chosen based on the results of the sensitivity study (i.e., some fractions may be too slow to obtain data with within the experimental window).

> *Basis:* Fernandez et al. (1999) showed that particle size affects the carbonation rate of MgO slurries.

5.8 Sample Collection and Analysis

After the experiments have commenced, we will remove samples for analysis at particular times. In the experiments there will be two classes of sample bottles: bottles which have been previously analyzed and those that have not yet been analyzed. Most analyses will be performed on bottles which have not yet been analyzed, and these virgin sample bottles will be analyzed at a staggered set of times covering the experimental time period. However, a subset of bottles that have been previously analyzed (after the experiment has commenced) will be returned to the experiment and analyzed subsequently. In this way we will determine the variance between those sample bottles that are only analyzed once and those sample bottles that are measured more than once. If the variance is found to be small, we will set up the experiment such that samples can be taken multiple times from the same bottle. We will carefully distinguish and label which sample bottles are virgin and which have been previously analyzed. There will be duplicate (or triplicate) samples for each staggered time period.

Samples of the MgO will be withdrawn from the bottles. The solids will be vacuum filtered using Whatman No. 40 filter paper (or other filter paper), and rinsed with DI water to remove any remaining brine. Other filtration procedures may be used including (but not exclusively) rinsing the solids with methanol, and centrifuging. The filtered solids will then be dried at room temperature at least overnight, or placed in an oven at an appropriate temperature and time to be determined (temperatures around 60 °C for 2 hours have been shown to be effective Wall, 2005). Some samples will then be ground and characterized by XRD, and some samples will be analyzed by SEM as described in 4.2.1 and 4.2.2. The amount of brucite and Mg-Cl-OH hydrate will be determined by LOI using the procedures described in Subsections 5.8.1–5.8.2.

Although we assume that only hydration takes place in these experiments, and efforts will be made to seal containers such that air (and CO_2) cannot enter, some carbonation of the MgO may still occur. Therefore, we will analyze some samples with a carbon coulometer (Subsection 6.2.2.1) to determine the quantity of carbonates formed.

A portion of the liquid from the sample bottles will be analyzed by ICP-AES to determine the concentration of dissolved Mg. An Orion EA 940 pH/ion analyzer (Mettler – Toledo MA 235 pH/ion analyzer or other pH meter) will be used to measure solution potential. The pH meter will be calibrated by Fisher certified pH buffers (pH = 4, 7, and 10) prior to measurement. The solution potential will yield information on the timescale for the solution to reach equilibrium. For example, we know that with Premier MgO, Mg-Cl-OH-hydrate formed and then decayed to brucite. Monitoring the solution potential versus time may be a means of tracking the kinetics of this process. In samples where the solid-to-liquid ratio is high, there may not be enough liquid to do any liquid analysis. Other ion specific electrodes (such as Cl⁻, discussed below) may also be used for this purpose.

In order to gain more information on Mg-Cl-OH-hydrate formation, Cl⁻ concentration will be monitored by an Orion EA 940 pH/ion analyzer (or another pH meter) using a Cl⁻ ion-selective electrode (Orion model 96/7B, or other Cl⁻ electrode). We will perform this analysis on

the matrix solution, or on a solution in which we have dissolved (all or a portion of) the washed solids.

5.8.1 Determination of Wt % of Brucite

To determine the weight fraction of brucite and periclase in hydrated samples, we will use two techniques: LOI and thermogravimetric analysis/differential scanning calorimetry (TGA/DSC). We will use a Netzsch TGA/DSC connected to a MS (mass spectrometer) to determine the fraction of brucite that is converted to periclase as a function of temperature and sample conditions. When brucite is heated to temperatures at or above 500 °C, it is converted to periclase:

$$Mg(OH)_2(s) \rightleftharpoons MgO(s) + H_2O(gas). \tag{3}$$

We will use the TGA/DSC to determine the fraction of brucite that is converted to periclase as a function of temperature and time. This information will then be used to develop an accurate LOI procedure that can be used on many samples simultaneously. It is not efficient to use the TGA on all samples because the TGA can only analyze one sample at a time. Nonetheless, even after an adequate LOI procedure has been developed, the TGA will be used periodically on samples to monitor the LOI procedure.

