

5.0 MgO Hydration and Carbonation at SNL/Carlsbad

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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 barrier 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, it maintains the pH and CO₂ fugacity (P_{CO_2}) 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, although it indicated that conversion of MgO to hydroxycarbonate was limited by formation of mineral rinds to about 25% of the total material present (Papenguth, et al., 1997, 1999). Presently, four times more MgO is scheduled to be emplaced in the WIPP than mass balance calculations suggest would be necessary if all organic materials in the waste were converted, through microbial respiration, to CO₂. 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. First, the MgO supplier for the WIPP has changed since the previous experiments were run, from National Refractory Minerals to Premier Chemicals, Inc. The new material is manufactured using a different process than the old. It 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 wetted system. Sandia is characterizing the new material chemically and physically, and is performing experiments to evaluate its ability to sequester water and CO₂ relative to the material used in previous experiments.

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 currently performing experiments to assess this using a variety of WIPP-relevant brines and cellulosic materials.

A third issue concerns the actual hydration/carbonation pathway that MgO follows under repository conditions (Wilson et al., 1997). The P_{CO_2} predicted from repository certification calculations in the CCA is based upon the assumption of equilibrium with magnesite ($MgCO_3$). 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_{CO_2} at values significantly higher than those used in the CCA. Previous work with MgO has been heavily criticized for failing to consider the potential effect of metastable hydroxycarbonates on repository chemistry. 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.

Because of the volume of MgO to be placed in the repository, sequestration of actinide metals through sorption onto or coprecipitation with MgO hydration/carbonation products could potentially have a significant effect on the concentration of radionuclides in repository solutions, and on releases should the repository be breached. The MgO reaction pathway is complex — MgO \square brucite [$Mg(OH)_2$] or Mg-hydroxychloride [$Mg_3(OH)_5Cl \cdot 4H_2O$] \square unknown Mg-hydroxycarbonate \square magnesite [$MgCO_3$] — and actinides may be either sequestered or released at each step of the reaction. Sandia is initiating a series of sorption experiments with both actinides and non-radioactive analogs to investigate the role of MgO and its reaction products as sinks for actinides in the repository.

Finally, Sandia is investigating the potential uses of MgO as an additive to waste drums to prepare them for transport. Portland cement is currently being added to some drums to adsorb fluids and to neutralize corrosive acidic solutions produced in some cases through radiolysis. However, cement in large amounts has the potential of locally raising the pH in the repository, increasing the solubility of the actinides. MgO could perform a similar function in the drums, albeit perhaps more slowly than CaO, without perturbing the repository chemistry.

The experiments described here are under the purview of test plan TP 00-07 "Experimental Study of WIPP MgO Backfill at Sandia National Laboratories Carlsbad Facility." The current revision (Rev. 0) is being modified to include the sorption/coprecipitation studies with radionuclides.

The objectives of these experiments are multifold. MgO hydration/carbonation rates vary greatly with the properties (temperature of calcination, porosity, impurities) of the MgO

used. Hydration/carbonation rate efficiencies will be determined by characterizing the Premier Chemicals MgO and performing hydration/carbonation rate experiments. Should carbonation reactions go to a greater degree of completion than with the previous material, this could result in reductions in required volume of MgO backfill and significant cost savings. Experiments to identify the hydration/carbonation reaction pathway are in response to criticisms leveled at the program in the (Wilson et al., 1997) and by Oversby (2000), and also supports the MgO sorption/coprecipitation experiments, by identifying the hydroxycarbonate phase that forms. The sorption experiments could potentially result in greatly lowered estimates of actinide concentrations in repository solutions. This, in turn, could reduce concerns about the effects of organic ligands (humics, citrate, ISA) or even repository redox conditions on actinide solution concentrations. Sandia is investigating the potential formation of ISA by degradation of cellulosic materials because such materials comprise a significant fraction of the waste inventory, and complexation with ISA could significantly raise actinide solution concentrations. Exploring the potential uses of MgO as a waste drum additive could result in new treatments for orphaned wastes, potentially helping "fill the waste pipeline."

Premier Chemicals MgO

The hydration/carbonation experiments which generated parameters for the CCA 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 wetted system. Sandia is characterizing the new material chemically and physically, and is performing experiments to evaluate its ability to sequester water and CO₂ relative to the material used in previous experiments.

