

## 5.0 MgO Experimental Work Conducted at SNL/CB

### Continuing Investigations with Premier Chemicals MgO<sup>1</sup>

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#### Abstract

The Carlsbad Programs Group of Sandia National Laboratories (SNL/CB) is currently investigating several issues with respect to the effect of MgO on repository conditions. Initial work was described in the January, 2001 Status Report (Milestone RI010) to the DOE. Characterization of Premier Chemicals MgO, with respect to both mineralogy and composition, and its ability to absorb water and CO<sub>2</sub> under repository conditions, continues. Sandia is currently carrying out a series of experiments to measure hydration rates for Premier MgO under both inundated and humid conditions. Results to date suggest that, in general, the hydration rate can be modeled as a diffusion-limited reaction, although interpretation of the hydration results in GW (synthetic Salado) brine is complicated by the formation of a second hydration phase, a magnesium chloride hydroxide hydrate.

In addition, MgO carbonation rates are being measured at partial pressures of CO<sub>2</sub> ranging from 5 % to 1/10 atmospheric ( $P_{CO_2} = \sim 10^{-4.5}$  atm). These experiments have just begun. Sandia is also working to determine the MgO hydration/carbonation pathway relevant to repository conditions. Of particular importance is the magnesium hydroxycarbonate mineral that forms initially, as this mineral may control the  $P_{CO_2}$  in the repository, an important parameter for estimating actinide solubilities. Sandia is also carrying out experiments to evaluate the generation of isosaccharinic acid, a potentially strong complexant for the actinides, under MgO-buffered conditions; this experimental work has been ongoing for nearly one year.

#### Introduction and Objectives

In the Compliance Certification Application (CCA) for the Waste Isolation Pilot Plant (WIPP), the Environmental Protection Agency concurred with the Department of Energy (DOE) that MgO backfill is an effective engineered backfill that will prevent or delay the movement of radionuclides toward the accessible environment. MgO sequesters carbon dioxide generated by microbial degradation of organic materials in the waste, in addition to reducing the amount of free liquid in the repository through hydration reactions. Thus,

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<sup>1</sup> This work is covered by BOE #1.3.05.04.03 and WBS #1.3.5.4.3. A more recent description of this work appears in Sandia National Laboratories WIPP/NTP Work Scope for FY01, December 14, 2000.

it maintains the pH and CO<sub>2</sub> fugacity (P<sub>CO2</sub>) in the repository at an optimal range, in which actinide solubility in brine is at a minimum.

Experimental work carried out previously at Sandia has shown that MgO is effective at adsorbing water and carbon dioxide (Papenguth, et al., 1997, 1999). Currently, almost four times more MgO is scheduled to be emplaced in the WIPP than gas generation calculations suggest will be necessary to absorb CO<sub>2</sub> generated through microbial degradation of organic materials. In total, nearly 80,000 tons of MgO will be placed in the WIPP repository.

Although the work done to date on MgO is sufficient to show that it is effective as a backfill material in buffering repository conditions and limiting actinide solubility, Sandia is currently examining several additional issues, as discussed in the January, 2001 Status Report (Milestone RI010) to the DOE. Experimental programs are evaluating the ability of the new material to sequester water and CO<sub>2</sub>, and are determining the hydration and carbonation pathways that Premier MgO will follow under WIPP-relevant conditions. The P<sub>CO2</sub> predicted from repository certification calculations in the CCA is based upon the assumption of equilibrium with magnesite (MgCO<sub>3</sub>). However, metastable hydromagnesite phases commonly form upon initial carbonation of MgO/brucite, and these phases have higher solubilities than magnesite. Thus, they might buffer the P<sub>CO2</sub> at values higher than those used in the CCA. Previous work with MgO has been criticized for failing to consider the potential effect of metastable hydroxycarbonates on repository chemistry. Sandia is currently working to identify the hydroxycarbonate phase(s) that might form.

Sandia is also evaluating the production of isosaccharinic acid (ISA) under repository conditions. ISA is a degradation product of cellulosic materials under alkaline conditions (Glaus et al., 1999), and is a strong complexant for the actinide metals (Greenfield et al., 1992). Cellulosic materials are a significant part of the waste inventory, and the production of ISA could significantly affect the solubilities of the actinides in the repository. However, it has never been demonstrated that ISA forms under the mildly alkaline conditions typical of MgO-dominated systems. Sandia is continuing experiments to assess this using a variety of WIPP-relevant brines and cellulosic materials.

The experiments described here are under the purview of the Sandia National Laboratories Nuclear Waste Management Program (NWMP) test plan TP 00-07 "Experimental Study of WIPP MgO Backfill at Sandia National Laboratories Carlsbad Facility."