LOI has been used previously to determine the brucite-to-periclase conversion rate in Premier-MgO hydration experiments. In the previous work, MgO was first heated at 60 °C for 2 hours to remove moisture, and was then heated at 500 °C for 3 hours to convert the brucite to periclase (Wall, 2005). Assuming periclase is the only reactant and brucite is the only product, the weight difference before and after heating to temperatures at or above 500 °C for several hours is equal to the water lost and can be related to the amount of brucite initially present. At higher temperatures (700 °C), decrepitation of the hydrated MgO was observed (Wall, 2005), leading to erroneous weight measurements. Higher temperatures could yield more accurate measurements, but a heating procedure must be developed that will avoid decrepatation. The TGA will be used to develop this procedure.

5.8.2 Determination of Wt % of Mg-Cl-OH-hydrate

There are many known crystalline forms of Mg-Cl-OH-hydrate, such as $Mg_3(OH)_5Cl \cdot 4H_2O$ (Bryan and Snider, 2001), $Mg_2(OH)_3Cl \cdot 4H_2O$ (Altmaier et al., 2003), and MgOHCl (Kashani-Nehad et al., 2004). While various Mg-Cl-OH-hydrates have been studied since 1906, the literature on these compounds remains rather sparse. As described below, techniques will be developed to separate and analyze the Mg-Cl-OH hydrate from the other magnesium compounds in the resulting solids. These techniques used in conjunction may yield a great deal of information on the processes and the products associated with Mg-Cl-OH-hydrate.

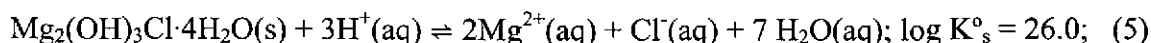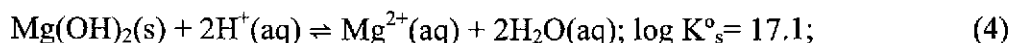#### 5.8.2.1 SEPARATION BY SOLUBILITY

It has been shown that MgOHCl can be separated from $MgCl_2$ by washing the solid mixture in methanol. $MgCl_2$ has a much larger solubility (10 times) in methanol compared to MgOHCl (Kashani-Nehad et al., 2004), and MgOHCl has a much larger (10 times) solubility in methanol compared with MgO and possibly brucite as well. This difference in solubility could

be exploited by first washing away the $MgCl_2$, then dissolving a portion of the remaining MgOHCl in methanol followed by re-crystallization (evaporation). The recrystallized fractions could then be weighed to determine wt %. Recrystallization may convert amorphous forms of the Mg-Cl-OH-hydrate to a crystalline form or vice versa. TGA/DSC and or other techniques, listed herein, before and after recrystallization may allow us to determine whether we have artificially created a phase change. At a minimum it will be important to remove the $MgCl_2$ for possible TGA/DSC or LOI experiments because $MgCl_2 \cdot 6H_2O$ dehydrates to MgOHCl at temperatures below 376 °C (Kashani-Nehad et al., 2005).

5.8.2.2 SEPARATION AND ANALYSIS BY TITRATION

Brucite buffers pH to a slightly higher value compared to some Mg-Cl-OH hydrates such as $Mg_2(OH)_3Cl \cdot 4H_2O$ (Altmaier et al., 2003). Thus titration of the methanol-washed solids,

$$Mg(OH)_2(s) + 2H^+(aq) \rightleftharpoons Mg^{2+}(aq) + 2H_2O(aq); \log K^o_s = 17.1; \qquad (4)$$

$$Mg_2(OH)_3Cl \cdot 4H_2O(s) + 3H^+(aq) \rightleftharpoons 2Mg^{2+}(aq) + Cl^-(aq) + 7 H_2O(aq); \log K^o_s = 26.0; \quad (5)$$

and subsequent methanol washing may allow us to separate and quantify the brucite from the Mg-Cl-OH hydrate, and quantify alkalinity. The solubility products for brucite and $Mg_2(OH)_3Cl \cdot 4H_2O$ in the presence of acid are found in Altmaier et al. (2003). Titration of the methanol-washed solids with a chloride-free acid (nitric acid or sulfuric acid), followed by measuring the chloride concentration using a chloride electrode will allow us to determine the total mass of chloride. ICP-AES can be used on the liquid to determine the total mass of magnesium.

5.8.2.3 SEPARATION AND ANALYSIS BY TGA/DSC

We will also perform TGA/DSC experiments on the solids after washing with methanol and subsequent drying. We will be able to discern the mixture of components if the decomposition temperature of a particular Mg-Cl-OH-hydrate is known or can be determined. The decomposition temperature of pure crystalline MgOHCl has been determined to be 376 °C (Kashani-Nehad et al., 2005). We will continue to search the literature for the decomposition temperatures of other known Mg-Cl-OH-hydrates. XRD analysis will be performed on samples before and after heating to determine reaction and formation products.

