Sandia National Laboratories
Waste Isolation Pilot Plant

# Continuing Investigations of
# The Hydration and Carbonation of
# Premier Chemicals MgO

Work carried out under the Test Plan for the Experimental Study of
WIPP Engineered Barrier MgO at Sandia National Laboratories' Carlsbad Facility,
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# TABLE OF CONTENTS

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# 1 ABSTRACT

This report presents new results on: (1) inundated hydration experiments to extend the original experiments with magnesium-oxide (MgO) in synthetic Castile- and Salado-Formation brines, to determine the effects of various factors on the extent of *MgO hydration in deionized* (DI) water ($H_2O$) and these brines, and to determine the effects of various factors on the reproducibility of MgO hydration in Castile brine; and (2) inundated carbonation of MgO at ambient-laboratory-atmospheric carbon-dioxide ($CO_2$) partial pressure ($p_{CO_2}$) and ambient-laboratory temperature (referred to in this report as "atmospheric $p_{CO_2}$" and "room temperature," respectively), or with an atmosphere consisting of 5% $CO_2$ at room temperature.

The inundated hydration experiments demonstrated that the *measured* extent of hydration of Premier Chemicals MgO in DI $H_2O$ depends on the temperature of posttest loss-on-ignition (LOI) analysis. LOI analysis carried out for 3 h at 500 °C yielded 83.0 and 84.2 mol % brucite ($Mg(OH)_2$) (equivalent to 87.6 and 88.5 wt % brucite); however, LOI at 750 °C yielded 88.7 and 89.4 mol % brucite (91.9 and 92.4 wt % brucite). This shows that hydrated Premier MgO does *not release all $H_2O$ during LOI analysis at 500 °C*, and that the extent of hydration of Premier MgO observed in new accelerated experiments analyzed by LOI at 750 °C (about 89 mol % brucite) is now essentially equal to that expected based on chemical analyses (about 89 or 90 mol % brucite).

Inundated carbonation experiments at atmospheric $p_{CO_2}$ and room temperature indicate that carbonation is proceeding in both Castile and Salado brines, although the rates are slow. The only Mg carbonate produced at atmospheric $p_{CO_2}$ is hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), referred to in this report as "hydromagensite (5424)." Carbonation experiments at 5% $CO_2$ and room temperature proceeded faster than those at atmospheric $p_{CO_2}$; the final carbonation product is also hydromagnesite (5424), although nesquehonite ($MgCO_3 \cdot 3H_2O$) appeared as a transient phase in runs with Castile brine. The replacement of nesquehonite by hydromagnesite (5424) in Castile brine shows that hydromagnesite (5424) is more stable than nesquehonite under these conditions.

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# 2 INTRODUCTION

The U.S. Department of Energy is emplacing magnesium oxide (MgO) in the Waste Isolation Pilot Plant (WIPP) disposal system to decrease the solubilities of the actinide elements in transuranic (TRU) waste in any brine present in the repository after closure. MgO will decrease actinide solubilities by consuming essentially all carbon dioxide ($CO_2$) that would be produced by microbial consumption of all cellulosic, plastic, and rubber materials in TRU waste or waste containers in the repository. Consumption of $CO_2$ will prevent the acidification of brine or the production of significant quantities of carbonate ion ($CO_3^{2-}$), both of which could increase actinide solubilities.

The geochemical functions that MgO must perform to decrease actinide solubilities and serve as an effective engineered barrier are to: (1) consume essentially all $CO_2$ that could be produced in the repository, and (2) buffer (control) the $CO_2$ partial pressure ($p_{CO_2}$) and pH within ranges favorable from the standpoint of actinide solubilities.

The effects of MgO carbonation (consumption of $CO_2$) have been included in performance-assessment (PA) calculations since the CCA by: (1) removing $CO_2$ from the gaseous phase in PA calculations, thereby reducing somewhat the predicted pressurization of the repository; (2) using the values of $f_{CO_2}$ (similar to $p_{CO_2}$) and pH established by reactions among MgO, brine, and aqueous or gaseous $CO_2$ to calculate actinide solubilities.

Another function that MgO will perform in the repository is to consume water ($H_2O$) in brine, or $H_2O$ vapor in the gaseous phase. MgO hydration ($H_2O$ consumption) could consume $H_2O$ in quantities that are potentially significant from the standpoint of PA. Subsequent carbonation of hydrated MgO will not necessarily release this $H_2O$. Potentially beneficial effects of MgO hydration include reductions in gas production, pressurization caused by gas production, and direct-brine and spallings releases. However, MgO hydration is not included in PA at present.

In its May 1998 certification rulemaking, the U.S. Environmental Protection Agency (EPA) specified MgO as the only engineered barrier in the WIPP disposal system.

Subsection 5.2 of this report contains a detailed review of the use of MgO as the WIPP engineered barrier.

Experimental work carried out at Sandia National Laboratories (SNL) in Albuquerque showed that MgO from National Magnesia Chemicals, emplaced in the WIPP from 1999 to 2000, consumes $CO_2$ and $H_2O$ effectively (Papenguth et al., 1997; 1999).

Ongoing work at SNL in Carlsbad is evaluating the efficacy of MgO from Premier Chemicals, the supplier of MgO since 2000. These experiments also include some experiments with reagent-grade periclase (MgO) and brucite ($Mg(OH)_2$) purchased from Fisher Scientific. The long-term objectives of this work include: (1) continued characterization of Premier MgO, (2) quantification of carbonation rates and pathways, (3) quantification of hydration rates and pathways; (4) determination of the effect(s) of possible lithification on

carbonation and hydration. Snider and Xiong (2002) described the current plans for these experiments in detail. Subsection 5.2 of this report reviews the results of this work.

All technical results reported in the document were obtained from experiments performed under the Sandia National Laboratories WIPP Quality Assurance Program. The test plan for this work is Snider et al. (2004). The laboratory notebooks that contain the results described in the report are: WIPP-MGO-CBD-1, WIPP-MGO-CBD-2, WIPP-MGO-CBD-3, WIPP-MGO-CBD-5, WIPP-MGO-CBD-6, WIPP-MGO-CBD-8, WIPP-MGO-CBD-10, WIPP-MGO-CBD-11, WIPP-MGO-CBD-13, and WIPP-MGO-CBD-16.

# 3 INUNDATED MgO HYDRATION EXPERIMENTS

Bryan and Snider (2001a, 2001b) and Snider (2002, 2003a, 2003d) have carried out humid and inundated hydration experiments with Premier Chemicals MgO and – to a lesser extent – with Fisher Scientific reagent-grade MgO. Most of these experiments have been completed.

The first objective of the hydration experiments still under way is to explain why the extent of hydration observed in accelerated experiments appears to be less than that expected based on chemical analyses of Premier MgO. Snider (2003a, 2003d) used inductively coupled plasma-optical emission spectroscopy (ICP-OES) and gravimetric analysis to quantify the mineralogical composition of one of the lots of Premier MgO used for experiments at SNL in Carlsbad. Based on the assumption that the silicate is forsterite, this lot of MgO contains 86.86±0.05 wt % periclase, 2.386±0.040 wt % lime, 2.071±0.043 wt % spinel, and 5.027±0.092 wt % forsterite. If the silicate is monticellite, this lot contains 88.73±0.53 wt % periclase, 1.273±0.059 wt % lime, 2.071±0.043 wt % spinel, and 5.756±0.105 wt % monticellite. Given the uncertainties inherent in quantifying the mineralogical composition of materials such as Premier MgO by X-ray diffraction (XRD) analysis, it is reasonable to conclude that this material contains about 89 or 90 wt % reactive phases (periclase + lime) and 10 or 11 wt % nonreactive phases (oxides and silicates). However, Snider (2002, Figures 1, 2, 6, and 7) observed that hydration of Premier MgO appeared to reach completion after formation of about 85 mol % brucite in accelerated experiments. Snider (2003c, p. 9) calculated that the average brucite content is 84.6 mol % after (apparently) complete hydration, based on the last 8 data points of the inundated-hydration run with DI $H_2O$ at 90 °C (Snider, 2002, Figures 1 and 2) and the last 16 data points of the humid-hydration run at 80 °C and 95% RH (Snider, 2002, Figures 6 and 7).

The second objective of the ongoing hydration experiments is to examine the reproducibility of experiments with ERDA-6, a synthetic brine representative of fluids in brine reservoirs in the Castile Formation (Popielak, et al., 1983).

The third objective of these experiments is to determine if hydration in Generic Weep Brine (GWB), a synthetic brine typical of intergranular (grain-boundary) fluids from the Salado at or near the stratigraphic horizon of the repository (Snider, 2003b), continues after hydration slows to a very low rate. Results of previous XRD analysis indicate that, despite the appearance of this "plateau," the concentration of brucite is still increasing with time (Snider, 2003d).

## 3.1 Experimental Methods

### 3.1.1 Extension of the Original Inundated Hydration Experiments

Snider (2002, 2003a) described additional experiments to extend the original inundated hydration experiments with Premier Chemicals MgO (Bryan and Snider, 2001a; 2001b; Snider, (2003c). Snider (2002, 2003a) placed 125-mL polypropylene bottles containing 5 g of Premier Chemicals MgO and 100 mL of ERDA-6 or GWB in ovens at room temperature, 50, 70, or 90 °C. The bottles were agitated frequently to prevent possible formation of lithified hydration products. Samples were taken and analyzed approximately once a month.