The objectives of these experiments are multifold. MgO hydration/carbonation rates vary greatly with the properties (temperature, porosity, impurities) of the MgO used. Hydration/carbonation rate efficiencies will be determined by chemically and mineralogically characterizing the Premier Chemicals MgO to determine reaction capacity, and performing hydration/carbonation experiments to determine reaction rate. Experiments to identify the hydration/carbonation reaction pathway are in response to criticisms of the previous MgO carbonation experiments by Wilson et al. (1997) and by Oversby (2000). They suggested that carbonation rates measured at high P<sub>CO2</sub> values are not valid for WIPP conditions, as the Mg-hydroxycarbonate mineral that forms (nesquehonite) is not typical of what will form under the lower P<sub>CO2</sub> values expected in



the WIPP. In addition, they argued that the  $P_{CO_2}$  values used in the CCA calculations are invalid, as they are based on the assumption that magnesite will be buffering the carbonate concentration, when in fact, a more soluble Mg-hydroxycarbonate may be the buffering phase. The ISA experiments will evaluate the potential effect of this organic acid on actinide mobility in WIPP near-field environment.

### **Premier Chemicals MgO**

The hydration/carbonation experiments, that supported the CCA calculations were carried out using MgO from National Refractory Materials, which, at that time, was the MgO supplier for the WIPP. However, a new vendor, Premier Chemicals, Inc., now supplies MgO for the repository. The new material is manufactured using a different process than the old, is dissimilar texturally, and contains higher levels of potentially reactive impurities, especially CaO. CaO hydrates more quickly than MgO, causing a transient initial rise in the pH of the solution. Sandia is characterizing the new material chemically and physically, and is performing experiments to evaluate its ability to sequester water and CO<sub>2</sub> relative to the material used in previous experiments

#### Characterization of Premier Chemicals MgO

As stated in the January, 2001 Status Report (Milestone RI010), a quantity of the reported MgO and CaO in Premier MgO is present as magnesium and calcium silicates. Two batches of Premier MgO have been analyzed to date, containing over 95% MgO plus CaO chemically, but containing 9–12 weight % non-reactive silicates and aluminates. Potentially this could significantly effect the capacity of the Premier MgO to sequester water and CO<sub>2</sub>. Both of these samples were obtained from Premier Chemicals Company before they began shipping material to WIPP. However, when shipments began, the purity of the MgO was increased slightly. This new material has not yet been fully analyzed.

#### Evaluation of hydration/carbonation rates of Premier Chemicals MgO

A large experimental matrix has been initiated to investigate both inundated and humid hydration rates of the Premier material, and to identify the hydration pathway in WIPP brines. A second matrix investigates carbonation rates and pathways for inundated material under several different partial pressures of CO<sub>2</sub>.

##### *Inundated hydration experiments*

Inundated hydration experiments are currently being run to evaluate several factors affecting MgO hydration rate. Experimental conditions for these are summarized in Table 1.

In the first experiment, Premier MgO was placed in four electrolytes—deionized (DI) water, 4.0 M NaCl, and synthetic Salado (GW) and Castile (ERDA-6) brines. The first two simple electrolytes were included in an effort to help develop a mechanistic understanding of the hydration process. Samples were aged in ovens at 25-90° C, and were agitated frequently. Sample agitation was performed to eliminate the formation of a cemented cake of hydration products, removing the possibility that cake formation will inhibit hydration by limiting brine access to the bulk MgO (the effects of cake formation

**Table 1. Experimental Matrix for Inundated Hydration Experiments**

Experiment	T, °C	Premier MgO, g	Electrolyte
Inundated hydration, samples agitated frequently	25°	5 g	DI water, 100 ml
	50°		4.0 M NaCl, 100 ml
	70°		ERDA-6 (Castile) brine, 100 ml
	90°		GW (Salado) brine, 100 ml
Experiment to evaluate the effects of GW brine/ MgO ratio	70°	5 g	GW brine (60, 90, 120, 160, 200, 240 ml)
Inundated hydration, samples not agitated ("cake" experiment)	25°	15 g (~5 mm thick)	ERDA-6 brine (100 ml) GW brine (100 ml)
	50°	30 g (~10 mm thick)	
	70°	45 g (~15 mm thick)	
	90°		

are being examined in a separate experiment). However, hydration products may still inhibit hydration by coating individual particles, or by plugging the internal porosity in the MgO grains. Periodically, samples are removed from the ovens, cooled, and the pH measured. The solid fraction is then filtered out using Whatman #40 filters, rinsed with deionized water to remove any remaining brine, dried, crushed, and characterized by X-ray diffraction. The loss on ignition (LOI) at 500° C (brucite dehydrates at ~350°C) is used to calculate the amount of hydrated material in each sample.