6 TASK #3 CARBONATION OF MG MATERIAL

The reaction of periclase with CO_2 can produce a series of magnesium carbonate minerals with magnesite as the most thermodynamically stable phase (Konigsberger et al., 1999). Different magnesium carbonates impose different values of CO_2 fugacity, which affects actinide speciation and solubility. These phases include magnesite ($MgCO_3$), nesquehonite ($MgCO_3 \cdot 3H_2O$), lansfordite ($MgCO_3 \cdot 5H_2O$), hydromagnesite ($Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$ or $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$), and others. With the Premier-MgO carbonation experiment carried out at room temperature using compressed lab air as a CO_2 source, hydromagnesite was the only Mg carbonate identified by XRD analysis (Snider and Xiong, 2002)

$$5Mg(OH)_2(s) + 4CO_2(aq \text{ or } gas) \rightleftharpoons Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O(s) \qquad (6)$$
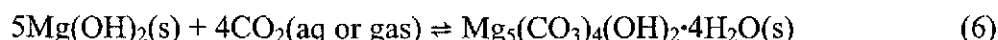
The main objective of this experiment is to gain a more mechanistic understanding of Mg carbonation and determine which magnesium carbonate phase will eventually control the P_{CO_2}. The experiment will help determine the carbonation rates of the MgO under various conditions. Two types of starting material will be used, MgO and hydrated MgO; hydrated MgO will be obtained from independent accelerated inundated hydration experiments in DI water.

Two sets of experiments are planned: atmospheric control by means of an environmental chamber to which a premixed gas is supplied; and solution control by means of an excess of a carbonate salt.

6.1 Chemical Solution Phase Control of Carbon Dioxide Partial Pressure

We will achieve various concentrations of carbon dioxide in the aqueous phase by adding an excess of a carbonate salt directly to the brine (GWB, ERDA-6, or other brine). MgO or hydrated MgO enclosed in a poly vinyldiene difluoride (PADF) dialysis bag or silver membrane capsules will be submerged in the brine, as shown in Figure 3. The container will be purged under argon, and capped with a rubber septum and an aluminum crimp. Headspace gas analysis (Subsection 6.2.2.2) will determine whether a particular carbonate salt-brine solution is maintaining the P_{CO_2} at a fixed level.
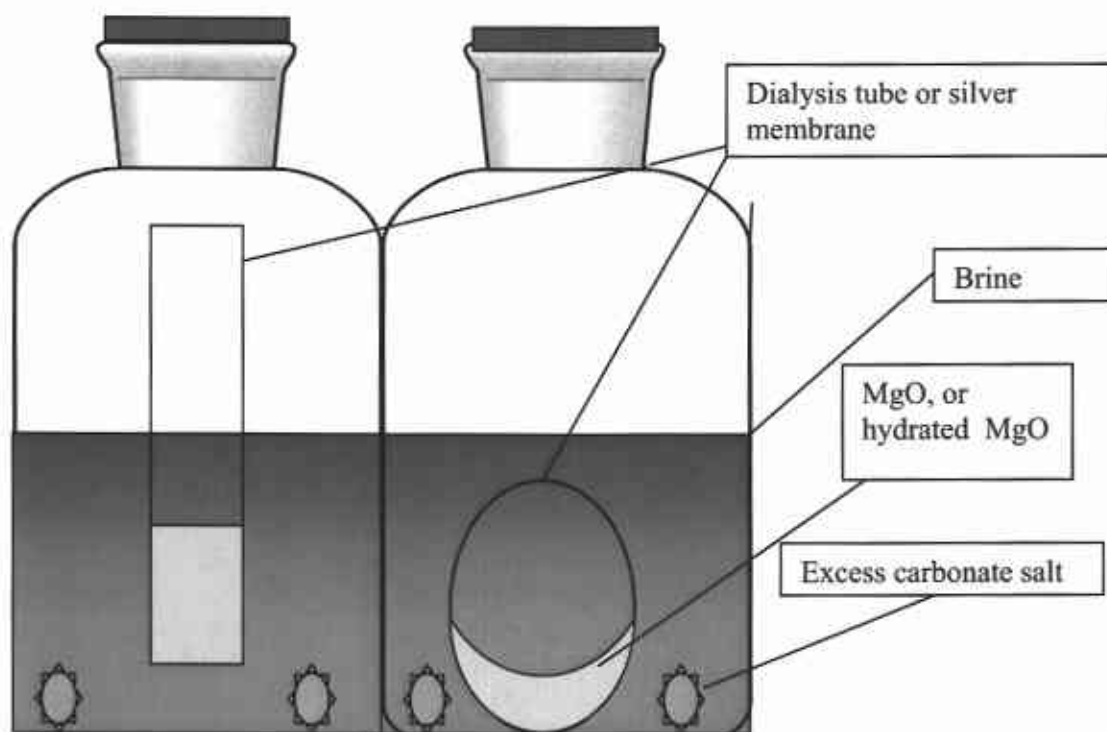
Figure 3. Diagram of septum bottle containing either a dialysis tube or a silver membrane.

