

Hydration of Magnesium Oxide in the Waste Isolation Pilot Plant

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ABSTRACT

Magnesium oxide (MgO) is the only engineered barrier being emplaced in the Waste Isolation Pilot Plant (WIPP), a U.S. Department of Energy repository for transuranic waste. MgO will lower dissolved concentrations of actinides by consuming CO₂ from possible microbial activity, by buffering the pH between 8.5 and 9.5, and by reducing the amount of free water in the repository. This paper discusses results from experiments measuring the hydration of MgO. Results suggest that periclase (MgO) hydrates rapidly to brucite (Mg(OH)₂) in de-ionized water and 4 M NaCl solution at 90°C; the hydration rate decreases as temperature decreases. In ERDA-6, a NaCl-rich WIPP brine, MgO hydrates directly to brucite; in GWB, a high-Mg brine, periclase hydrates to magnesium chloride hydroxide hydrate(s) until the dissolved Mg²⁺ concentration decreases, and brucite becomes the stable phase. Under humid conditions MgO fully hydrates at higher humidities (> 50%). All data are consistent with diffusion-limited hydration reactions.

INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy repository designed for the disposal of defense-related transuranic waste. The WIPP is located in southeast New Mexico at a depth of 655 m in the Salado Formation, a Permian bedded salt formation. Magnesium oxide (MgO) is currently the only engineered barrier certified by the U.S. Environmental Protection Agency. The MgO currently being emplaced is supplied by Premier Chemicals of Gabbs, Nevada. MgO emplaced in the WIPP will lower dissolved concentrations of actinides by consuming CO₂ from possible microbial degradation of organic material (cellulose, plastic, and rubbers), and buffer the brine system between pH 8.5 and 9.5 and P_{CO₂} at 10^{-5.5} atm. MgO will reduce the amount of water in the repository if subsequent carbonation produces hydrous magnesium carbonates, however formation of magnesite (MgCO₃) would release water. Water (brine) within the WIPP is postulated to derive from the surrounding Salado Formation or from human drilling intrusion penetrating underlying brine pockets of the Castile formation.

Investigations on the efficacy of MgO are underway at Sandia National Laboratories' Carlsbad Programs Group. Experiments include possible repository conditions. The ambient temperature of the Salado Formation at the depth of the repository (655 m) is 28 °C [1]. Studies focus on hydration and carbonation rates, and characterization of the products formed under humid and inundated conditions. This paper describes chemical and mineralogical characterization of MgO and the hydration experiments. These experiments help determine hydration rates and pathways, and whether the reaction products passivate MgO.

EXPERIMENTS

Characterization of Premier Chemicals MgO by physical and chemical analyses determined mineralogy and quantity or impurities. Bulk MgO and uncrushed sieved fractions were analyzed. Physical analyses utilized a JEOL 5900LV scanning electron microscope (SEM) and a Bruker powder X-ray diffractometer (XRD). The SEM was used to identify major and minor mineral phases and to document grain textures, such as the physical distribution of minerals and intergranular porosity. SEM analysis was performed in backscatter electron mode at 15 kV in order to emphasize compositional variation. Analysis by XRD was run using CuK_α wavelength at 40 kV and 30 mA. Data from all samples was collected from 10° to $90^\circ 2\theta$, with a step size of 0.0200° at 1.000 second per step. Chemical analyses included gravimetric determination of silica coupled with analysis by a Perkin Elmer Optima 3300 DV inductively coupled plasma optical emission spectrometer (ICP-OES) [2]. These analyses determine the amount of relatively unreactive silicates and aluminates present in Premier Chemicals MgO.

Inundated hydration experiments are currently being run, under agitated conditions, to evaluate MgO hydration rates. In the first series of hydration experiments, 5 g of Premier MgO was placed in 125-mL polypropylene bottles, each containing either deionized (DI) water or one of three solutions: 4 M NaCl, ERDA-6 (a synthetic NaCl brine representing the Castile brine), or Generic Weep Brine (GWB, a synthetic brine high in Mg representing the Salado brine). The first two liquids were included in an effort to gain a more fundamental understanding of the hydration process. Samples were kept in ovens at 25, 50, 70, or 90 °C, and were agitated daily by hand. Sample agitation was performed to eliminate the formation of lithified hydration products, minimizing the likelihood that cake formation would inhibit hydration by limiting brine access to unhydrated MgO. The effects of caking are being examined in a separate series of experiments, not presented here. However, hydration products may still inhibit hydration by coating individual particles, or by plugging the internal pores in the MgO grains.