Results of the agitated, inundated hydration experiment are shown in Figure 1. In DI water, 4.0 M NaCl, and in ERDA-6 brine, X-ray diffraction (XRD) studies indicate that brucite is the only hydration phase present. It is detectable by XRD once the degree of hydration reaches several percent. Thus, in Figure 1, hydration rate is given as the mole percent brucite in the solid fraction. However, in the GW brine, a different hydration phase, probably a magnesium chloride hydroxide hydrate (Sorel cement) precipitates rapidly and early; brucite becomes the stable hydration phase only at higher degrees of hydration. As the Sorel cement and brucite lose different amounts of water upon ignition, the actual degree of MgO hydration is difficult to calculate, and the vertical axis on the GW results in Figure 1 is wt% lost on ignition. This value is proportional—not necessarily linearly, since two hydration phases are forming—to the degree of hydration.

There are several features of interest in these plots. To date, hydration has proceeded to completion for only one set of samples—those in deionized water at 90° C. These samples reached a plateau of 80-90% hydration, at which point XRD analysis indicated that no periclase remained. This is consistent with the suggestion, made in the January, 2001 Status Report (Milestone RI010) that non-reactive silicates and aluminates constitute 10-15% of Premier MgO.

All plots except for the GW brine samples show increasing hydration rates with increasing temperature, as expected. The results for the GW brine samples, however, are not consistent. The 70° and 90° C hydration curves track each other closely, rising very rapidly initially, and then flattening and changing very little for over 2 months before again beginning to rise. In contrast, at 50° C, the hydration rate was initially slow, and



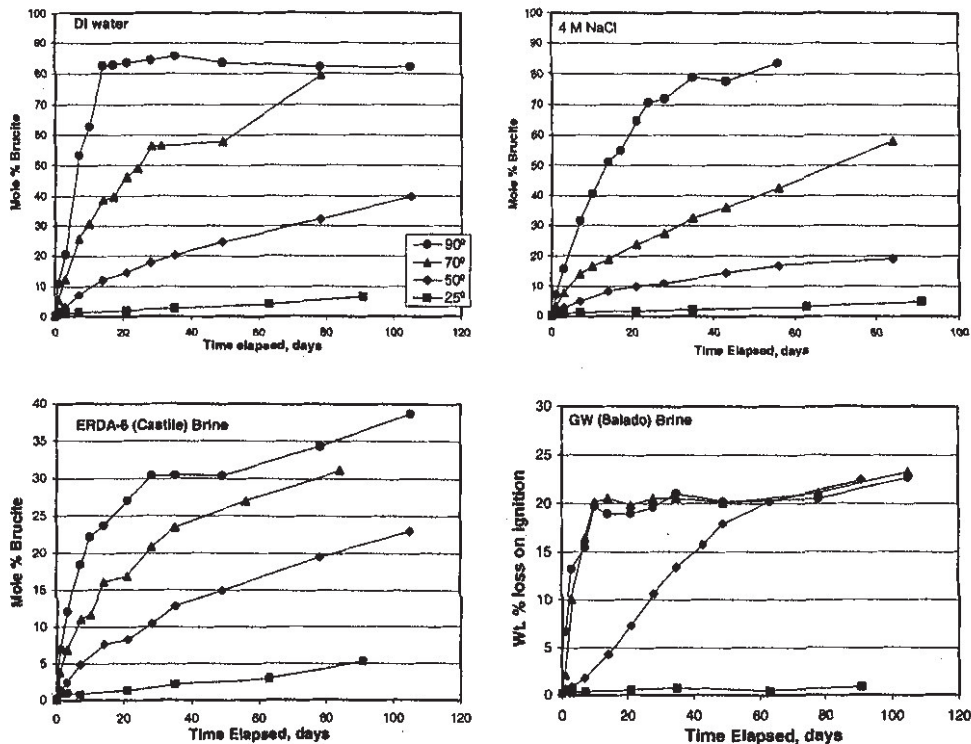


Figure 1. Results of the inundated hydration experiments with Premier MgO.

then increased rapidly, resulting in a curve that is initially concave upwards—the only time this occurred in the current matrix of experiments.

Previous MgO hydration experiments, performed with National Magnesia MgO (the previous supplier for the WIPP) are described in Zhang et al. (2001, Milestone RI010). Zhang et al. divided their hydration curves into three different segments. The first segment was a period of slow hydration, which they attributed to kinetically inhibited nucleation. In the second segment, hydration was rapid and assumed to be reaction-limited. In the third segment, hydration slowed again. This was interpreted to represent the buildup of hydration products, coating and isolated the remaining non-reacted MgO. Eventually this results in hydration being limited by the rate at which water can diffuse through the hydration products to the remaining MgO.

Interpretation of the current matrix of MgO hydration experiments may be somewhat simpler. Except for the 50° C GW-brine hydration curve discussed above, none of the data sets show evidence of slow, nucleation-limited initial hydration. Several of the data sets are adequately described by assuming that hydration is a diffusion-limited reaction, in which build-up of the reaction product is limited by the rate at which water can diffuse through continuously-thickening hydrated mineral coatings on the MgO grains. The buildup of hydration products varies as a function of the square root of time ( $t^{1/2}$ ):

$$N = N_o + k \cdot t^{1/2}$$

where  $N$  is the amount of reaction product (brucite),  $N_0$  is the initial amount of brucite present (for Premier MgO, this is about 0.15 %), and  $k$  is reaction rate constant. When the product of a diffusion-limited reaction is plotted against  $t^{1/2}$ , the result is a straight line, the slope of which is the rate constant.