To determine whether and which carbonates can be used for this experiment, we will use the EQ3/6 geochemical software package (Wolery, 1992a; Wolery, 1992b; Wolery and Daveler, 1992) to theoretically calculate the equilibrium P_{CO_2} and pH in the closed system containing: (1) MgO or hydrated MgO, (2) a brine (GWB, ERDA-6, or another brine), and (3) an excess of carbonate salt. A separate analysis plan will be written to describe these calculations in detail.

Some of the carbonate salts that will be tested using EQ3/6 are listed in Table 4. We expect that salts with a smaller pK_{sp} will correspond to a higher P_{CO_2}. We will not use any carbonate salt that EQ3/6 predicts P_{CO_2} levels above 1000 ppm. If none of the salts listed in Table 4 yield acceptable P_{CO_2} levels, according to EQ3/6 or experimental measurement, we will look for other salts. Some carbonates such as siderite ($FeCO_3$) will rapidly decompose into iron oxides in the presence of small amounts of oxygen. This can be remedied by adding an oxygen scavenger to the container, which doesn't necessarily make contact with the brine. For example ultra fine iron powder (Fe°) will effectively scavenge all oxygen that enters the system.

Another strategy is to numerically titrate CO_2 into GWB and ERDA-6 using EQ3/6 and determine the brine composition as a function of P_{CO_2}. Once a desired P_{CO_2} (less than 1000 ppm) has been reached, we will evaluate the brine composition, especially the solid phases. If this composition and P_{CO_2} can be recreated by the addition of excess solids (in the absence of a external-gas-phase source of CO_2), then this would be an ideal brine to use because it maintains

fixed P_{CO_2} and corresponds to the correct brine chemistry as if one maintained fixed P_{CO2} using a gaseous-phase source.

Table 4. Carbonate Minerals and Associated Solubility Product ($p_{K_{sp}}$).

Formula	$p_{K_{sp}}$ [1] (25 C, $\mu = 0$ M)
$CaCO_3$ (calcite or aragonite)	8.22 or 8.35
$FeCO_3$ (siderite)	10.68
Na_2CO_3	Unknown
K_2CO_3	Unknown
$NaHCO_3$	Unknown
$KHCO_3$	Unknown
Li_2CO_3	3.09

1. $p_{K_{sp}}$ obtained from Harris (1991) and CRC (2003).

6.2 Inundated Carbonation with solution controlled P$_{CO2}$

In the inundated carbonation experiments, the carbonate salt selected using EQ3/6 (Subsection 6.1) will be placed in a sealed serum bottle (or other container). MgO retained in a dialysis tube or silver membrane capsule will be emplaced in brine saturated with an excess of carbonate salt. To prepare this brine, an excess amount of carbonate salt will be added to the brine with continuous stirring and heating, if necessary. The heated brine will subsequently be cooled to room temperature. MgO will be enclosed in a dialysis tube (Spectra, 1000,000 daltons, 100 nm pore size) or silver membrane capsule (Millipore, 0.8 μm pore size). Both the dialysis tube and silver membrane have a pore size small enough to prevent the mixing of solids, yet large enough to allow free movement of dissolved species. A small amount of brine will be initially placed in the dialysis tube with the MgO. As the concentration gradient generated by the dissolved Mg and carbonate salt will be small, a low osmotic pressure crossing the tube is expected. Thus an extended working life is expected for the dialysis tube.