Characterization of Premier Chemicals MgO

Previously, National Refractory Materials MgO was produced by mixing calcined limestone with seawater, and processing the resulting precipitate in a rotary kiln. The resulting product is porous (~50% porosity) pellets, ≤3/8 inch in diameter, consisting of sintered MgO crystallites on the order of several micrometers in size. It contains relatively low concentrations of CaO (0.5% typically, with a maximum of 1%). However, National Refractory Minerals is no longer supplying MgO for the WIPP. The new vendor is Premier Chemicals, which is already in use at the WIPP. Premier Chemicals MgO differs significantly from the previous material. This material is produced by calcining magnesite ore, mined at Gabbs, NV, in a rotary kiln, and consists of angular grains of material ≤ 3/8 inch in diameter (much of the material is fine powder.) The material is a minimum of 90% MgO (as stated on the Material Safety Data Sheet), and is relatively impure, containing up to 10 percent Mg-Ca silicates. As of October 2000, Premier Chemicals has adjusted the chemical composition to a minimum of 95% MgO+CaO.

The purpose of this study is to analyze Premier Chemical's MgO to determine what impurities might be present and in what quantities, and to describe the granular texture of Premier Chemical's MgO. Analyses were done using the JEOL 5900LV scanning electron microscope (SEM), and the Bruker X-ray Diffraction unit (XRD).

Chemistry

The chemical makeup of a typical sample of Premier MgO, as listed in the Material Safety Data Sheet, is as follows: 2.8 % SiO₂, 1.3 % Fe₂O₃, 0.8 % Al₂O₃, 3.9 % CaO, and 91.0 % MgO (90 % minimum). Note that the impurity oxides listed here do not exist as free oxides in the MgO (with the exception of a fraction of the CaO and SiO₂) but are combined mineralogically as calcium-magnesium silicates, aluminates, and ferrites.

Size distribution

Two different batches of Premier MgO were received from the supplier. Both are poorly sorted and ranged in grain size from > 2 mm to < 0.15 mm. Results of sieve analysis are shown in Figure 1. Batch 2 is somewhat better sorted than Batch 1. Approximately 60 % of the total weight from Batch 2 is between 0.50 and 0.15 mm, whereas Batch 1 displays a bimodal size distribution, with ~70% of the total weight in the largest and smallest size fractions.

Mineralogical analysis

All samples and size fractions were analyzed using the SEM and the XRD. The XRD was used for quantitative bulk mineralogical analyses. The SEM was utilized to identify major and minor mineral phases, and to document the grain textures—the physical distribution of the minerals, and the intergranular porosity.

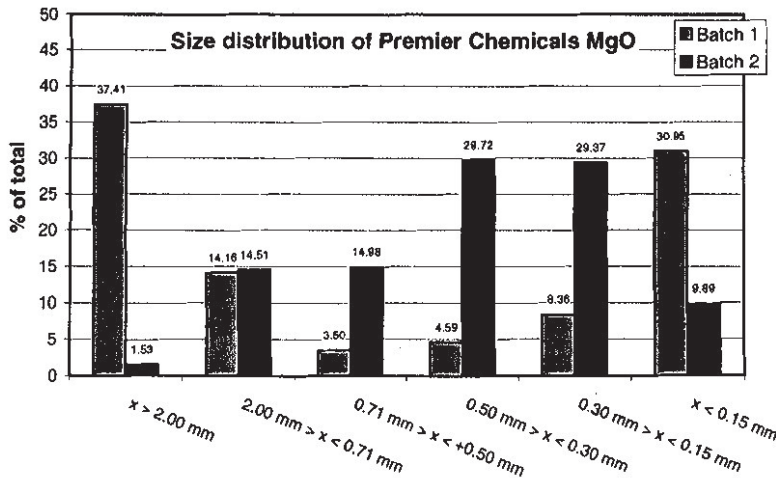


Figure 1. The size distribution of 2 batches of Premier Chemicals MgO.

XRD Analysis

Bruker D8 Advance X-ray Diffractometer (XRD) was used to determine what mineral phases are present in each size fraction, and a quantitative analysis was performed with GSAS, (this software has not been qualified as per NP 19-1) a Reitfeldt structural refinement software package developed by LANL to determine what percent of each phase occurs in each size fraction. Samples were prepared for analysis by crushing/powdering using a mortar and pestle. Thomas Hartmann, of Los Alamos National Laboratories performed the analysis and data refinement.

A typical XRD pattern for the Premier Chemicals material is shown in Figure 2. Periclase (MgO) dominates the pattern, constituting more than 85% of each sample. Other major and minor phases are forsterite (Mg_2SiO_4), lime (CaO), monticellite ($CaMgSiO_4$), spinel ($MgAl_2O_4$) and ulvospinel ($FeTi_2O_4$). The amount present varies with the particle size (see Table 1). Note that the finest material has the highest concentration of periclase. It is speculated that the less pure material, which loses less CO_2 and undergoes less volume change during calcination, has less tendency to decrepitate, and is hence preferentially enriched in the larger size fractions.