Data for all four electrolytes are plotted as a function of  $t^{1/2}$  in Figure 2. The hydration curves for several of the electrolytes form linear trends on these plots, the slopes of which represent the rate constants at each temperature. These rate constants are plotted against  $1/T(^{\circ}\text{K})$  ("Arrhenius" plots) in Figure 3. The measured rate constants for DI water and 4M NaCl vary linearly with  $1/T$ , suggesting that MgO hydration in these systems can be modeled successfully as a simple, diffusion-limited reaction. The data for ERDA-6 brine are not quite as linear—the 25° C rate constant falls below the trend defined by the other, higher temperature systems. However, hydration is slower in ERDA-6 than in other brines, and the 25° C data are scattered. As more long-term hydration data are collected, the validity of a diffusion-limited reaction model for MgO in ERDA-6 brines will be tested.

It is apparent that, although a diffusion-limited hydration rate model may be sufficient for three of the electrolyte systems examined, it is inadequate for describing hydration in GW brine. Much of the difficulty in interpreting the GW brine results is caused by the presence of two hydration phases (Sorel cement and brucite), rather than just one. As the degree of hydration in the sample is determined by weight loss upon ignition, the presence of a second hydration phase, containing a different amount of stoichiometric

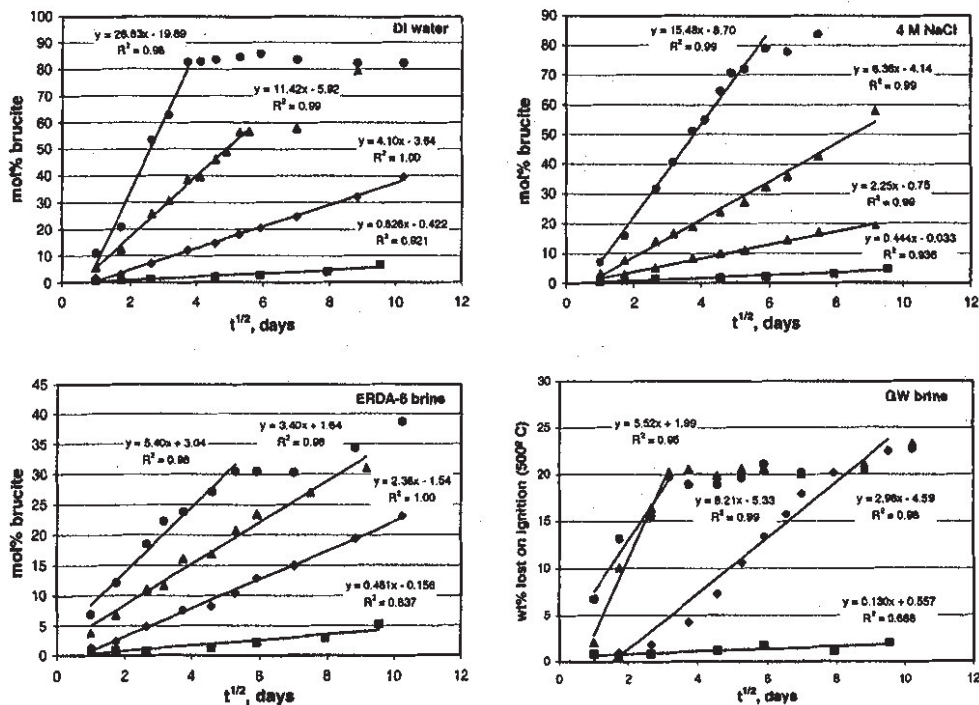


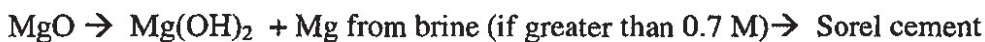
Figure 2. Inundated hydration data plotted as a function  $t^{1/2}$ . Symbols are as shown in Figure 1.



water, complicates interpretation of the results.

It should be noted here that the second hydration phase *has not been identified*. However, there is strong indirect evidence that it is a Sorel cement of some type, and that assumption will be made in the following discussion.

In brines containing high concentrations of Mg, brucite formed by hydration of MgO dissolves and reprecipitates as Sorel cement. This reaction, which consumes excess Mg in the brine, continues until the Mg concentration drops to ~0.7 M (GW brine is initially 1 M). At this point, brucite becomes the stable solid hydroxide phase. Thus, the greater the volume of brine in the sample, the greater the fraction of magnesium chloride hydroxide hydrate in the hydration products. This is very important for proper interpretation of the experimental results, and for application of those results to repository conditions.