The amount of brine (GWB or ERDA-6) added to the sample bottles (solid-to-liquid ratio), the stir speed, and particle size may be varied depending on the results of the accelerated hydration sensitivity study described in Subsection 5.4. The serum bottles (or other containers)

will be purged under argon, capped with a rubber septum and an aluminum crimp (or other sealing mechanisms). Samples will be analyzed according to the procedures described in Subsection 6.2.2. Headspace gas analyses in the sample bottles will be performed by removal of small amounts of gas using a syringe and analysis using GC/MS. We may also analyze the amount of carbon dissolved in brine using the carbon coulometer if the amount of dissolved carbonate is above the detection limit of the carbon coulometer.

6.2.1 Inundated Carbonation Test Matrix

Below is the expected test matrix for the long-term inundated sensitivity study. Duplicate experiments will be set up. Changes to this matrix may be required. We expect this experiment will take three years.

- *Temperature:* ~25 °C

  ➤ *Basis:* This is the ambient laboratory temperature, which is about 3 °C below the in situ WIPP temperature.

- *Solvents:* GWB + carbonate salt, ERDA-6 + carbonate salt. The brines will be in equilibrium with given partial pressure of CO_2 (see Subsection 6.1).

  ➤ *Basis:* GWB and ERDA-6 represent brines that are relevant to expected WIPP conditions.

- *Particle Size:* If the accelerated-inundated sensitivity study (Subsection 5.4) shows this to be an important parameter, then at least two levels will be chosen. These levels will be chosen based on the results of the sensitivity study (i.e., some fractions may be too slow to obtain data with within the experimental window).

  ➤ *Basis:* Fernandez et al. (1999) showed that particle size affects the carbonation rate of MgO slurries.

- *Solid-to-Liquid Ratio:* If the accelerated-inundated sensitivity study (Subsection 5.4) shows this to be an important parameter, then at least two levels within the range of 10^{-3} to 10^1 g/ml will be used These levels will be chosen based on the results of the sensitivity study.

  ➤ *Basis:* Fernandez et al. (1999) showed that the solid-to-liquid ratio affects the carbonation rate of MgO slurries. Nemer (2006) showed that this range brackets the expected range of solid-to-liquid ratios in WIPP.

- *Stir Speed:* If the accelerated-inundated sensitivity study (Subsection 5.4) shows this to be an important parameter, then at least two levels within the range of 0 to 300 rpm will be used.

  ➤ *Basis:* Fernandez et al. (1999) showed that stir speed affects the carbonation rate of MgO slurries. This may yield information on the transport mechanisms of MgO hydration.

- *CO₂ partial pressure:* Up to 1000 ppm. The number of levels and their P_{CO_2} will depend strongly on the results of EQ3/6.

  ➢ *Basis:* We need to vary the P_{CO_2} to determine the impact of this parameter. Partial pressures below the detection limit of the GC/MS (< 50 ppm) or the carbon coulometer (detection limit to be determined) are not feasible. Snider (2003a) showed that the carbonation rate of Premier MgO at 25 °C and fixed P_{CO_2} decreased with increasing ionic strength of the brine. The carbonate concentration in the brine decreases with increasing ionic strength at a fixed P_{CO_2} due to the salting out effect.

6.2.2 Periodic Sample Collection and Analysis

Sample collection and analysis procedures will follow that given in Subsection 5.8 with the addition of carbon analysis using a carbon coulometer (Subsection 6.2.2.1) and headspace gas monitoring (subsection 6.2.2.2). We may also attempt to use the TGA/DSC to measure the weight fraction of carbonate for comparison purposes.

6.2.2.1 CARBON COULOMETER ANALYSIS

A carbon coulometer from UIC Inc (Model CM5014 coulometer, CM 5130 Acidification Module and CM 5120 Furnace Apparatus) will be used to determine the amount of carbonates formed during the carbonation reaction(s). A sample will be ground with a mortar and pestle after it has been dried in air at least overnight. Then, the ground sample will be dried in an oven at 60 °C for 2 hours prior to the coulometer analysis. TGA analysis described in Subsection 5.8.1 may suggest other temperatures and or times for drying samples prior to coulometer analysis.

6.2.2.2 HEADSPACE GAS MONITORING

A Varian GC/MS will be used to periodically measure the CO_2 concentration above the brine in the serum bottles. Two methods may be employed. In both methods, a gas sample is taken by syringe from the serum bottles (or other container). In the first method the gas is directly injected into the GC/MS by means of an injector port. Standards are similarly injected. This method is low cost but generates uncertainties on the order of 20%. In the second method the gas sample and standard are injected into a multiport valve with sample loop(s) of prescribed internal volume. A mechanical mass flow controller may be used to maintain prescribed internal pressure within the sample loop. This type of setup can decrease errors to below 20%. While multiple sampling of samples and standards can reduce uncertainty, we wish to minimize the number of punctures to the septum, which could contaminate the atmosphere in the serum bottles (or other containers).