It must be noted that the weight percent of periclase (MgO in pure mineral form) and lime (CaO in pure mineral form) in a sample, as presented below, is different from the oxide weight percent of MgO and CaO in a chemical analysis, as listed on the specification or material safety data (MSD) sheets for Premier Chemicals MgO. The chemical analysis does not distinguish between MgO present as periclase, and that present in non-reactive silicate minerals such as forsterite. For example, the Batch 1 material in Table 1 contains 91.9 wt% (periclase + lime), but a chemical analysis of the same material would yield 96.3 wt% (MgO + CaO, calculated assuming the ideal chemical formulas for the phases listed above); Batch 2 contains 88.3 wt% (periclase + lime) but 95.1 wt% (MgO + CaO).

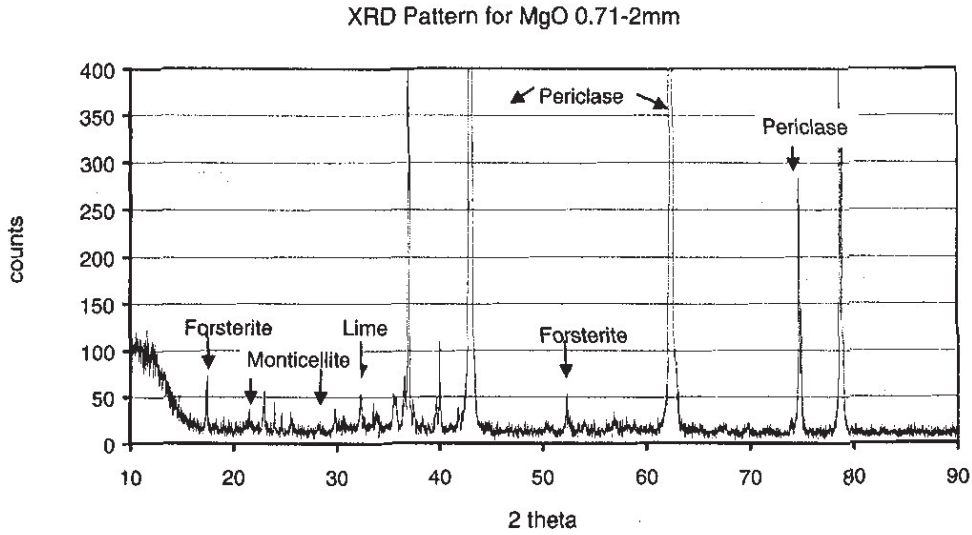


Figure 2. XRD pattern. Arrows indicate mineral refraction peaks.

Table 1. The mineral composition, as determined by X-ray diffraction, of different size fractions of Premier Chemicals MgO.

Size Fraction (μm)	Periclase %	Forsterite %	Lime %	Monticellite %	Spinel %	Ulvospinel %
<i>Batch 1</i>						
< 150	95.1	2.75	1.22	0	0	0.93
150 - 130	93.6	4.82	1.62	0	0	0
300 - 500	92.1	5.83	1.10	0.98	0	0
500 - 710	88.5	7.86	0.92	2.68	0.08	0
710 - 2000	88.3	9.19	0.21	2.28	0	0
> 2000	88.7	8.50	0.25	2.02	0.52	0
Bulk	91.2	6.34	0.73	1.23	0.2	0.3
<i>Batch 2</i>						
Bulk	87.6	8.74	0.74	2.92	0	0

Both of these samples meet the WID (1997) specification that the backfill material be a minimum of 95% MgO (chemical composition) if CaO is included. However, they are on the average only 89.9% "reactive MgO," where "reactive MgO" is periclase plus lime recalculated into the mole-equivalent wt% periclase. MgO density and volume calculations indicate that it might be necessary to increase the volume of the Premier Chemicals MgO to be placed in the repository by ~7.4%, or to obtain an agreement with the EPA to reduce the amount required.

SEM Analysis

A JEOL 5900LV scanning electron microscope (SEM) was used to examine the grain textures and to identify what impurities might be present in each size fraction from Batch 1 and in a homogeneous sample from Batch 2. The samples were prepared for analysis by vacuum impregnating each sample with epoxy, then cutting and polishing using diamond laps and oil-based grits. Water was not used to avoid leaching any components out of the samples. All samples were coated with carbon for imaging and elemental analysis by SEM.

Samples were examined under backscatter electron mode, in order to emphasize compositional differences, at 15kV. Texture and mineralogy were fairly consistent throughout all size fractions. The grains display a high internal porosity, caused by the phase change from magnesite to periclase during calcination and the resulting degassing of CO₂. A considerable volume change (~60%; MgCO₃ → MgO) occurs during this reaction.