Two Sorel cements were observed in early-inundated hydration experiments using pure Fisher Scientific MgO and crushed Premier MgO (see Milestone RI010 for more details). These are:

- a)  $\text{Mg}_3(\text{OH})_5\text{Cl} \cdot 4 \text{H}_2\text{O}$  (crushed Premier MgO)
- b)  $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4 \text{H}_2\text{O}$  (high purity MgO from Fisher Scientific)

However, the Sorel cement phase that is forming in the current experiments has not yet been identified. The phase has not been observed in XRD patterns of the hydrated materials, and it may be going structurally amorphous when the samples are dried. Its existence is inferred from two lines of evidence. First, GW-brine hydration samples

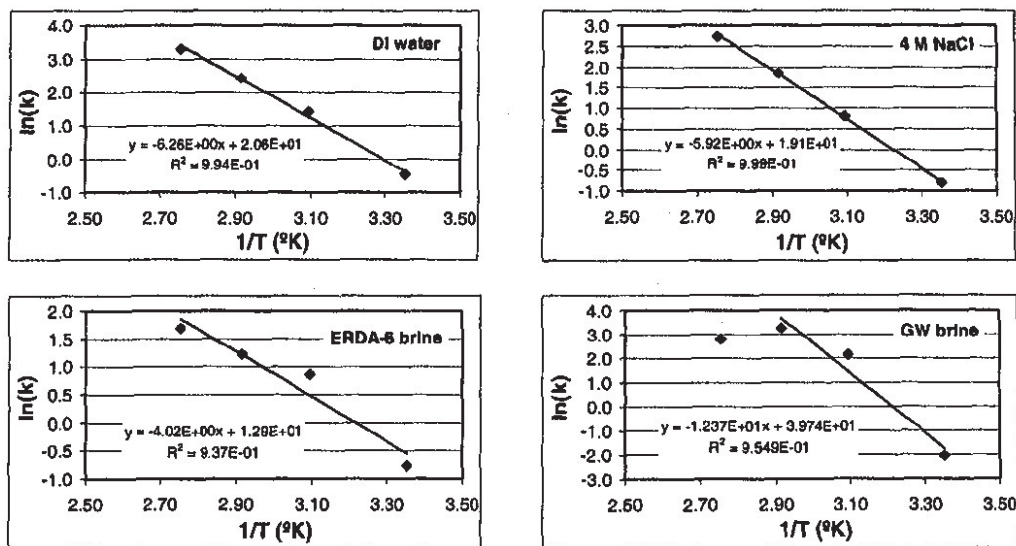
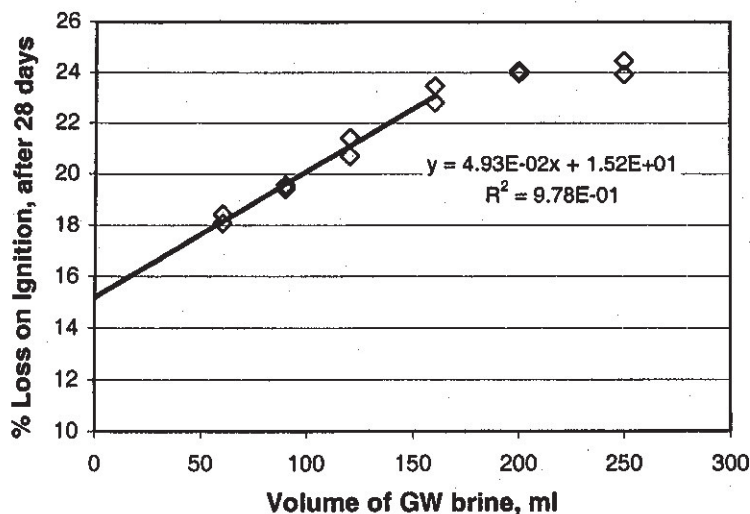


Figure 3. Arrhenius plots of the inundated hydration data.

collected early in the experiment show considerable LOI even though no brucite is present in the XRD patterns. Second, Mg, Cl-rich phase(s?) have been observed by scanning electron microscope, in one of the samples from the cake experiment (the only sample examined to date). Experiments are being carried out to identify this phase. As the degree of hydration in the sample is determined by LOI, and the Sorel cement phases lose more weight than brucite, this phase must be identified in order to quantify the amount of MgO hydration that occurs with time.

A second experiment evaluated the effect of the brine volume present in GW brine/MgO systems. The greater the volume of brine in the sample, the greater the fraction of Sorel cement in the hydration products. Five grams of MgO was placed in GW brine volumes ranging from 60-250 ml, and aged for 28 days. The results of this experiment are shown in Figure 4. As predicted, the relative proportions of brucite and Sorel cement in each sample, and the weight loss upon ignition, vary with the volume of brine present. At low brine volumes, the brine represents only a small reservoir of excess Mg, and brucite rapidly becomes the stable phase and constitutes most of hydration product formed. With increasing brine volume, the fraction of the Sorel cement in the hydration product increases, and brucite becomes progressively less abundant. This is manifested in two ways. First, the partially hydrated solids show progressively higher LOI as the brine volume in the system is increased, because Sorel cement loses more weight than brucite (on a mole% basis) when it dehydrates. Second, XRD patterns have progressively smaller brucite peaks with increasing brine in the system. The systems with the most brine (250 ml) contain no detectable brucite, indicating that the excess Mg in the brine was never exhausted, and brucite never became the stable hydration phase.