6.3 Environmental Chambers with Fixed Humidity and P_{CO2}

In this set of experiments, MgO carbonation under humid and inundated conditions will be investigated inside environmental chambers with fixed humidity and P_{CO2}. The design of the environmental chamber is copied from TP 06-02, *Iron and Lead Corrosion in WIPP-Relevant Conditions*, Subsection 9.2.2 (Wall and Enos, 2006). In our experiment we will use chambers with fixed humidity and P_{CO2} instead of the four chambers used in TP 06-02 with fixed humidity

and P_{CO2}, P_{H2S}. We will investigate P_{CO2} from atmospheric concentration (350 ppm) up to several times atmospheric concentration (1000 ppm) at 72% RH. All the experiments will take place at room temperature.

Prior to sample emplacement, the functionality of the environmental chambers will be verified according to TP 06-02 section 9.2.3. If the humidity of the environmental chambers is difficult to maintain with the system described in TP 06-02, humidity may be controlled by passing the inlet gas stream through a pan of brine solution (GWB or EDRA-6) that matches the solutions in the sample bottles (in the chambers). The brine in the pan will first be acidified with phosphoric acid to a pH of around 4.5 to minimize CO_2 uptake by the pan. The gas will be bubbled through the pan using a gas diffuser tube which produces very small bubbles and hence maximizes the production of water vapor into the environmental chamber. A small fan may also be placed into the chamber to circulate gas.

6.4 Carbonation in Environmental Chambers

MgO carbonation under humid and inundated conditions will be investigated inside environmental chambers with 72%RH and P_{CO2} between 350 ppm and 1000 ppm at room temperature. In the inundated carbonation experiments, samples of MgO or hydrated MgO will be placed in open containers with various brines inside an environmental chamber. The amount of brine added to the sample bottles (solid-to-liquid ratio), and particle size may be varied depending on the results of the accelerated-hydration sensitivity study described in Subsection 5.4.

In the humid carbonation experiment, open containers with MgO or hydrated MgO will be in placed inside the environmental chambers. If the results of the accelerated humid sensitivity study (Subsection 5.5) shows that MgO particle size is a sensitive factor, MgO or hydrated MgO with various particle sizes may be tested.

Samples will be collected from the sample bottles and analyzed according to the procedures in Subsection 5.8 with the addition of carbon analysis using a carbon coulometer (Subsection 6.2.2.1).

6.4.1 Test Matrix for Environmental Chambers

Below is the expected test matrix for the environmental chambers for both the humid and inundated carbonation.

- *Temperature:* Room temperature (~25 °C)

  ➢ *Basis:* This is the ambient laboratory temperature, which is about 3 °C below the in-situ WIPP temperature.

- *RH:* 72%

  ➢ *Basis:* The anticipated RH in WIPP is 72%.

- *CO_2 partial pressure:* between 350 ppm to 1000 ppm.

  ➢ *Basis:* We need to vary the P_{CO_2} to determine the impact of this parameter. 350 ppm is the atmospheric partial pressures of CO_2.

6.4.2 Test Matrix for Inundated Carbonation

Below is the expected test matrix for the inundated carbonation study. Duplicate experiments will be set up. Changes to this matrix may need to be made. We expect this experiment to take no longer than three years.

- *Solvents:* GWB, ERDA-6, GWB and ERDA-6 that has first been equilibrated with WIPP-relevant minerals (see Subsection 5.6).

  ➢ *Basis:* GWB, ERDA-6, and brines that are first equilibrated with WIPP-relevant minerals represent brines under expected WIPP conditions.

- *Particle Size:* If the accelerated-inundated sensitivity study (Subsection 5.4) shows this to be an important parameter, then MgO or hydrated MgO with two different sizes will be chosen.

  ➢ *Basis:* Fernandez et al. (1999) showed that particle size affects the carbonation rate of MgO slurries.

- *Solid-to-Liquid Ratio:* If the accelerated-inundated sensitivity study (Subsection 5.4) shows this to be an important parameter, then at least two levels within the range of 10^{-3} to 10^1 g/ml will be used. The two levels will be chosen based on the results of the sensitivity study.

  ➢ *Basis:* Fernandez et al. (1999) showed that the solid-to-liquid ratio affects the carbonation rate of MgO slurries. Nemer (2006) showed that this range brackets the expected range of solid-to-liquid ratios in the WIPP.