Individual grains are angular (Figure 3) and are generally highly porous. Two types of intergranular porosity are recognized. A fracture texture is observed in several forms. Some grains contain a random array of interconnected fractures that extend through the entire grain (Figures 3 and 4). Other grains (Figure 3) show elongate fractures that are either sub parallel and extend across the entire grain or that cross-cut each other at fixed angles. These may represent relict cleavage planes in grains that were originally single crystals of magnesite. A second type of porosity, present on a much smaller scale, is a pocketed or vermicular appearance within the grain (Figure 5). The channels appear to have formed by removal of an intergrown phase by volatilization or dissolution during or after calcination or the magnesite ore. Alternatively, the channels may have formed as pathways for CO₂ degassing during calcination. The abundance of fractures and channels in the grains indicates that they have a high internal surface area.

The grains have an intragranular composition consisting of sub-rounded crystals of MgO (Figure 6), with interstitial matrix material consisting of calcium/magnesium silicates or lime (this generally absorbs water from the air after the final step of polishing, forming calcium hydroxide and swelling slightly). Typically, in MgO-rich grains, the intergranular material is calcium-magnesium silicate. In relatively periclase-poor areas, the MgO is matrix-supported, and calcium oxide is usually the dominant matrix phase. The major mineralogical phase present in each size fraction is MgO (periclase). Other identified

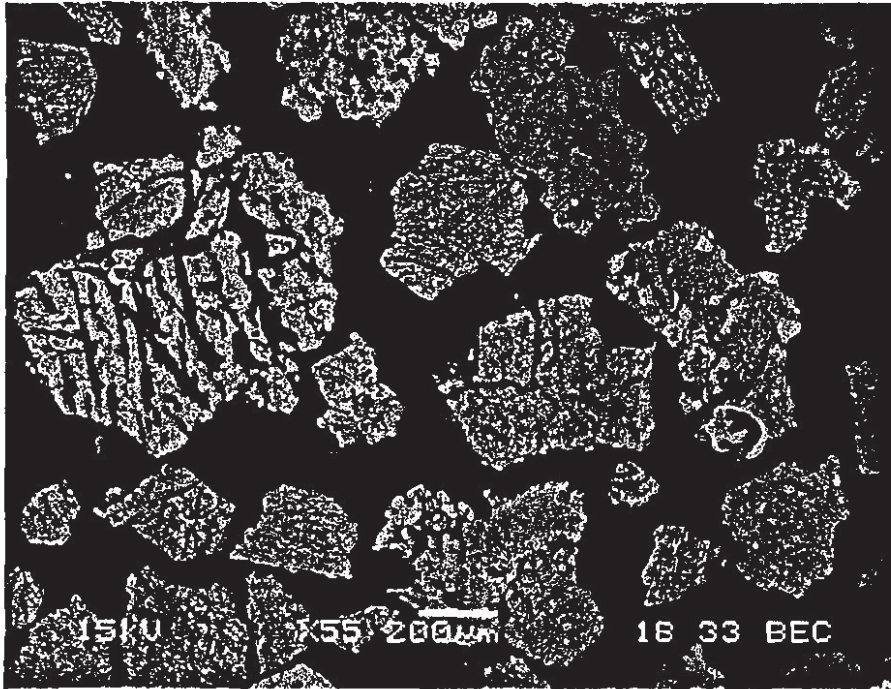


Figure 3. SEM backscattered electron image of Premier Chemicals MgO. Note the highly fractured grains and presence of impurities.

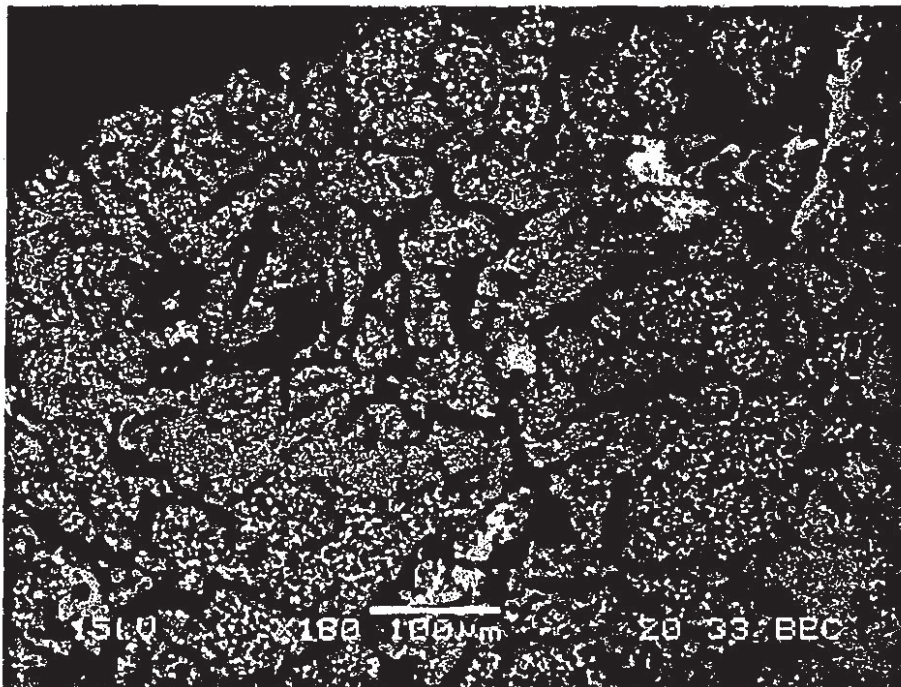


Figure 4. Close up of a highly fractured grain of Premier Chemicals MgO.