In Figure 4, the samples that contain both brucite and Sorel cement form a linear trend with respect to the brine volume in the system, as they should, if they consist of binary



**Figure 4.** The results of varying the brine content in GW brine/Premier MgO systems. The greater the volume of brine in the system, the greater the loss on ignition (LOI) of the separated and dried, and crushed solid phase. Samples were aged for 28 days at 70° C prior to sampling.



mixtures of those two phases. This trend should continue to lower brine volumes, so long as enough brine is added such that the number of moles of water present does not become a limiting factor. For five grams MgO, this would be two to three milliliters of brine. The y-intercept of this trend represents the LOI that would correspond the formation of brucite only. This value, 15.2% LOI, corresponds to 49.2 mol% brucite in the solid. Conversely, the sample with the most brine contains only Sorel cement. LOI for this sample is ~24.2%. *If the hydration rate is independent of the product formed*, then 24.2% Sorel cement represents the equivalent amount of hydration as 15.2% brucite (this is based upon an OH<sup>-</sup> mass balance). This is almost exactly the ratio one would expect if the Sorel cement phase forming is that described as (b) above.

Understanding the formation of magnesium chloride hydroxide hydrate is important for Performance Assessments considerations. Identifying this phase is critical to deconvolving the GW-brine hydration data and determining hydration rates. In addition, if Sorel cement and brucite exhibit different carbonation rates, then the GW brine/MgO ratio is an important consideration in designing and interpreting carbonation experiments. Sorel cement also serves as an immediate sink for hydroxide in GW brine. It buffers the pH to near-neutral values—an important consideration for Premier chemicals MgO, which contains minor CaO, and raises the pH in unbuffered systems to as high as 11.5.

The effects of formation of a cemented cake of hydration products are being examined in a third experiment, which was started in June. In this experiment, 5, 10, and 15 mm thick layers of Premier MgO were placed in containers with GW or ERDA-6 brine, and the samples were aged in ovens at 25°–90° C. The samples are not agitated. To date, too little data have been collected to evaluate the effects of cake formation on hydration.

#### *Humid Hydration experiments*

Humid hydration experiments were started June 6, 2001. The experimental setup differs slightly from experiments previously described by Zhang et al. (Milestone RI010). Samples consist of uncrushed Premier chemicals MgO and are being run at temperatures of 25°, 40°, 60°, and 80°C and relative humidities of 35%, 50%, 75%, and 95%. Premier Chemicals MgO is contained in 6-well polycarbonate trays, with three grams of MgO in each well. Four trays are stacked in sealed polypropylene containers. Each container contains a saturated salt solution providing the desired relative humidity (Table 2).

**Table 2. Saturated Salt Solutions and the Relative Humidity Values They Produce.**

Salt	RH Value, %*
K <sub>2</sub> SO <sub>4</sub>	95
NaCl	75
NaBr·2H <sub>2</sub> O	50
MgCl <sub>2</sub> ·6H <sub>2</sub> O	35

\* RH values vary a few % with temperature

The trays in each container are elevated above the salt solution on plastic blocks. Holes have been drilled in the bottom and top of each tray; and the upper lip of each well is notched. The holes and notches allow for circulation through each sample well. The

experiment consists of 384 samples (four temperatures, four relative humidities, four trays, six wells per tray).

Samples will be periodically collected over a period of months to years. Each sample is dried and analyzed by loss on ignition and X-ray diffraction. Brucite concentration will be determined by weight loss at 500°C. This technique assumes that MgO hydration to brucite is the only reaction that occurs; a few samples will be analyzed by X-ray diffraction to verify that carbonate formation is not significant under humid conditions.

A few data points have been collected and the following are preliminary results at this early stage in the experiment (Figure 5). Hydration is relatively slow at lower temperatures and humidities, but appears to occur readily at elevated temperature. After four weeks, the degree of hydration reached up to 80% in higher humidity samples at 80°C.