### 3.1.2 Experiments on the Extent of Hydration

Experiments were carried out to determine the effects of three factors on the extent of MgO hydration: (1) grain size, (2) the type of MgO (Premier Chemicals or Fisher Scientific reagent grade), and (3) the temperature of loss-on-ignition (LOI) analysis (500 or 750 °C).

#### 3.1.2.1 EXPERIMENT 1

This experiment was carried out to determine the effect of grain size. Thirty 125-mL polypropylene bottles containing 5 g of bulk (unsieved) Premier MgO or sieved (grain size < 150 $\mu$m) Premier MgO and 100 mL of DI $H_2O$, ERDA-6, or GWB were placed in an oven at 90 °C. Five bottles containing bulk MgO and five bottles with sieved MgO were prepared for each of the three solutions. Each bottle was agitated daily by hand. One bottle containing bulk MgO and one with sieved material were sampled after 7, 14, 21, 28, and 35 days. Posttest LOI analysis was conducted at 500 °C.

#### 3.1.2.2 EXPERIMENT 2

This experiment was conducted with Fisher reagent-grade MgO at 90 °C to test the validity of LOI analysis at 500 °C. (It was expected that hydration of Fisher MgO at 90 °C would yield 100 mol % brucite, because this reagent-grade material comprises pure, crystalline MgO with an XRD pattern identical to that of periclase.) Twenty-two 125-mL polypropylene bottles containing 5 g of Fisher MgO and 100 mL of DI $H_2O$ were placed in an oven at 90 °C. Each bottle was agitated daily by hand. One or two bottles were sampled daily for 15 days. Posttest LOI analysis was performed at 500 °C.

#### 3.1.2.3 EXPERIMENT 3

This experiment extended Experiment 2 by hydrating both Fisher and Premier MgO, and by running for 29 days to ensure 100% hydration of the Fisher MgO. Furthermore, all samples were analyzed by LOI at both 500 and 750 °C to further test the validity of LOI analysis at 500 °C. Eight 125-mL polypropylene bottles containing 5 g of either Fisher or Premier MgO and

100 mL of DI H$_2$O were placed in an oven at 90 °C. The bottles were agitated daily by hand. All eight bottles were sampled after 29 days.

During all three experiments, the pH of all solutions was measured at the time of sampling. The samples were vacuum-filtered and rinsed with DI H$_2$O on Whatman #40 filter paper (particle retention > 8 μm). After rinsing, the filter papers containing the solids were placed on watch glasses to dry in room air. Once dry, the solids were ground using a mortar and pestle, and stored in plastic bottles for subsequent LOI and XRD analyses.

## 3.1.3 Experiments on the Reproducibility of Hydration

Experiments were conducted to examine the effects of ionic strength and batch-to-batch variations in Premier MgO on the reproducibility of MgO hydration in ERDA-6.

### 3.1.3.1 EXPERIMENT 1

This experiment was carried out in DI H$_2$O, which was expected to have a relatively constant ionic strength, to determine if possible batch-to-batch variations in the ionic strength of ERDA-6 or changes in the ionic strength of this brine during a run caused the poor reproducibility observed in previous experiments with this brine. Eight 125-mL polypropylene bottles containing 5 g Premier MgO and 100 mL of DI H$_2$O were placed in an oven at 70 or 90 °C. Each bottle was agitated daily by hand. One bottle at 70 °C and one at 90 °C were sampled after 7, 14, 21, and 28 days. Posttest LOI was carried out at 500 °C.

### 3.1.3.2 EXPERIMENT 2

This experiment was conducted to compare results obtained with two batches of Premier MgO supplied to SNL at different times. Forty-eight 125-mL polypropylene bottles containing 5 g of MgO from one or the other batch and 100 mL of ERDA-6 or GWB were placed in an oven at 90 °C. Twelve bottles were prepared with MgO from each batch and each of the two brines. The bottles were agitated daily by hand. Three bottles containing MgO from each combination of batch and brine were sampled after 1 week, 1 month, 3 months and 5 months. Duplicate LOI analyses were performed at 500 °C.

During both experiments, the pH was measured at the time of sampling and samples were vacuum-filtered, rinsed, and dried for LOI and XRD analyses as described above for the experiments on the extent of MgO hydration.

## 3.2 Analytical Methods

### 3.2.1 LOI Analysis

LOI analysis is carried out to determine the concentration of brucite, reported in mol % and wt %. Crushed samples with masses of 1-3 g are placed in porcelain crucibles. The crucibles are placed in a furnace at 60 °C for approximately 2 h to evaporate any $H_2O$ adsorbed from the atmosphere. After 2 h, the crucibles are removed from the furnace and transferred to a desiccator to cool. The crucibles are reweighed and placed back in the furnace at 500 °C for 3 h to drive off bound $H_2O$. In some cases, such as the third experiment described under "Experiments on the Extent of Hydration", to determine the extent of MgO hydration, samples were heated at 750 °C instead of 500 °C. The crucibles are then placed back in a desiccator to cool for at least 30 min prior to final weighing.

### 3.2.2 XRD Analysis

Powdered samples are run on a Bruker D8 X-ray diffractometer to identify crystalline constituents of solid starting materials or reaction products. The X-ray source is $Cu_{K\alpha}$ and patterns are collected from 10–90° 2θ.

## 3.3 Results

### 3.3.1 Extension of the Original Inundated Hydration Experiment

Figures 1, 2, 3, and 4 present the results of hydration of Premier Chemicals MgO in DI $H_2O$, 4-M NaCl, ERDA-6, and GWB, respectively, at room temperature, 50, 70, and 90 °C. Most of the bottles used to extend the original inundated hydration experiment with Premier MgO (Bryan and Snider, 2001a; 2001b; Snider, (2003c) have been opened and analyzed, with the exception of several bottles at room temperature. Note that no new experiments were carried out in DI $H_2O$ or 4-M NaCl (Figures 1 and 2); these figures are included for comparison with ERDA-6 and GWB. Furthermore, the original results for ERDA-6 and GWB are shown for comparison with the new results for these brines. Also note that the abscissa in Figure 4 (GWB) is labeled "LOI (wt %)" instead of "Brucite (mol %)," because two hydration products form in GWB: brucite and an amorphous or (less often) a crystalline Mg-Cl-OH-$H_2O$ phase. The first 12 data points (solid symbols) for ERDA-6 and GWB (Figures 3 and 4, respectively) are from the original inundated hydration experiment (Bryan and Snider, 2001a; 2001b; Snider, (2003c). The new results (open symbols) include some data obtained after periods identical to those of the original experiment to test the reproducibility of hydration in these brines.

Both the original results (Figures 1 and 2) and the new and original results (Figures 3 and 4) with Premier MgO demonstrate that the hydration rate of this material increases significantly with temperature, and that Premier MgO hydrates slowly – relative to the duration

of typical laboratory experiments - at room temperature, the experimental temperature closest to the in situ temperature of 28 °C observed in the Salado at a subsurface depth of 655 m (Munson et al., 1987).

Furthermore, at any given temperature, the Premier-MgO hydration rate decreases in the following order: DI $H_2O$ > 4 M NaCl > ERDA-6 > GWB. In general, the Premier-MgO hydration rate decreases as the solutions become more complex and hence more representative of WIPP brines. (ERDA-6 and GWB closely simulate typical Castile and Salado brines, respectively.)

The new results for Premier MgO in ERDA-6 (Figure 3) show that MgO has continued to hydrate during the extended period covered by this experiment. The new results at room temperature and 50 °C correspond relatively closely to the original results at room temperature and 50 °C during the period of overlap. Furthermore, hydration at these temperatures has now proceeded to an extent similar to that at 70 °C, and to the same extent as that in the original runs at 90 °C. At both 70 and 90 °C, however, the extended data plot below the original data during the period of overlap. After 370 days, hydration at 70 °C did not proceed as far as it did in the original runs at 70 °C, but hydration at 90 °C did exceed that in the original runs.