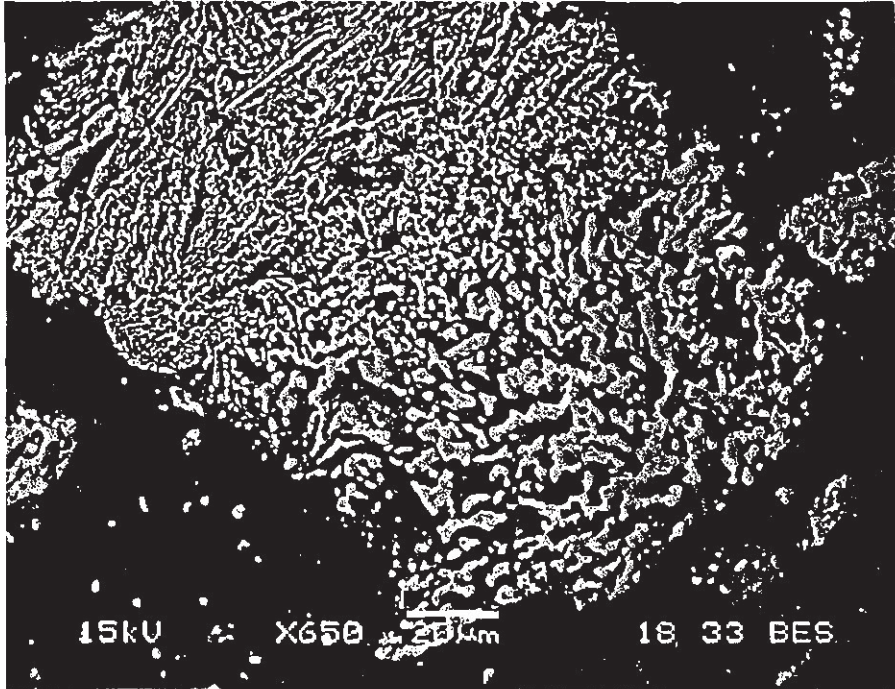


Figure 5. SEM backscattered image of a MgO grain exhibiting a channeled or vermicular porosity.

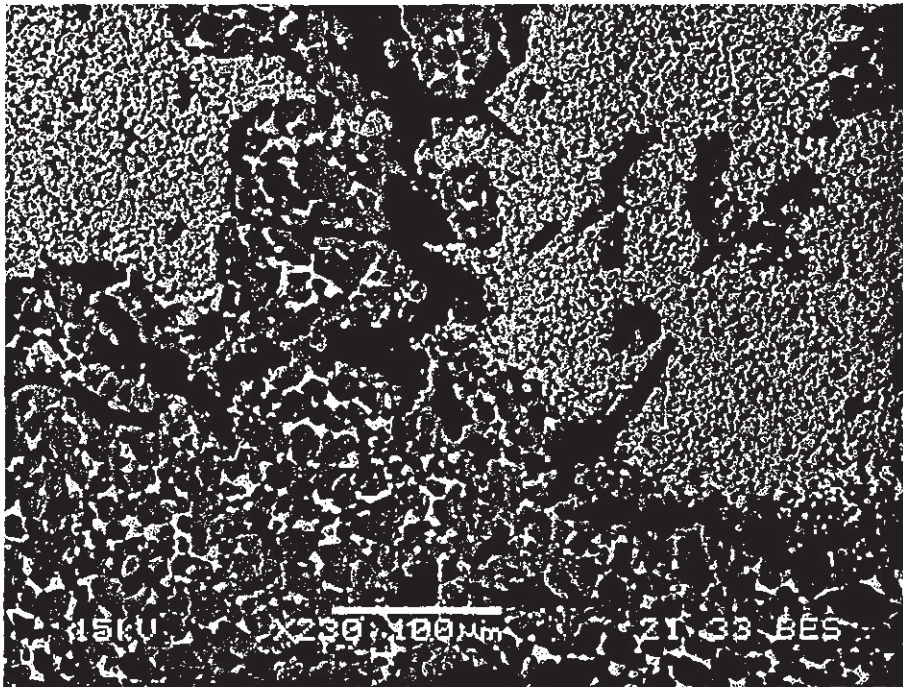


Figure 6. SEM close up of a MgO grain. Note the dark MgO crystals in the lower half of the photo, with interstitial by white calcium-rich silicate. The large white areas in the upper half of the photo are dominated by calcium oxide (hydrated after polishing to form calcium hydroxide).

phases include: CaO (lime), calcium silicate (probably Ca-rich monticellite), CaMgSiO₄ (monticellite), Mg₂SiO₄ (forsterite), and spinel (MgAl₂O₄).