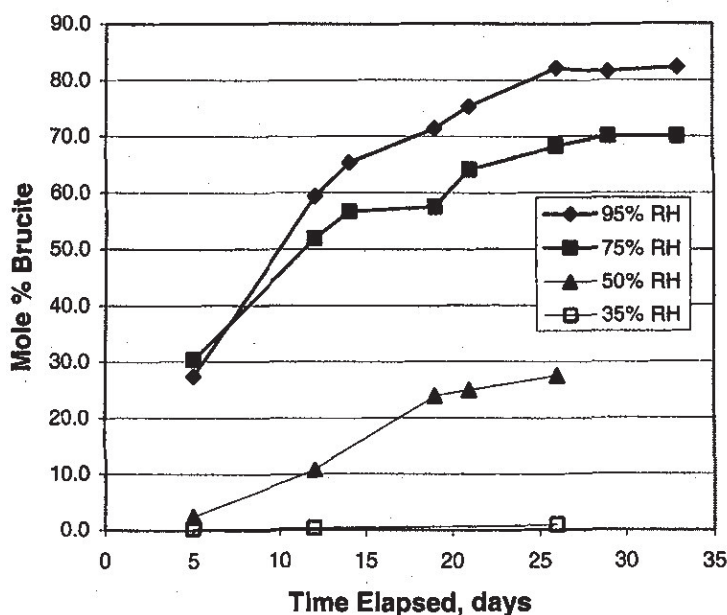


Figure 5. Results from the humid hydration experiment after four weeks at 80°C.

#### Carbonation Rate experiments

As of June 14, 2001 64 carbonation rate samples (four brines, sixteen samples) have been running on the bench top under atmospheric  $P_{CO_2}$  ( $10^{-3.5}$ ) conditions. In the near future carbonation rate experiments will be started at partial pressures of  $CO_2$  of 5% and  $1/10$  atmospheric ( $\sim 10^{-4.5}$  atm  $CO_2$ —room air will be diluted by a factor of 10 with nitrogen). These experiments do not duplicate those run previously in Albuquerque (TP 97-01 “Confirmation of the Ability of a Designed Backfill to Control the Chemical Environment of the WIPP”), which used very high concentrations of  $CO_2$ . Rather,



Sandia will attempt to examine carbonation under conditions more similar to those expected in the repository.

The current experiment, as well as the future ones, uses four different electrolytes: DI water, 4 M NaCl, GW seep brine, and ERDA-6 brine. Each sample bottle includes five grams Premier Chemicals MgO and 100 ml of electrolyte. Room air is bubbled continuously through the samples using a gas manifold. Each manifold holds 24 samples. To minimize evaporation, the air is humidified by bubbling through water prior to entering the manifold. Future carbonation experiments will be conducted in a similar manner, except the samples and manifolds will be inside glove boxes. A purchased mixture of 5% CO<sub>2</sub> in nitrogen gas and room air diluted to 1/10 of its original concentration with inert N<sub>2</sub> will be pumped into the glove boxes and bubbled through the samples.

Samples will be collected at weekly and eventually monthly intervals. Samples will be dried and crushed. Carbonate conversion rates will be ascertained by using a carbon coulometer and X-ray diffractometer. The carbon coulometer will determine the percent carbon, whereas the X-ray diffractometer will identify the carbonate phase present. Samples analyzed to date from the experiment run at atmospheric P<sub>CO2</sub> indicate less than 1% carbonate conversion in 30 days.

### **ISA Generation Under MgO-Buffered Conditions**

Sandia is continuing to evaluate the production of isosaccharinic acid (ISA) under repository conditions. In August 2000, cellulosic materials and MgO were placed in bottles containing three different electrolytes. The samples were placed in ovens ranging from 25°C to 90°C in temperature. A detailed description, recounting the importance of the experiment and the experimental method used are found in the January, 2001 Status Report (Milestone RI010). At this time, the experiment has been sampled seven times, and will be sampled again in August, 2001. No samples have been analyzed to date, because access to a gas chromatograph-mass spectrometer (GC-MS) has not been available. However, at each sampling, pH has been monitored. Values are stabilizing at measurements similar to those of the pure MgO systems.

### **Hydration/Carbonation Pathway Experiments**

The P<sub>CO2</sub> assumed for repository certification calculations in the CCA is based upon the assumption of equilibrium with magnesite (MgCO<sub>3</sub>). However, metastable hydromagnesite phases commonly form upon initial carbonation of MgO/brucite, and these phases have higher solubilities than magnesite. Thus, they might buffer the P<sub>CO2</sub> at values significantly higher than those used in the CCA. Previous work with MgO has been criticized for failing to consider the potential effect of metastable hydroxycarbonates on repository chemistry (Wilson et al., 1997). Sandia is currently working to identify the MgO hydration/carbonation pathway that is relevant to the WIPP, and to evaluate the hydroxycarbonate phase(s) that might form.

MgO in the repository is expected to follow two possible hydration/carbonation pathways. In the E2 scenario, slow influx of Salado brines results in a humid repository with little free water; the MgO hydrates under humid conditions, and is hydrated prior to being inundated with brine. Carbonation occurs after inundation, as microbial action increases due to the presence of free liquid. The hydrated products of the MgO adsorb CO<sub>2</sub>, and form hydroxycarbonate, which slowly dehydrates to form stable magnesite. In the second, E1, scenario, the dry MgO is inundated directly with brine, and then follows the rest of the reaction path given above.