6.4.3 Test Matrix for Humid Carbonation

Below is the expected test matrix for the humid carbonation study. Duplicate experiments will be set up. Changes to this matrix may need to be made. We expect this experiment to take no longer than three years.

- *Particle Size:* If the accelerated-humid sensitivity study (Subsection 5.5) shows this to be an important parameter, then MgO or hydrated MgO with two different sizes will be chosen.

7 SCIENTIFIC NOTEBOOKS

Quality control of the scientific notebooks will be established by the SNL Nuclear Waste Management Procedure (NP) 20-2, "Scientific Notebooks." Justification, evaluation, approval, and documentation of deviations from this TP will be documented in the scientific notebooks. Significant deviations from this TP will be captured in revisions of this TP.

Procedures, including use of replicates, spikes, split samples, control charts, blanks and reagent controls, will be determined during the development of experimental techniques, and will be documented in the scientific notebooks.

8 SAMPLE CONTROL

The sample control for the work under this TP will follow NP 13-1, "Control of Samples and Standards." Each sample will be appropriately labeled. 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 in a secure area with associated documentation.

9 DATA QUALITY CONTROL

9.1 Measuring and Test Equipment (M&TE)

A calibration program will be implemented for the work described in this TP 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. In addition, NP 13-1 and SNL Activity/Project Specific Procedures (SP) 13-1, "Chain of Custody," identify requirements and appropriate forms for documenting and tracking sample possession. Computer-based data handling will follow NP 9-1, "Analyses."

9.2 Data Acquisition Plan

Data collection procedures are specific to individual instruments. For details of the data acquisition for a particular instrument, see the Activity Specific Procedures (SP) or Users 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 following the requirements in NP 20-2. If the instrument allows data to be recorded electronically, copies of the data disks will be submitted to the WIPP Records Center according to procedure NP 17-1 "Records." If possible, data files may be transferred to ZIP disks or a CD ROM for submittal to the SNL/WIPP Records Center. For instruments that do not have direct data output (print or electronic), the instrument readings will be recorded directly into the scientific notebook.

The numerical data will be transferred from data printouts, electronic media, and scientific notebooks to Microsoft Excel spreadsheets and/or other commercial software. Data transfer and reduction shall be performed in such a way to ensure that data transfer is as accurate, avoiding information loss in the transfer, and that the input is completely recoverable.

9.3 Data Qualification

All hand calculations performed as part of the activities in this TP will be documented in a scientific notebook or in a report format that will be submitted to the records center. The notebook will be reviewed periodically according to procedure NP 20-2.

10 EQUIPMENT

A variety of measuring and analytical equipment will be used for the work described in this TP. This equipment includes that listed below, as well as equipment not yet purchased. A complete equipment list, including serial numbers, will be maintained in the scientific notebooks. The equipment uncertainties are defined in their SPs. They are acceptable for this TP.

10.1 Weighing Equipment

Several balances may be used for this project. These include a Mettler AT-261 five-decimal-place electronic balance, an ANC three-decimal-place balance, and top-loading balances and scales with maximum ranges of 2-30 kg. Balance calibration checks will be performed according to procedure SP 12-1, "Use of Laboratory Balances and Scales." Balance calibration checks will be recorded in the "Balance Calibration Logbook," which will be referenced in the scientific notebooks.

10.2 Oven and Temperature Measuring Equipment

Six Precision Thelco ovens and one VWR oven are used in the facility. They display the set-point temperature (the desired temperature) and the actual oven temperature. The accuracy of the actual temperature displayed by an oven is verified on a weekly to daily schedule and recorded in the "Oven Temperature Logbook" using a mercury thermometer with a unique identifier. The thermometers used to check the accuracy of the oven display are checked on an annual basis against an ERTCO High Precision digital thermometer (model 4400), calibrated by the SNL Primary Standards Laboratory every year.

We also have a Fisher Isotemp furnace and a Barnstead muffle furnace in the facility. The actual temperature of the furnace is verified regularly by a VWR expanded range thermometer at time of use and recorded in the scientific notebook. The thermometer is calibrated by the SNL Primary Standards Laboratory every year. The acceptance criteria for oven temperature is $\pm 5\,^{\circ}C$ of the set temperature.