Evaluation of hydration/carbonation rates of Premier Chemicals MgO

To date, only a few scoping hydration experiments have been run, to investigate the effects of Premier Chemicals MgO on solution pH and to assist in developing an experiment design and sampling schedule. A large experimental matrix has been planned to investigate both humid and inundated hydration rates of the Premier material.

Humid experiments will be conducted as described in Zhang et al. (this report). Experiments will be conducted using samples of both Premier chemicals MgO and a pure, finely powdered MgO, obtained from Fisher Scientific, and will be run at ~25°C (room temperature), 50°C, and 80°C, over saturated salt solutions that will provide relative humidity (RH) values as listed in Table 1. In all 42 containers (7 different brines, 2 different substrates, and 3 temperatures) will be prepared and sampled regularly over a period of months to years to generate a humid hydration rate data set. These experiments will be started in February, 2001.

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

Salt	RH Value, %*
K ₂ SO ₄	95
BaCl·2H ₂ O	90
NaCl	75
KI	70
NaBr·2H ₂ O	50
MgCl ₂ ·6H ₂ O	35

* RH values vary a few % with temperature

Samples will be periodically collected, dried and analyzed by thermogravimetric analysis—brucite concentration will be determined by weight loss at 600°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.

Inundated condition experiments are considerably more complex. The experimental matrix is shown in Table 3. Experiments will be run at ~25°C (room temperature), 50°C, and 80°C, and will be sampled over periods or months or years to generate a data set for hydration under inundated conditions. To minimize the formation of carbonate minerals, these experiments will be run in PETG plastic and glass bottles, which are resistant to CO₂ diffusion. The Fisher MgO and crushed Premier MgO samples will be agitated regularly, in an effort to evaluate potential kinetic effects independently of formation of cemented cake of hydration minerals. The intact Premier MgO samples will not be agitated, but will be allowed to hydrate and form a cake as expected in the repository.

Table 3. Experimental Matrix for Inundated Condition Experiments

Solid	Brine
Fisher MgO	DI water
Premier MgO	4.0 M NaCl
Intact Premier MgO	4.0 M NaCl + 0.1 M MgCl ₂
	4.0 M NaCl + 1.0 M MgCl ₂
	Synthetic ERDA-6 (Castile) Brine
	Synthetic GW (Salado) Brine

The complexity of these experiments comes in analyzing the hydration minerals that form and quantifying the hydration rate. Scoping experiments run to date suggest that MgO placed in brines containing elevated concentrations of Mg in solution (e.g. GW-brine and the NaCl + 1.0 M MgCl₂ brine) will react to form a gel-like mass of amorphous material—possibly magnesium hydroxychloride and other salts that precipitate as the water in the brine reacts with the MgO. In one sample of Premier MgO, crystalline Mg-hydroxychloride was observed by XRD and SEM (Figures 7 and 8). Quantifying the amount of brucite and hydroxychloride that forms is difficult; with two hydrated phases present, weight loss upon ignition can no longer be clearly interpreted, and the poor crystallinity of the material makes quantification by XRD difficult. We are currently investigating methods to quantify the mass of the hydration products formed.

An additional complexity is that the hydration rate will probably vary with the MgO/brine ratio, as Mg-hydroxychloride formation ceases once the concentration of Mg in solution drops to less than 0.7 M (Wang, personal communication). The experimental matrix described in Table 3 will be run using an excess of MgO to duplicate the conditions most likely to occur in the repository.

The full experimental matrix for the inundated hydration experiments will be started in February, 2001, and will be sampled regularly until completion, in months or years.

Carbonation experiments will be run in batch systems at room temperature, using both Fisher MgO and Premier chemicals MgO. Samples will be run in the same set of brines as listed in Table 2. Two sets of samples will be run; in the first case, room air ($P_{CO_2} = 10^{-3.5}$) will be bubbled through the samples using a gas manifold. The second set will be run in a glove box, through which room air diluted 1/10 with inert N₂ will be pumped. These experiments do not duplicate those run previously, which used very high concentrations of CO₂, but rather attempt to examine carbonation under conditions more nearly similar to those expected in the repository.