Efforts to determine the hydration/carbonation pathway are currently underway at Sandia. Initial experiments, have merely confirmed modeling results that magnesium chloride hydroxide hydrate will be an important solid phase in systems with Mg-rich brines, and that there are no apparent kinetic barriers to reaction of MgO or brucite with brine to produce it.

Efforts to identify the hydroxycarbonate phase that forms under the low P<sub>CO2</sub> values expected in the repository have only just begun. The carbonation experiments at atmospheric P<sub>CO2</sub> and 1/10 atmospheric P<sub>CO2</sub> will produce only very small amounts of carbonate over very long periods. Identification of these phases by XRD may prove impossible if they do not comprise a significant fraction of the total solid. However, it may be possible to identify the hydroxycarbonate phase indirectly. Samples will be removed from the gas manifolds, sealed, and allowed to equilibrate for a few days. Samples of the brine will then be extracted, and analyzed for carbonate content. Brine samples will also be equilibrated with hydroxycarbonate mineral standards. Ideally, comparing the results from the known and unknown samples will allow identification of the carbonate phase present in the unknowns. The hydroxycarbonate minerals currently in our possession include:

Magnesite	MgCO <sub>3</sub>
Nesquehonite <sup>†</sup>	MgCO <sub>3</sub> ·3H <sub>2</sub> O
Lansfordite	MgCO <sub>3</sub> ·5H <sub>2</sub> O
Pokrovskite*	Mg <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub> ·0.5H <sub>2</sub> O
Artinite	Mg <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub> ·3H <sub>2</sub> O
Hydromagnesite <sup>†</sup>	Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> ·4H <sub>2</sub> O
Dypingite*	Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> ·5H <sub>2</sub> O

\* these rare minerals may not be available in sufficient amounts for experimental use.

† these minerals have been observed in previous WIPP-related carbonation experiments.

## Summary

Since the January 2001 Status Report (Milestone RI010), Sandia has continued to perform experimental work to characterize the hydration/carbonation rates of Premier Chemicals MgO, and to determine the probable hydration/carbonation pathway MgO will take under repository conditions. This work is covered under Test Plan TP 00-07 "Experimental Study of WIPP MgO Backfill at Sandia National Laboratories Carlsbad Facility."



In inundated experiments, Premier MgO was placed in four electrolytes—de-ionized (DI) water, 4M NaCl, GW brine, and ERDA-6 brine—and placed in ovens at temperatures ranging from 25°C to 90°C. Brucite is the only hydration phase present in three of the brines; in GW brine, a second, heretofore unidentified, hydration phase forms. In most electrolytes, hydration appears to be readily modeled as a diffusion-limited reaction. Hydration ceased in samples immersed in DI water at 90°C after ~85% of the material converted to brucite. Non-reactive silicates and aluminates probably make up the remaining 10-15%.

Samples submerged in GW brine are difficult to quantify. Due to the high magnesium content in solution an unidentified phase, most likely an amorphous phase of magnesium chloride hydroxide hydrate, forms until the excess magnesium is depleted and brucite becomes the stable phase. The unidentified hydration phase contains a different amount of stoichiometric water compared to brucite, making it difficult to determine, from LOI data, the actual degree of MgO hydration that has occurred.

The ratio of MgO to volume of GW brine impacts the amount of each hydration product formed. After samples were aged for 28 days at 70°C, data indicated that the greater the volume of brine in the sample, the greater the fraction of magnesium chloride hydroxide hydrate relative to brucite.

The cemented “cake” experiments look at three different thickness of MgO in two brines (GW and ERDA-6) at temperatures between 25°C and 90°C. Samples are not agitated. The study will examine how the formation of a cemented cake of hydration products will affect the rate at which water can diffuse into the sample and hydrate the remaining MgO. At this time little data has been analyzed.

Humid hydration and carbonation experiments are still in the early stage, thus little data have been acquired. However, at higher temperatures and humidities, the humid hydration experiments are readily converting to brucite. At 80°C, the higher humidity samples have converted to over 80% brucite after only four weeks. In the coming months, continued sampling should supply the necessary data to determine rate constants at lower temperatures.

It may be months before the carbonation experiments, running under atmospheric  $P_{CO_2}$ , show any results (currently, samples show less than 1% carbonate conversion). Experiments running with 5%  $CO_2$  and  $1/10^{th}$  atmosphere will be started within the next few weeks.

ISA experiments continue at Sandia, and have been sampled seven times since initiation in August 2000. Samples are currently being stockpiled until the gas chromatograph-mass spectrometer (GC-MS) becomes available for sample analysis.

Finally, Sandia will start experiments to identify the magnesium hydroxycarbonate phase that will form under WIPP-relevant  $P_{CO_2}$  conditions. Known hydroxycarbonate minerals will be used as standards to help identify the carbonate phase that forms in these experiments.

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