The new GWB results at 50, 70, and 90 °C (Figure 4) follow the same trend as the original data. After a period of rapid hydration that is inversely proportional to temperature, Premier MgO in both the new and original experiments appear to hydrate very slowly once the LOI attains a value of about 24 wt %. Hydration in the new experiment at room temperature now exceeds that in the original experiment after about 600 days, but may be proceeding slower now that the LOI has reached about 30 wt %. Again, XRD analysis of the original hydration products indicated that, despite the appearance of this "plateau," the concentration of brucite is still increasing with time (Snider, 2003d).
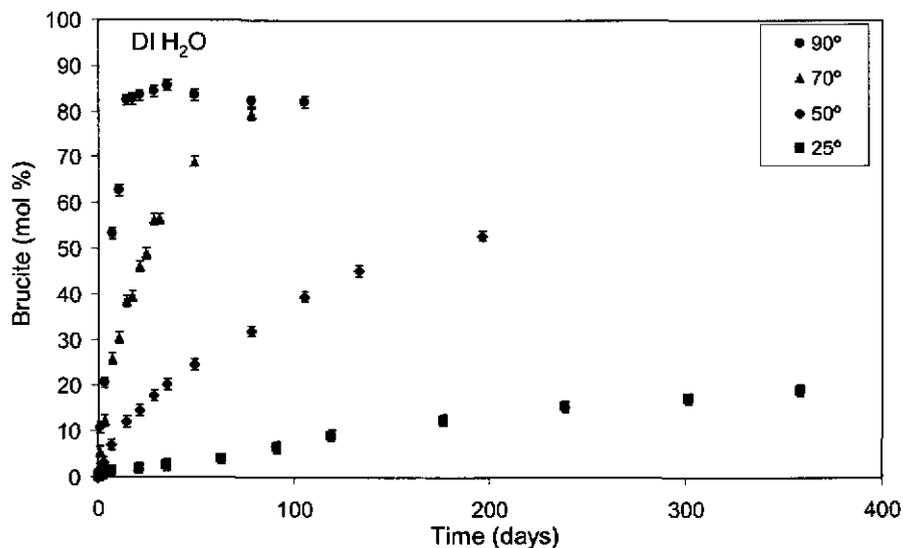


Figure 1. Hydration of Premier MgO in DI $H_2O$ at room temperature, 50, 70, and 90 °C.
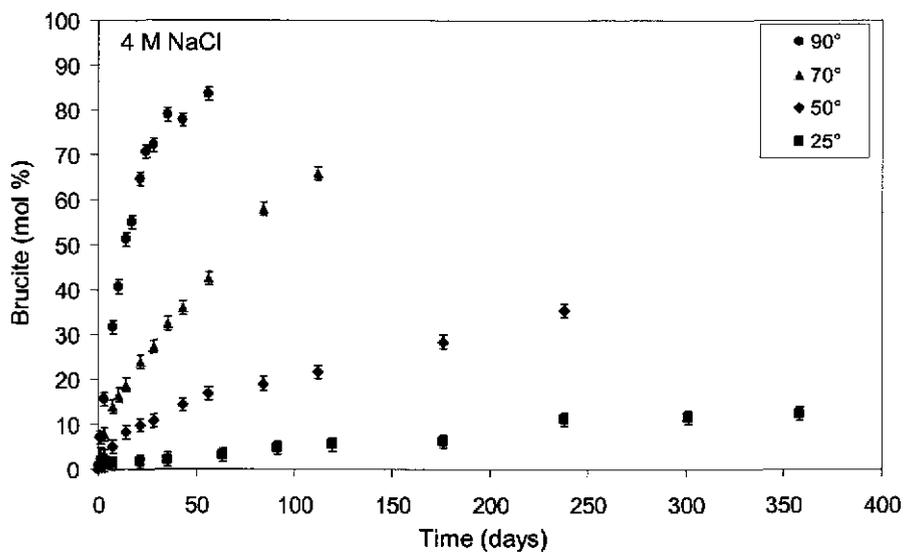
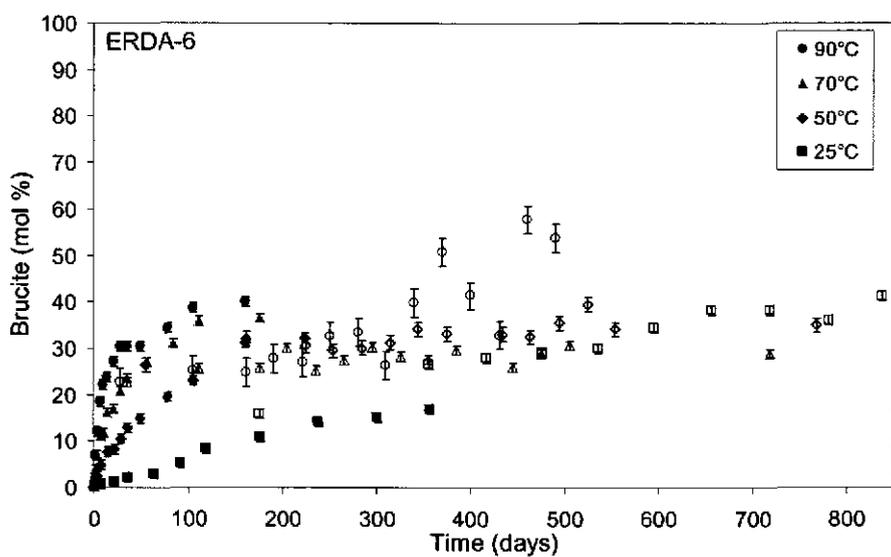Figure 2.  Hydration of Premier MgO in 4 M NaCl at room temperature, 50, 70 and 90 °C.



Figure 3.  Hydration of Premier MgO in ERDA-6 at room temperature, 50, 70, and 90 °C (solid symbols: original data; open symbols: new data).
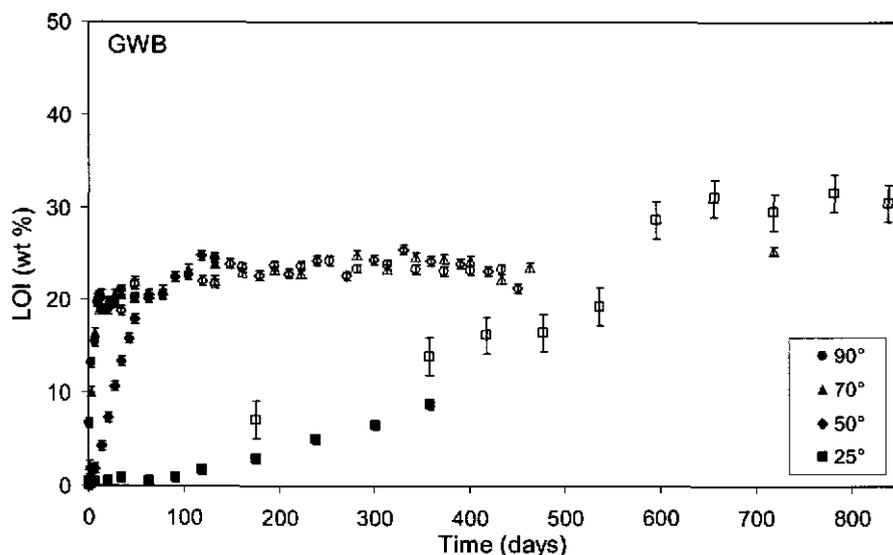
Figure 4. Hydration of Premier MgO in GWB at room temperature, 50, 70, and 90 °C (solid symbols: original data; open symbols: new data).


## 3.3.2 Experiments on the Extent of Hydration

The results of this experiment demonstrated that the *measured* extent of hydration of Premier Chemicals MgO in DI $H_2O$ depends on the temperature of posttest loss-on-ignition (LOI) analysis: LOI analysis carried out at 750 °C yields hydration results much closer to those that expected based on ICP-OES and gravimetric analysis of Premier Chemicals MgO than does LOI conducted at 500 °C.


### 3.3.2.1 EXPERIMENT 1

Figures 5, 6, and 7 present the results of hydration of bulk (unsieved) Premier MgO or sieved (<150 μm) Premier MgO in DI $H_2O$, ERDA-6, or GWB, respectively, at 90 °C for 7, 14, 21, 28, or 35 days. Again, note that the abscissa in Figure 7 (GWB) is labeled "LOI (wt %)" instead of "Brucite (mol %)," because two hydration products (brucite and a Mg-Cl-OH-$H_2O$ phase) form in GWB. These figures include data from the original hydration experiment with DI $H_2O$, ERDA-6, and GWB (Figures 1, 3, and 4) for comparison.

The new results for DI $H_2O$ (Figure 5) indicate that both the bulk and sieved Premier MgO apparently hydrated slightly less than the Premier MgO in the original experiment (Bryan and Snider, 2001a; 2001b; Snider, (2003c). Both the new and the original results appear to indicate less hydration than that expected based on XRD analysis of Premier MgO. However, LOI analysis for both of these experiments was carried out at 500 °C.

The new results for ERDA-6 (Figure 6) indicate that the sieved Premier MgO hydrated slower than the bulk Premier MgO, and slower than bulk Premier MgO in the original experiment. The new hydration rate of bulk Premier MgO is within the experimental error of the

previous rate for this material. It is unclear why the finer-grained Premier MgO hydrated slower than the bulk material.

The new GWB results (Figure 7) indicate that the sieved Premier MgO hydrated faster than the bulk Premier MgO in this or the original experiment. However, both the sieved and the bulk materials appear to be hydrating very slowly, as observed in previous experiments after an initial period of rapid hydration. Note that the extent of hydration attained in the new experiment after 7 days is similar to that reached in the original experiment after 100 days. Again, XRD analysis of the original hydration products indicated that, despite the appearance of this "plateau," the concentration of brucite is still increasing with time (Snider, 2003d).

### 3.3.2.2 EXPERIMENT 2

Figure 8 provides the results, obtained by LOI analysis at 500 °C, of hydration of Fisher Scientific reagent-grade MgO in DI $H_2O$ at 90 °C for 1 to 15 days. Symbols with different colors plotted at identical times represent results from LOI analyses of hydration products from duplicate bottles; identical symbols plotted at identical times represent duplicate LOI analyses of hydration products from the same bottle. All results are between 87 and 99 mol % brucite; there appears to be no increase in the extent of hydration from 1 to 15 days. Most of the duplicate LOI analyses yielded results that did not differ significantly. The most likely explanation for why hydration of Fisher MgO did not produce 100 mol % brucite in this experiment is that LOI analysis at 500 °C did not drive off all bound $H_2O$ see Experiment 3 below).