ISA Generation Under MgO-Buffered Conditions

Sandia is 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 increase the solubility of the actinides in the

XRD Pattern for P. MgO I-41a

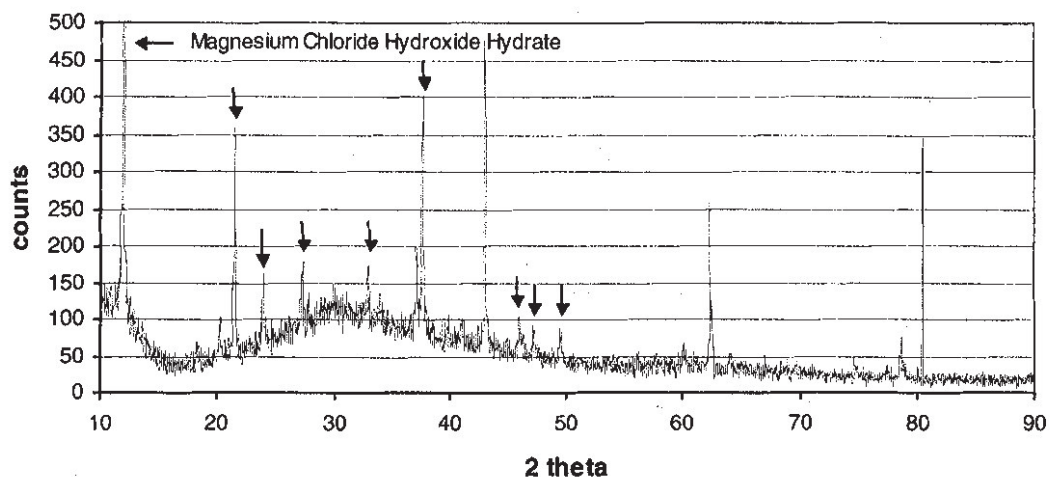


Figure 7. An XRD pattern of the solids present after aging Premier Chemicals MgO aged in 4M NaCl + 1.0 M MgCl₂ for one week. Arrows indicate Magnesium Chloride Hydroxide Hydrate diffraction peaks.

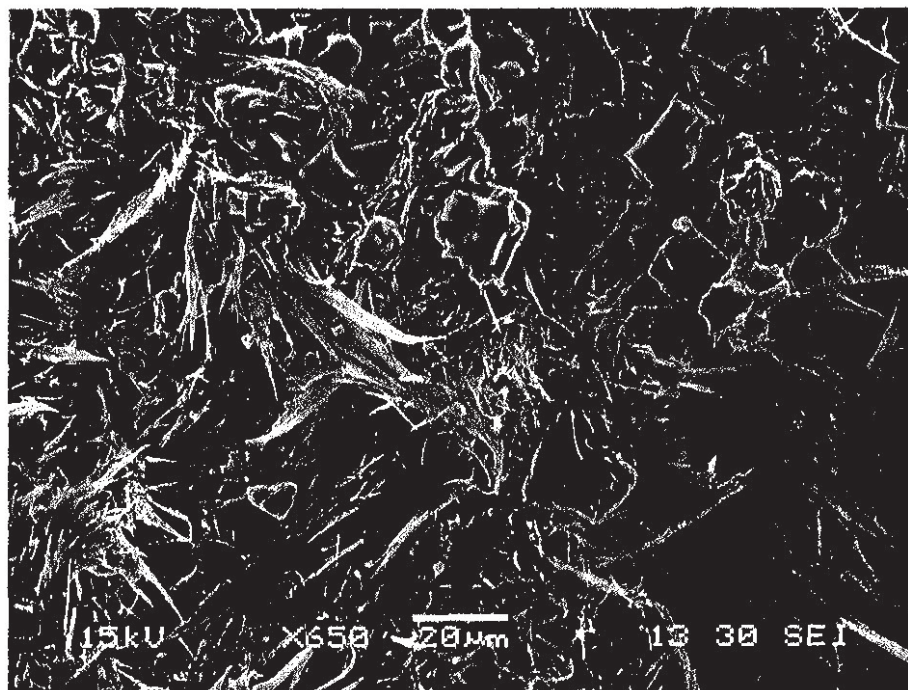


Figure 8. SEM image of the material analyzed in figure 7. Note the fibrous Mg hydroxy-chloride ($Mg_3(OH)_5Cl \cdot 4H_2O$) and cubic salt crystals.

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repository. However, it has never been demonstrated that ISA forms under the mildly alkaline conditions typical of MgO-dominated systems. Sandia is currently performing experiments to assess this using a variety of WIPP-relevant brines and cellulosic materials.