10.3 Volumetric Measuring Equipment

Standard Laboratory Class A glassware (pipettes, volumetric flasks, etc.) will be used at all times. In addition, several adjustable Eppendorf pipettes are available for use in the laboratory. The calibration of Eppendorf pipettes will be checked routinely against a calibrated balance and documented in the scientific notebook.

10.4 Other Analytical Equipment

- *pH Meters/ion analyzer and autotitrators* – An Orion EA 940 pH/ion analyzer (Mettler – Toledo MA 235 pH/ion analyzer or other pH meter, autotitrator) will be used to measure pH. The range for all pH meters is 0.00 to 14.00. Electrodes will be calibrated according to SP 12-14, *Use of pH Meter and Electrodes.* The Cl⁻ concentration will be monitored by Orion EA 940 pH/ion analyzer (or other pH meter/ion analyzer) using a Cl⁻ ion selective electrode (Orion model 96/7B, or other Cl⁻ electrode). Electrodes will be calibrated daily or before each use (whichever is less frequent) with a blank and three Cl⁻

standard solutions. Calibration checks will be recorded in the "Cl⁻ Ion Electrode Log Book."

- *Equipment for chemical analysis* – Several instruments may be used for chemical analyses. These include a Perkin Elmer Optima 3300 DV ICP/AES; a UIC, Inc. carbon coulometer, consisting of an acidification module, a furnace module; a Netzsch STA 409 TGA/DSC; and a Varian GC/MS. These instruments will be calibrated or a calibration check will be performed as applicable and documented in the appropriate instrument log books.

- *Equipment for mineralogical, and textural characterization* – The mineralogy and texture of solid samples may be characterized using an Olympus BX60 polarizing microscope, a Fisher Scientific Stereomaster stereo microscope, or a JEOL JSM 5900LV SEM. Bulk sample mineralogy will be determined using a Bruker AXS D-8 Advance XRD. A mineral standard (quartz) will be run periodically to verify diffraction line positions. Calibration results will be documented in the appropriate instrument log book.

- *Equipment for particle size analysis* – A Malvern Instruments Mastersizer laser-scattering particle-size analyzer will be used to obtain particle-size distributions.

11 TRAINING

All personnel involved in the experiments described in this TP will be trained and qualified for their assigned work. This requirement will be implemented through procedure NP 2-1, "Qualification and Training." Evidence of training will be documented through Form NP 2-1-1, "Qualification and Training" and/or Form NP 2-1-2, "Training Record."

Sample preparation procedures, which may vary from sample to sample as work scope evolves, will be detailed in scientific notebooks, in accordance with procedure NP 20-2.

12 HEALTH AND SAFETY

All of the health and safety requirements relevant to the work described in this TP and the procedures that will be used to satisfy these requirements are described in ES&H standard operating procedures. SP473548, "ES&H Standard Operating Procedure," describes the nonradiological 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.

13 PERMITTING/LICENSING

There are no special licenses or permit requirements for the work described in this TP.

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APPENDIX A: BRINE COMPOSITION

Synthetic WIPP brines are used in all the experiments except those run under humid conditions. ERDA-6 is a saturated brine that contains mainly NaCl along with minor amounts of other solutes and represents fluids from reservoirs in the Castile Formation. ERDA-6 has 4.85 M of sodium, 4.64 M of chloride, and 167 mM of sulfate. GWB is a saturated brine with 3.54 M of sodium, 1.02 M of magnesium, 467 mM of potassium, 5.61 M of chloride, and 178 mM of sulfate, and represents intergranular brines from the Salado Formation at or near the stratigraphic horizon of the repository.

Synthetic WIPP brines are mixed following the technical operating procedure described by Robinson (1996). Brine formulas are shown below in Table 5 and Table 6. The ERDA-6 brine composition is from Popielak et al. (1983). The GWB is from Snider (2003b).

Table 5. Brine Formulas for Synthetic ERDA-6

Compound	Concentration (g/l)
MgCl$_2$ .6H2O	3.86
NaCl	261.64
KCl	7.23
Na$_2$SO$_4$	23.70
Na$_2$B$_4$O$_7$ .10H2O	6.00
CaCl$_2$ .2H2O	1.76
NaBr	1.13

Table 6. Brine Formulas for Synthetic GWB.

Compound	Concentration (g/l)
$MgCl_2 \cdot 6H_2O$	207.05
NaCl	179.61
KCl	34.84
Na_2SO_4	25.23
$Na_2B_4O_7 \cdot 10H_2O$	15.06
$CaCl_2 \cdot 2H_2O$	2.03
NaBr	2.74
LiCl	0.19

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