### 3.3.2.3 EXPERIMENT 3

Table 1 shows the effects of the temperature at which posttest LOI analysis was performed on the extent of hydration of Fisher Scientific reagent-grade MgO and Premier Chemical MgO in DI $H_2O$ at 90 °C for 29 days. These results indicate that all bound $H_2O$ is not released during LOI analysis at 500 °C.
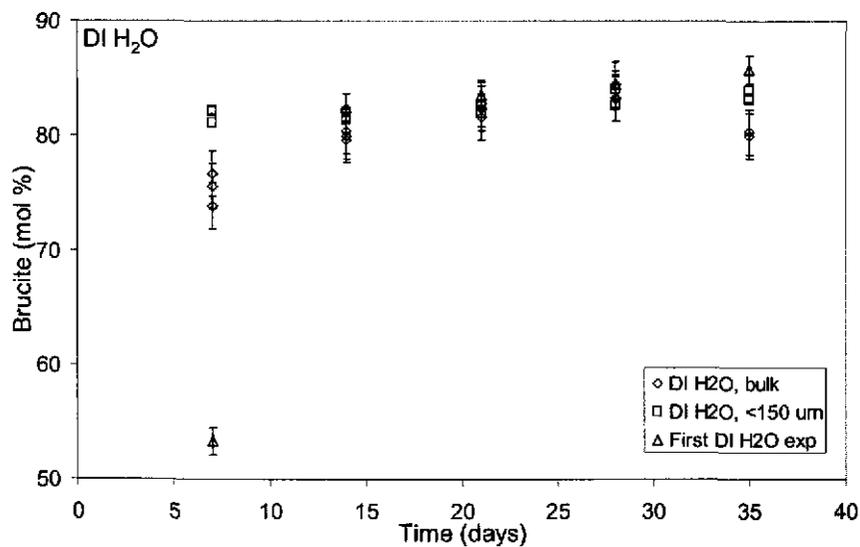
Figure 5. Hydration of bulk (unsieved) or sieved (<150 μm) Premier MgO in DI H₂O at 90 °C for 7, 14, 21, 28, or 35 days (LOI analysis at 500 °C).
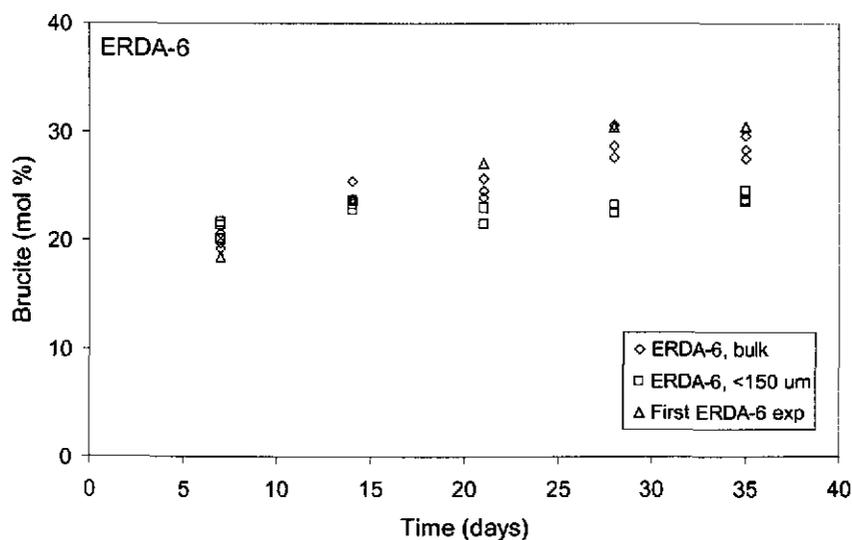


Figure 6. Hydration of bulk (unsieved) or sieved (<150 μm) Premier MgO in ERDA-6 at 90 °C for 7, 14, 21, 28, or 35 days (LOI analysis at 500 °C).
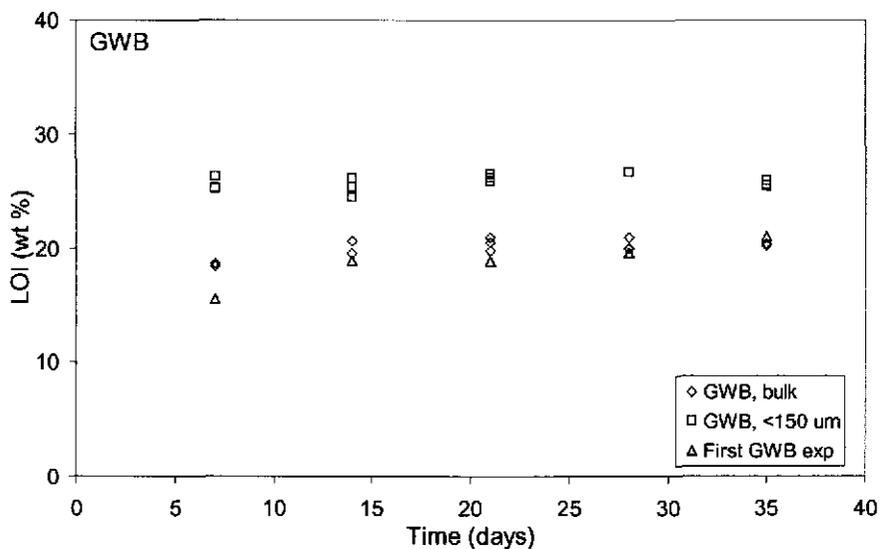
Figure 7.  Hydration of bulk (unsieved) or sieved (<150 μm) Premier MgO in GWB at 90 °C
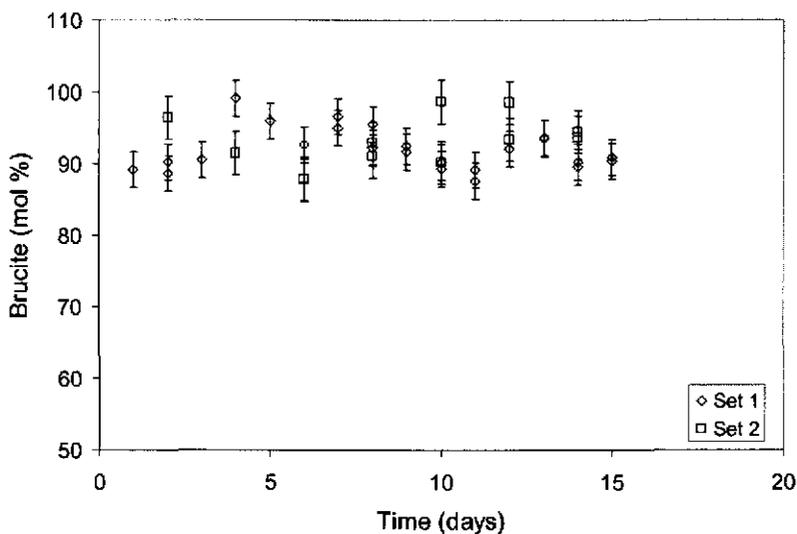for 7, 14, 21, 28, or 35 days (LOI analysis at 500 °C).



Figure 8.  Hydration of Fisher MgO in DI H₂O at 90 °C for 1 to 15 days (LOI analysis at
500 °C).

Table 1. Effects of the Temperature of LOI Analysis on the Extent of Hydration of Fisher and Premier MgO under Accelerated Conditions.

| Type of MgO | Mol % Brucite, 500 °C | Wt % Brucite, 500 °C | Mol % Brucite, 750 °C | Wt % Brucite, 750 °C |
|---|---|---|---|---|
| Fisher | 90.5 | 93.2 | NA | NA |
| Fisher | 90.2 | 93.0 | NA | NA |
| Fisher | NA | NA | 97.3 | 98.2 |
| Fisher | NA | NA | 98.5 | 99.0 |
| Premier | 84.2 | 88.5 | NA | NA |
| Premier | 83.0 | 87.6 | NA | NA |
| Premier | NA | NA | 88.7 | 91.9 |
| Premier | NA | NA | 89.4 | 92.4 |

NA = not analyzed.

The extent of hydration of both Fisher and Premier MgO inferred from LOI analysis at 750 °C, about 97-98 mol % or 98-99 wt % brucite in the case of Fisher and 89 mol % or 92 wt % in the case of Premier, is slightly more than that expected based on ICP-OES and gravimetric analysis of these materials.

Furthermore, it is possible that a very small amount of the increase in the extent of hydration inferred from the results of LOI at 750 °C is the result of decarbonation of the hydration products. This is because: (1) atmospheric $CO_2$ was not excluded from this or other MgO hydration experiments; (2) calcite decarbonates at 670 °C (Bruni et al., 1998). However, the effect of decarbonation on the increase in the extent of hydration is probably very small, because the $CO_2$ present in the headspaces of the 125-mL polypropylene bottles at the start of these runs was very limited, and it is unlikely that significant quantities of $CO_2$ entered the bottles after they were sealed and placed in the ovens. Experiments are under way to quantify how much, if any, of the increase in the extent of hydration inferred from the results of LOI at 750 °C is the result of decarbonation; results will be reported as soon as they become available.