Experimental Method

To examine the degradation of cellulose under repository conditions, a large experimental matrix has been initiated. This matrix is summarized in Table 4. Samples of cellulosic materials were placed in bottles containing three different electrolytes, and MgO was added. The dominant cellulosic material used was a mixture of four paper types—white paper towels, brown paper towels, kimwipes®, and filter paper—cut into 1 cm squares. A few samples were run with cotton squares (cut from a clean 100% cotton laboratory coat), and with wood (sawdust filed from a clean pine 2"x 4" board). Fisher pure MgO, and Premier MgO were used; metallic Fe was added to some samples to evaluate the effect of Eh. CaO was used in a few samples to verify that the cellulose would generate ISA under high pH conditions. PETG plastic and glass bottles were used to minimize CO₂ and O₂ diffusion into the systems.

Table 4. Experimental Matrix for ISA Generation Experiments

Temp, °C	Reactant (15 g)	Brines (150 ml)	Cellulose (20 g)
~25	Fisher MgO	Deionized water	Paper mixture
40	Premier MgO	ERDA-6 — Castile	(Cotton)
50	(Fisher MgO + Fe metal)	GW-brine — Salado	(Wood)
60	(Premier MgO + Fe metal)		
70	(CaO)		
80			
90			

Materials in () are part of a comparison matrix of limited extent.

The samples are being aged at temperatures ranging from 25°C to 90°C, and were started August 2000. They have been sampled 4 times, and will be sampled again in Feb, 2001. Sampling will continue for at least one year. No samples have been analyzed to date, because access to a gas chromatograph-mass spectrometer (GC-MS) has not been available. However, LANL is moving a GC-MS to Carlsbad in February, and it is anticipated that the current backlog of stored samples will be analyzed by April, 2001.

The pH in the samples has been monitored, and is useful in evaluating the effect of the relatively minor amount of CaO present in the Premier MgO (Figure 9). Initial pH values are elevated relative to those in the pure MgO systems, but the values drop as the Premier MgO continues to react, eventually stabilizing at values similar to those of the pure MgO systems. The initial pH difference was greater in the DI water systems (~ 1.5 pH units), than in the brine systems (<0.5 units for Salado). With aging, the pH dropped more rapidly at elevated temperatures because the MgO reacted more quickly. *It must be noted that any effect of cellulosic degradation is not being considered here, and that no attempt has been made to correct the measured pH values for Na interference to yield the true pH.*

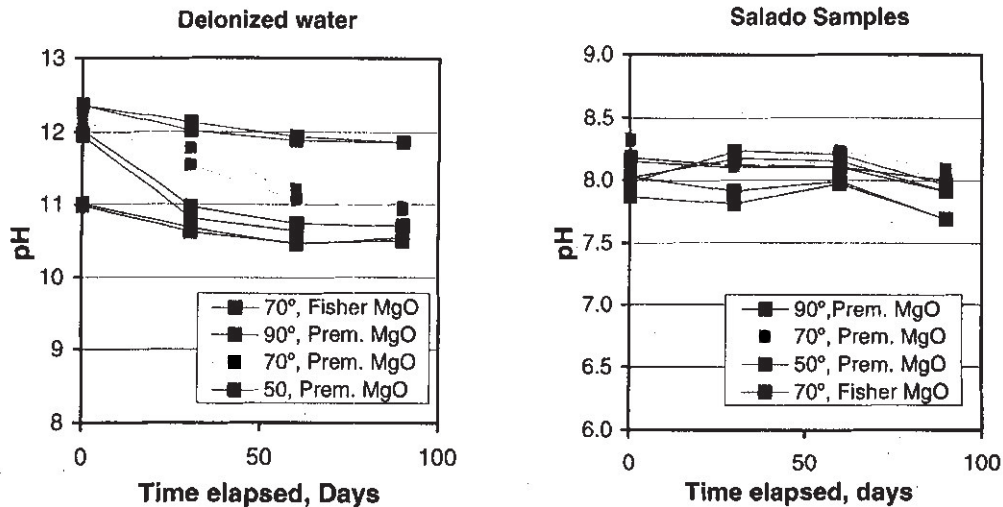


Figure 9. The pH of DI water and Salado brine solutions aged in the presence of Premier Chemicals MgO at elevated temperature. Note transient initial temperature rise.

Hydration/Carbonation Pathway Experiments

The P_{CO_2} assumed for repository certification calculations in the CCA is based upon the assumption of equilibrium with magnesite ($MgCO_3$). 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_{CO_2} at values significantly higher than those used in the CCA. Previous work with MgO has been heavily 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_2 , 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 rest of the reaction path given above.

Efforts to determine the hydration/carbonation pathway are currently underway at Sandia. Batch experiments have been prepared using the brines listed in Table 2, Section 2.2., and with brucite, Fisher MgO, and Premier chemicals MgO. Initial experiments, in progress now, have merely confirmed modeling results that predict that Mg-hydroxychloride 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. Such systems, even those containing Premier Chemicals MgO, will form a