### 3.3.3 Experiments on the Reproducibility of Hydration in ERDA-6

The reproducibility experimental results detailed below indicate that ionic strength is not a factor. Data from different batches of MgO do not show distinct patterns; however, when compared to the original plots, the data follow the original trend.

#### 3.3.3.1 EXPERIMENT 1

Figure 9 presents the results of hydration of one batch of Premier Chemicals MgO in DI $H_2O$ at 70 or 90 °C for 7, 14, 21, or 28 days. The original results for hydration of Premier MgO in DI $H_2O$ at 70 and 90 °C are shown for comparison with the new results for these temperatures. The results for 70 °C suggest that hydration of Premier MgO in DI $H_2O$ is not more reproducible than hydration of Premier MgO in ERDA-6. However, most of the results for 90 °C, which appear to be more reproducible, appear to suggest that hydration of Premier MgO in DI $H_2O$ is more reproducible than hydration of Premier MgO in ERDA-6 at this temperature. Furthermore, most of the results of hydration of bulk (unsieved) Premier MgO or sieved (<150 μm) Premier MgO in DI $H_2O$ at 90 °C for 7, 14, 21, 28, or 35 days (Figure 6) also appear to support the hypothesis that hydration of Premier MgO is more reproducible in DI $H_2O$ than in ERDA-6 at this temperature. However, it is unclear whether the ionic strength varies less in experiments with DI $H_2O$ than in experiments with ERDA-6, because dissolution of brucite in DI $H_2O$ increases the ionic strength of the solution as these experiments proceed. Therefore, the implications of any conclusions that might be drawn from this experiment are also unclear.

#### 3.3.3.2 EXPERIMENT 2

Figures 10 and 11 present the results of hydration of two batches of Premier MgO in ERDA-6 or GWB at 90 °C for 1 week, 1 month, 3 months and 5 months. Each datum represents the results of duplicate LOI analysis at 500 °C of the sample from one of the three bottles with each of the two batches of ERDA-6 or GWB sampled at that time. The results shown in Figure 10 demonstrate that hydration of Premier MgO in ERDA-6 continued throughout this 5-month experiment, consistent with other experiments with ERDA-6 (Figures 3 and 6). In most cases, samples of the old batch of Premier MgO appeared to hydrate faster in ERDA-6 than samples of the new batch. The data in Figure 11 show that hydration of Premier MgO in GWB continued throughout this experiment, perhaps because it was not long enough to yield the "plateau" observed in other experiments with GWB (Figure 4). Comparison of Figure 10 and Figure 11 shows that the results for GWB data are more reproducible than those for ERDA-6. The variation among samples hydrated in ERDA-6 and sampled at the same time was about 4 to 7 mol % brucite; the corresponding variation for GWB was 2 to 4 mol %.
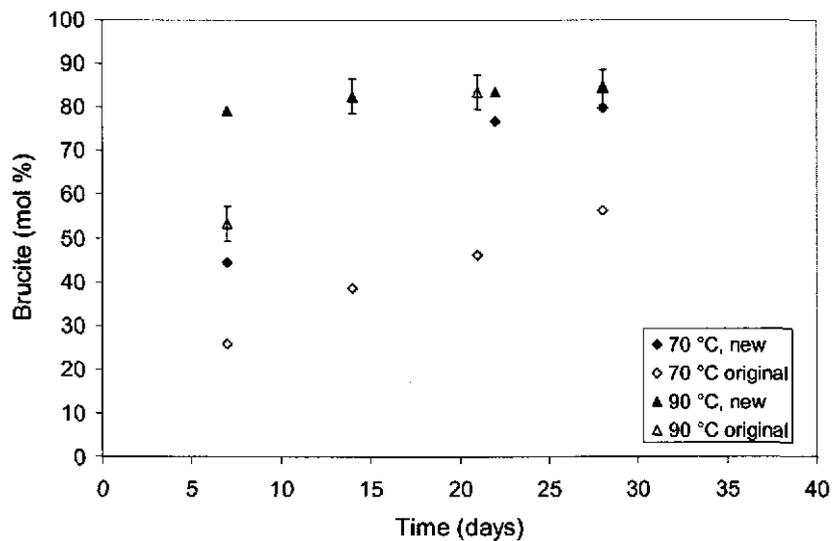
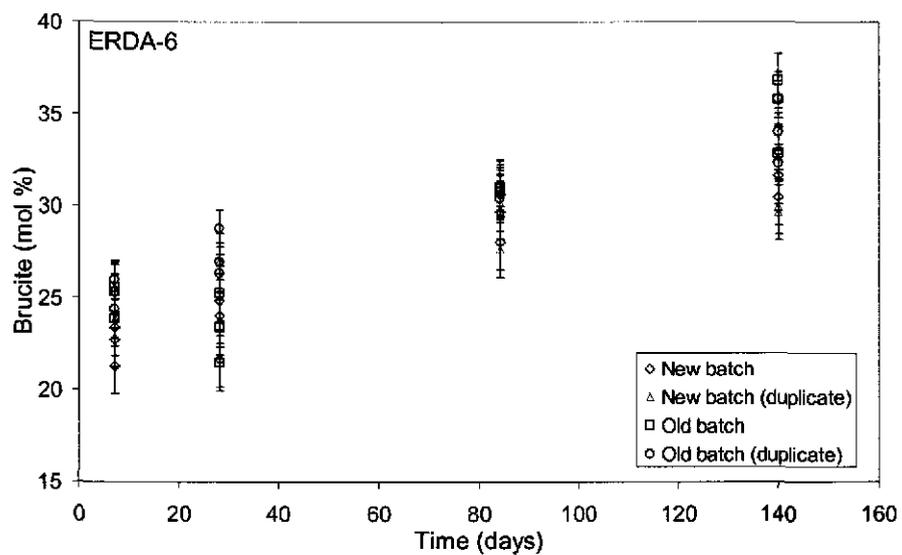Figure 9. Hydration of Premier MgO in DI H$_2$O at 70 or 90 °C for 7, 14, 21, or 28 days.



Figure 10. Hydration of two batches of Premier MgO in ERDA-6 at 90 °C for 1 week, 1 month, 3 months, and 5 months.
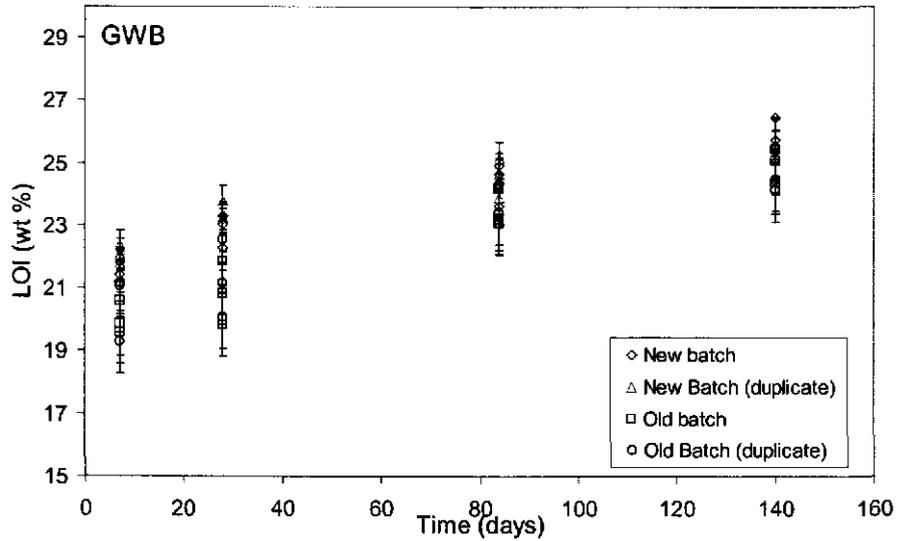
Figure 11. Hydration of two batches of Premier MgO in GWB at 90 °C for 1 week, 1 month, 3 months, and 5 months.

Figures 12 and 13 compare these new hydration results to those from the original and extended hydration experiments (see above). The new results for ERDA-6 (Figure 12) indicate that Premier MgO hydrated slower in this experiment than in the original experiment at 90 °C, but faster than in the extended experiment at this temperature, at least for comparable sampling times. The new results for GWB (Figure 13) suggest that Premier MgO hydrated somewhat faster in this experiment that in the original experiment at 90 °C, and that it hydrated significantly faster than it did in the extended experiment.
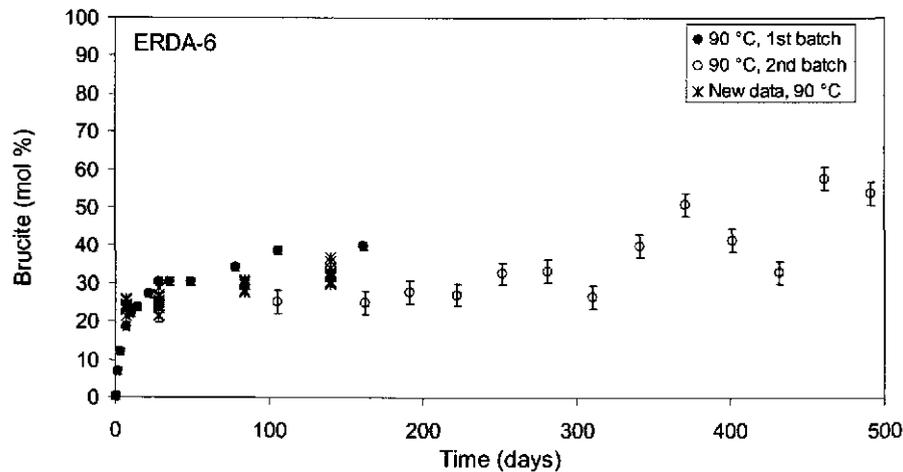


Figure 12. Comparison of data from the hydration of two batches of Premier MgO in ERDA-6 at 90 °C (Figure 10) and data from the original and extended hydration of Premier MgO in ERDA-6 at 90 °C (Figure 3).
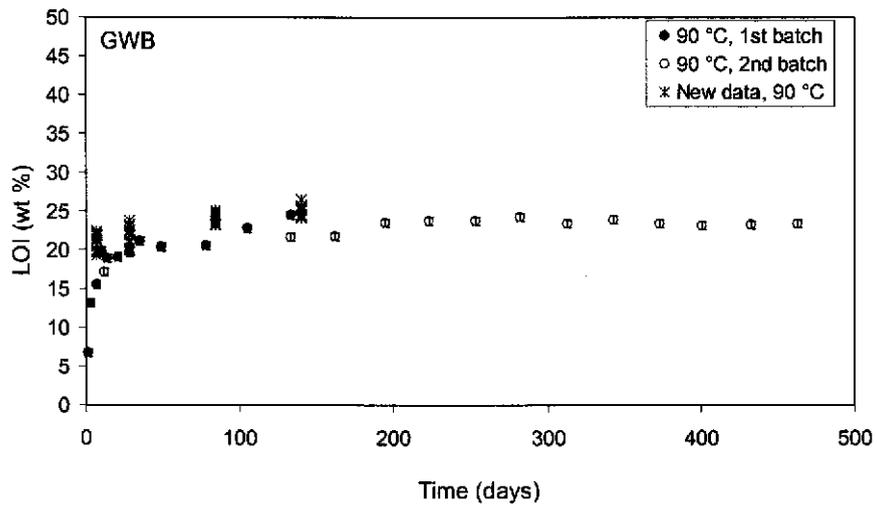
Figure 13. Comparison of data from the hydration of two batches of Premier MgO in GWB at 90 °C (Figure 11) and data from the original and extended hydration of Premier MgO in GWB at 90 °C (Figure 4).

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# 4 INUNDATED CARBONATION EXPERIMENTS

Bryan and Snider (2001a, 2001b), Snider (2002), and Snider and Xiong (2002a, 2002b) have carried out inundated MgO carbonation experiments with Premier Chemicals MgO at ambient-laboratory-atmospheric carbon-dioxide ($CO_2$) $p_{CO_2}$ and ambient laboratory temperature (referred to in this report as "atmospheric $p_{CO_2}$" and "room temperature," respectively), or with Fisher Scientific reagent-grade MgO, prehydrated Fisher MgO, Premier MgO, or prehydrated Premier MgO, at room temperature with an atmosphere consisting of 5% $CO_2$ (referred to as "5% $CO_2$"). The $p_{CO_2}$ in these experiments was about $3.5 \times 10^{-4}$ ($10^{-3.5}$) atm or $5 \times 10^{-2}$ ($10^{-1.3}$) atm.

The objectives of the inundated (and humid) carbonation experiments is to determine carbonation rates under conditions as close as possible to those expected in the WIPP after closure, and to identify the Mg-carbonate minerals that will result from carbonation and of MgO.

Since results on MgO carbonation were last reported (Snider and Xiong, 2002a), the experiment with 5% $CO_2$ - designed to accelerate the carbonation of MgO - has been completed, and the experiment at atmospheric $p_{CO_2}$ has been extended and is continuing. This report presents data acquired since July 2002.

## 4.1 Experimental Methods

### 4.1.1 Experiment at Atmospheric $p_{CO_2}$

This experiment is being carried out to determine the effects of solution composition and time on MgO carbonation rates and products at atmospheric $p_{CO_2}$. The current experiment is an extension of the original experiment at atmospheric $p_{CO_2}$, started in June 2001. The last bottle from the original experiment was sampled in June 2003. The original experiment has been extended because the last samples from that experiment were removed from test and analyzed in June 2003. Eighty-four 125-mL polypropylene bottles containing 5 g of Premier Chemicals MgO and 100 mL of DI $H_2O$, 4 M NaCl, ERDA-6, or GWB were placed on gas manifolds holding up to 24 samples each. Twenty-one samples were prepared for each solution. Compressed room air is bubbled continuously through the samples. To minimize evaporation, the air is humidified by bubbling through $H_2O$ prior to entering the manifold. The bottles are not agitated. Bottles were sampled weekly initially, and are now sampled monthly or bimonthly.

The pH of all solutions is measured at the time of sampling. The samples are vacuum-filtered and rinsed with DI $H_2O$ on Whatman #40 filter paper (particle retention > 8 μm). After rinsing, the filter papers containing the solids are placed on watch glasses to dry in room air. Once dry, the solids are ground using a mortar and pestle, and stored in plastic bottles for subsequent carbon (C) coulometric, XRD, and scanning-electron-microscope (SEM) analysis.

## 4.1.2 Experiment at 5% $CO_2$

This experiment was conducted to accelerate the slow carbonation of Premier MgO observed in the original inundated experiments at atmospheric $p_{CO_2}$. Sixty-four 125-mL polypropylene bottles containing 5 g of Fisher Scientific reagent-grade MgO, prehydrated Fisher MgO, Premier Chemicals MgO, or prehydrated Premier MgO; and 100 mL of ERDA-6 or GWB were placed in a controlled-atmosphere glove box. The prehydrated solids were prepared by adding 5 g of Fisher or crushed Premier MgO to 100 mL of brine and bottles placing them in an oven at 90 °C three to four weeks. (Note that samples of premier MgO that were not prehydrated were not crushed, and that none of the samples of Fisher MgO were crushed.) Samples of the prehydrated solids were analyzed by XRD prior to use. The glove box atmosphere was controlled by pumping in at 500 mL/min premixed gas consisting of 5% $CO_2$ and 95% $N_2$. To bring the atmosphere up to 5% $CO_2$ in a timely manner after the glove box was opened for start-up or sampling, dilute sulfuric acid ($H_2SO_4$) was mixed with sodium bicarbonate ($NaHCO_3$) within the glove box, which released a predetermined amount of $CO_2$ to the atmosphere. The atmosphere was monitored frequently with a Bacharach $CO_2$ analyzer. The bottles were not agitated during prehydration or during the carbonation experiment. Bottles were sampled after 1, 3, 7, 21, and 36 days, and monthly thereafter. Sampling was more frequent during this experiment than during the atmospheric-$p_{CO_2}$ experiment because it was expected that 5% $CO_2$ would accelerate carbonation. However, 48 new bottles were added at various times to extend this experiment. Samples were subject to the same analyses as the atmospheric $p_{CO_2}$ samples.

The pH was measured at the time of sampling and samples were vacuum-filtered, rinsed, and dried for C coulometric, XRD, and SEM analyses as described above for the atmospheric-$p_{CO_2}$ experiment.

## 4.2 Analytical Methods

### 4.2.1 XRD Analysis

XRD analysis is carried as described above for the hydration experiments.

### 4.2.2 C Coulometric Analysis

Portions of all samples are crushed, and the powders are analyzed for total C with a UIC C coulometer and furnace module. Approximately 80 mg of each sample is ignited at 900 °C in the furnace module and measured until the precision of the results is $\leq \pm 0.3$ wt %.

### 4.2.3 SEM Analysis

SEM analysis provides qualitative information on the composition of solid starting materials or reaction products, and reveals textural and other physical attributes of these solids. Selected samples were analyzed under a 15-kV electron beam in backscatter-electron mode to detect differences in elemental atomic weights.

## 4.3 Results

### 4.3.1 Experiments at Atmospheric $p_{CO_2}$

Figure 14 presents the results of carbonation of Premier Chemicals MgO in DI $H_2O$, 4-M NaCl, ERDA-6, or GWB at atmospheric $p_{CO_2}$ and room temperature. The concentrations of Mg carbonate shown in this figure were calculated based on the observation that hydromagnesite $(Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O)$ - and only hydromagnesite (5424) - was detected by XRD analysis of the solid samples obtained from this experiment (see Table 2 and the discussion below). In this report, hydromagnesite with the composition $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ is referred to as "hydromagnesite (5424)." Because hydromagnesite (5424) was the only Mg carbonate detected by XRD analysis and because the C:Mg molar ratio in hydromagnesite (5425) is 4:5, a value of 0.8 was used to calculate the Mg-carbonate concentrations shown in Figure 14. These results show that carbonation of Premier MgO is proceeding slowly in both ERDA-6 and GWB at atmospheric $p_{CO_2}$ and room temperature.

Table 2 provides the results of XRD analysis of Mg carbonate produced during this experiment. Hydromagnesite (5424) was detected by XRD analysis by 109 days in DI $H_2O$, 264 days in 4 M NaCl, and 327 days in ERDA-6 and GWB. XRD analysis has a detection limit of several percent. Therefore, it is unclear whether hydromagnesite (5424) was the first Mg carbonate to nucleate in these samples. Nevertheless, hydromagnesite (5424) was the only Mg carbonate detected by XRD analysis in the experiment at atmospheric $p_{CO_2}$.

Figure 14 and Table 2 show that, for the most part, the Premier-MgO carbonation rate decreases in the following order: DI $H_2O$ > 4 M NaCl > ERDA-6 > GWB. This is identical to the order observed for hydration (compare Figure 14 and Table 2 with Figures 1, 2, 3, and 4).
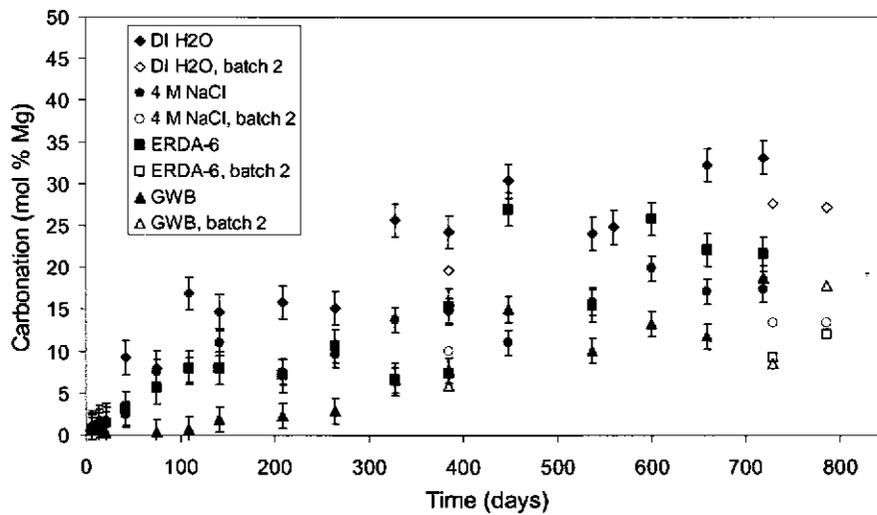
Figure 14. Carbonation of Premier MgO in DI H₂O, 4-M NaCl, EDRA-6 at atmospheric $p_{CO_2}$ and room temperature (Mg-carbonate concentrations calculated assuming hydromagnesite (5424)).

Table 2. Identity of the Mg Carbonate Identified by XRD Analysis of Run Products from Carbonation of Premier MgO in DI $H_2O$, 4-M NaCl, EDRA-6, and GWB at Atmospheric $p_{CO_2}$ and Room Temperature.

| Time (days) | DI $H_2O$ | 4 M NaCl | ERDA-6 | GWB |
|---|---|---|---|---|
| 6 | ND | ND | ND | ND |
| 13 | ND | ND | ND | ND |
| 21 | ND | ND | ND | ND |
| 41 | ND | ND | ND | ND |
| 75 | ND | ND | ND | ND |
| 109 | H | ND | ND | ND |
| 141 | H | ND | ND | ND |
| 208 | H | ND | ND | ND |
| 264 | H | H | ND | ND |
| 327 | H | H | H | H |
| 384 | H | H | H | H |
| 447 | H | H | H | H |
| 536 | H | H | H | H |
| 599 | H | H | H | H |
| 658 | H | H | H | H |
| 719 | H | H | H | H |

H = hydromagnesite (5425).
ND = no Mg carbonate detected.

## 4.3.2 Experiments at 5% $CO_2$

Figure 15 presents the results of carbonation of Fisher Scientific reagent-grade MgO, prehydrated Fisher MgO, Premier Chemicals MgO, or prehydrated Premier MgO in ERDA-6 at 5% $CO_2$ and room temperature. The concentrations of Mg carbonate shown in Figure 15 were calculated based on: (1) the observation that, although nesquehonite ($MgCO_3 \cdot 3H_2O$) was the first Mg carbonate detected by XRD analysis, it was replaced by hydromagnesite (5424); (2) the conclusion that, after about 200 days, hydromagnesite (5424) is the dominant Mg carbonate present (see Table 3 and the discussion below). Therefore, a C:Mg molar ratio of 1.0 (the C:Mg molar ratio of nesquehonite) was used to calculate the Mg-carbonate concentrations of solids sampled from 1 through 148 days in Figure 15, and a C:Mg molar ratio of 0.8 (the C:Mg molar ratio of hydromagnesite (5424)) was used to calculate the Mg-carbonate concentrations of solids sampled from 178 through 268 days in this figure. The data in Figure 15 show that, in most cases, prehydrated Premier MgO carbonated faster than Premier MgO. The data also show that Premier MgO carbonated faster at 5% $CO_2$ and room temperature than at atmospheric $p_{CO_2}$ and room temperature (compare the data for Premier MgO in ERDA-6 at 5% $CO_2$ and at atmospheric $p_{CO_2}$ after 268 and 264 days, respectively). Prehydrated Fisher MgO carbonated faster than Fisher MgO in some cases.
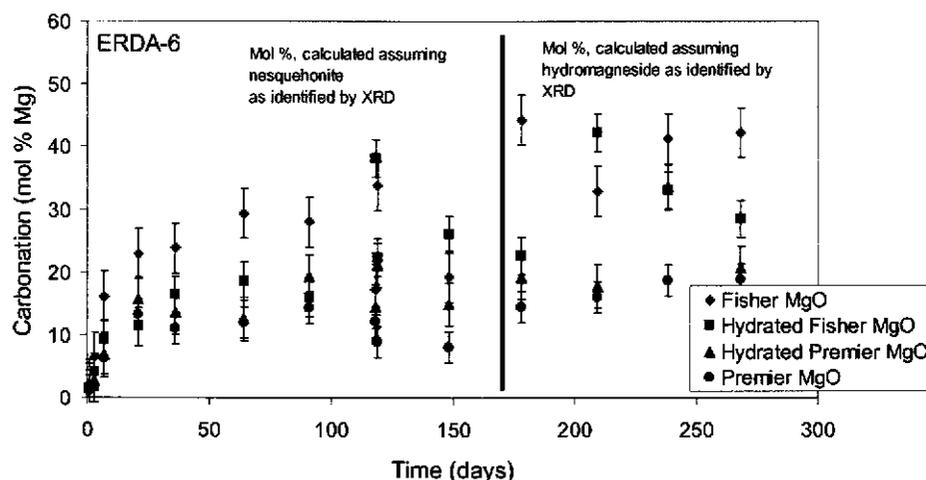


Figure 15. Carbonation of Fisher MgO, prehydrated Fisher MgO, Premier MgO, or prehydrated Premier MgO in ERDA-6 at 5% $CO_2$ and room temperature. (The vertical blue line at 150 days indicates that Mg-carbonate concentrations were calculated assuming nesquehonite from 1 through 148 days and hydromagnesite (5424) from 178 through 268 days).

The scatter displayed by the carbonation data for ERDA-6 may have resulted from failure to maintain continuous bubbling of $CO_2$ through all bottles at all times. Interruptions in bubbling that occurred in some cases may have caused $CO_2$ concentration gradients within the brines, thus preventing the solids from contacting brine in equilibrium with 5% $CO_2$ at all times.

Table 3 presents the results of XRD analyses of the Mg carbonates produced during the runs with ERDA-6. Nesquehonite was detected by 3 days in Fisher MgO and prehydrated Fisher MgO, by 21 days in Premier MgO, and by 7 days in prehydrated Premier MgO. Hydromagnesite (5424) appeared by 36 days in Fisher MgO, by 21 days in prehydrated Fisher MgO, and by 64 days in Premier MgO and prehydrated Premier MgO. Nesquehonite disappeared from the XRD patterns by 118 days in Fisher MgO, 91 days in prehydrated Fisher MgO, by 64 days in Premier MgO, and by 118 days in prehydrated Premier MgO. (Nesquehonite probably persisted for some period beyond the time of its disappearance from these XRD patterns, because XRD analysis has a detection limit of several percent.) Nevertheless, the replacement of nesquehonite by hydromagnesite (5424) constitutes conclusive evidence that hydromagnesite (5424) is thermodynamically stable with respect to nesquehonite under these conditions (ERDA-6 under 5% $CO_2$). Actually, hydromagnesite (5424) is *metastable* with respect to nesquehonite, because magnesite ($MgCO_3$) is stable with respect to both hydromagnesite (5424) and nesquehonite under these conditions (see Brush and Xiong, 2003).

The reaction path for MgO carbonation in ERDA-6 was clearly different at 5% $CO_2$ than at atmospheric $p_{CO_2}$. At 5% $CO_2$ ($p_{CO_2}$ = $10^{-1.3}$ atm), carbonation of periclase (MgO) and/or brucite initially produced nesquehonite or – perhaps - nesquehonite and hydromagnestie (5424). (Small amounts of hydromagnestie (5424) may have formed, undetected by XRD analysis, at the start of the runs at 5% $CO_2$.) Subsequently, hydromagnesite (5424) formed and eventually replaced nesquehonite (see Table 3). At atmospheric $p_{CO_2}$ ($10^{-3.5}$ atm), carbonation of periclase and/or brucite initially produced hydromagnesite (5424), which then persisted for the entire duration of the runs carried out to date (Table 2). (Small amounts of nesquehonite may have formed at the start of these runs; however, nesqeuhonite was either absent or much less significant at atmospheric $p_{CO_2}$ than at 5% $CO_2$.)

The XRD results within the 5% $CO_2$ experiment suggest carbonation reaction pathways are dependent on the combination of solids, and/or brine used. Between 21 and 36 days, Fisher "pre-hydrated" MgO and Fisher MgO converted to hydromagnesite (Table 3). ERDA-6 samples with Premier Chemicals MgO behave somewhat differently. Premier "pre-hydrated" MgO and Premier MgO form nesquehonite first. Between 36 and 64 days nesquehonite converts to hydromagnesite. Hydromagnesite is the first Mg-carbonate mineral to show strong peaks in Premier MgO at 21 days. However, there also appears to be a poorly developed nesquehonite peak in the same XRD pattern, but by 36 days this peak disappeared. Samples from the GWB react at a slower rate compared to the ERDA-6 samples.

Table 3. Identity of Mg Carbonates Identified by XRD Analysis of Run Products from Carbonation of Fisher MgO, prehydrated Fisher MgO, Premier MgO, or prehydrated Premier MgO in ERDA-6 at 5% $CO_2$ and Room Temperature.

| Time (days) | Fisher MgO | Prehydrated Fisher MgO | Premier MgO | Prehydrated Premier MgO |
|---|---|---|---|---|
| 1 | ND | ND | ND | ND |
| 3 | N | N | ND | ND |
| 7 | N | N | ND | N |
| 21 | N | N > H | N | N |
| 36 | N > H | H | N | N |
| 64 | N > H | N = H | H | N > H |
| 91 | N > H | H | H | N = H |
| 119 | N = H | H | H | N < H |
| 118 | H | H | H | H |
| 148 | H | H | H | H |
| 178 | H | H | H | H |
| 209 | H | H | H | H |
| 238 | H | H | H | H |
| 268 | H | H | H | H |

H = hydromagnesite (5425).
N = nesquehonite.
ND = no Mg carbonate detected.

Figure 16 presents the results of carbonation of Fisher Scientific reagent-grade MgO, prehydrated Fisher MgO, Premier Chemicals MgO, or prehydrated Premier MgO in GWB at 5% $CO_2$ and room temperature. The concentrations of Mg carbonate shown in Figure 15 were calculated based on the observation that hydromagnesite (5424) was the only Mg carbonate detected by XRD analysis (see Table 5 and the discussion below). Therefore, a C:Mg molar ratio of 0.8 (the C:Mg molar ratio of hydromagnesite (5424)) was used to calculate the Mg-carbonate concentrations of all solids sampled from the bottles with GWB at 5% $CO_2$. The data in this figure show that, in almost all cases, prehydrated Fisher MgO carbonated faster than Fisher MgO, and prehydrated Premier MgO carbonated faster than Premier MgO. The data also show that Premier MgO carbonated faster at 5% $CO_2$ and room temperature than at atmospheric $p_{CO_2}$ and room temperature. Finally, as observed in previous experiments, the data for ERDA-6 display more scatter than those for GWB. The scatter observed for GWB also may have resulted from failure to maintain continuous bubbling of $CO_2$ through all bottles at all times, thus preventing the solids from contacting brine in equilibrium with 5% $CO_2$ at all times.
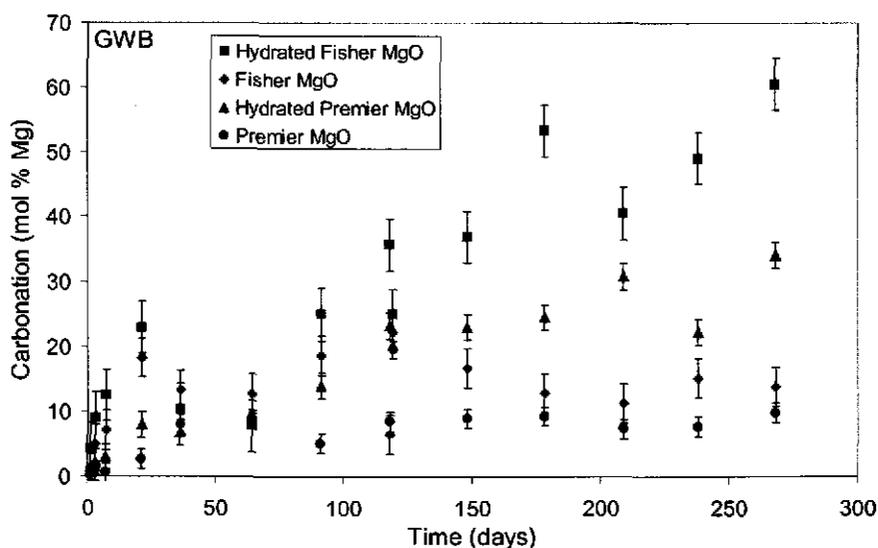


Figure 16. Carbonation of Fisher MgO, prehydrated Fisher MgO, Premier MgO, or prehydrated Premier MgO in GWB at 5% $CO_2$ and room temperature (Mg-carbonate concentrations calculated assuming hydromagnesite (5424)).

The results of XRD analysis provided by Table 4 show that, in the runs in GWB, hydromagnesite (5424) formed by 64, 7, 64, or 91 days in Fisher MgO, prehydrated Fisher MgO, Premier MgO and prehydrated MgO, respectively, and persisted for 268 days (the duration of this experiment). However, the hydromagnesite peak was not well developed, even after 268 days. No nesquehonite was observed in samples carbonated in GWB at 5% $CO_2$. It is not known why nesquehonite appeared as a transient phase in the runs with ERDA-6 at 5% $CO_2$, but not in the runs with GWB at 5% $CO_2$.

Table 4. Identity of the Mg Carbonate Identified by XRD Analysis of Run Products from Carbonation of Fisher MgO, Prehydrated Fisher MgO, Premier MgO, or Prehydrated Premier MgO in GWB at 5% $CO_2$ and Room Temperature.

| Time (days) | Fisher MgO | Prehydrated Fisher MgO | Premier MgO | Prehydrated Premier MgO |
|---|---|---|---|---|
| 1 | ND | ND | ND | ND |
| 3 | ND | ND | ND | ND |
| 7 | ND | H | ND | ND |
| 21 | ND | H | ND | ND |
| 36 | ND | H | ND | ND |
| 64 | H | H | H | ND |
| 91 | H | H | H | H |
| 119 | H | H | H | H |
| 118 | H? | H | H | H |
| 148 | H | H | H | H |
| 178 | H? | H | H | H |
| 209 | H | H | H? | H |
| 238 | H | H | H? | H |
| 268 | H | H | H? | H |

H = hydromagnesite (5425).
ND = no Mg carbonate detected.

# 5 SUMMARY

Hydration experiments demonstrated that the temperature of posttest loss-on-ignition (LOI) analysis affects the *measured* extent of hydration of Premier Chemicals MgO in DI $H_2O$. LOI analysis carried out for 3 h at 500 °C yielded 83.0 and 84.2 mol % brucite ($Mg(OH)_2$) (equivalent to 87.6 and 88.5 wt % brucite); however, LOI at 750 °C yielded 88.7 and 89.4 mol % brucite (91.9 and 92.4 wt % brucite). Apparently, hydrated Premier MgO does *not* release all $H_2O$ during LOI analysis at 500 °C. Furthermore, the extent of hydration of Premier MgO observed in new accelerated experiments analyzed by LOI at 750 °C (about 89 mol % brucite) is now essentially equal to that expected based on chemical analyses (about 89 or 90 mol %).

MgO carbonation is proceeding slowly in Castile and Salado brines at atmospheric $p_{CO_2}$ and room temperature. The only Mg carbonate produced at atmospheric $p_{CO_2}$ is hydromagnesite (5424). Carbonation at 5% $CO_2$ and room temperature proceeded faster than at atmospheric $p_{CO_2}$; the final carbonation product is also hydromagnesite (5424), although transient nesquehonite appeared in runs with Castile brine. The replacement of nesquehonite by hydromagnesite (5424) in Castile brine shows that hydromagnesite (5424) is more stable than nesquehonite under these conditions.

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**Xiong, Yongliang**
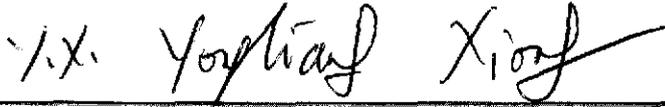
**From:** Snider, Anna C [acsnide@sandia.gov]

**Sent:** Monday, October 11, 2004 11:29 AM

**To:** Xiong, Yongliang

**Subject:** Signature authorization

Yongliang,

I am giving you signature authority to sign on my behalf the cover and approval page of the document entitled **Continuing Investigations of The Hydration and Carbonation of Premier Chemicals MgO.**

Thanks,
Anna

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