Periodically (i.e. weeks to months), samples are removed from the ovens, cooled, and the pH measured. The solid fraction is then filtered using Whatman #40 filters (particle retention $> 8\mu\text{m}$), rinsed with DI water to remove any remaining salts, and then dried, ground using mortar and pestle, and characterized by XRD and SEM. Samples for the SEM were vacuum impregnated in epoxy, polished, and coated with carbon. The loss on ignition (LOI) at 500 °C (brucite dehydrates at $\sim 290^\circ\text{C}$; temperature extrapolated from published data [3]) is used to calculate the mass of hydrated material in each sample.

The humid hydration samples consist of uncrushed Premier Chemicals MgO and are being reacted at temperatures of 25, 40, 60, and 80 °C and relative humidities of 35, 50, 75, and 95%. Samples of MgO are contained in six-well polycarbonate trays, with 3 g of MgO in each well. Four trays are stacked in sealed polypropylene containers. Each container holds a saturated salt solution providing the desired relative humidity. Relative humidity will vary a few percent with temperature, the exception being solutions of $\text{NaBr}\cdot 2\text{H}_2\text{O}$, which may vary as much as 8% at 25 °C [4]. The trays in each container are elevated on plastic blocks above the salt solution. 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 air circulation through each sample well.

The experiments are sampled over a period of months to years. Each sample is dried and analyzed by LOI and a few entirely reacted samples by XRD. We assume that MgO hydration is the only reaction that occurs to a significant extent during these experiments because MgO will only be in contact with water vapor. Analysis by XRD will test this assumption.

RESULTS

XRD powder patterns show that Premier Chemicals MgO is dominated by periclase (MgO) and contains other minor phases such as forsterite (Mg_2SiO_4), lime (CaO), monticellite (CaMgSiO_4), and spinel (MgAl_2O_4). In sieved batches of MgO the larger size fractions (> 0.50 mm) contain relatively more impurities than the smaller particle fractions (< 0.50 mm).

Quantitative mineral analysis results are shown in Table 1. Reactive minerals (MgO + CaO) constitute approximately 90 wt %, whereas the unreactive constituents constitute the remaining 10 wt %. Table 1 displays two separate calculations, both using data from gravimetric determination of silica. The major silicate phase is calculated as being entirely incorporated as either forsterite or monticellite. These two cases represent the two impurity end members in Premier Chemicals MgO.

Analysis of SEM images reveals that MgO grains are angular and highly fractured. Individual grains contain subrounded MgO grains surrounded by Ca-Mg silicates or lime.

Results from the inundated hydration experiments are expressed as hydration (mol % brucite or wt % LOI) vs. time (Figures 1 and 2). In DI water, 4 M NaCl, and in ERDA-6, XRD studies indicate that brucite ($\text{Mg}(\text{OH})_2$) is the only hydration phase present. In GWB a magnesium chloride hydroxide hydrate (probably $\text{Mg}_3(\text{OH})_5\text{Cl}\cdot 4\text{H}_2\text{O}$) precipitates initially; brucite becomes the stable hydration phase only at higher degrees of hydration. Because the magnesium chloride hydroxide hydrate and brucite lose different amounts of water upon ignition, the extent of hydration is expressed as wt % loss on ignition.

Table I. Mineral constituents of Premier Chemicals MgO

Premier MgO	A				B			
	wt % MgO (Periclase)	wt % Mg_2SiO_4 (Forsterite)	wt % CaO (Lime)	wt % MgAl_2O_4 (Spinel)	wt % MgO (Periclase)	wt % MgCaSiO_4 (Monticellite)	wt % CaO (Lime)	wt % MgAl_2O_4 (Spinel)
Results	86.86	5.027	2.386	2.071	88.73	5.756	1.273	2.071
Standard Deviation	0.05	0.092	0.040	0.043	0.53	0.105	0.059	0.043

Data compiled from ICP-OES and gravimetric silica method results. Scenario (A) is calculated assuming Mg_2SiO_4 is the only silicate present, (B) assumes MgCaSiO_4 is the only silicate occurring in the sample.

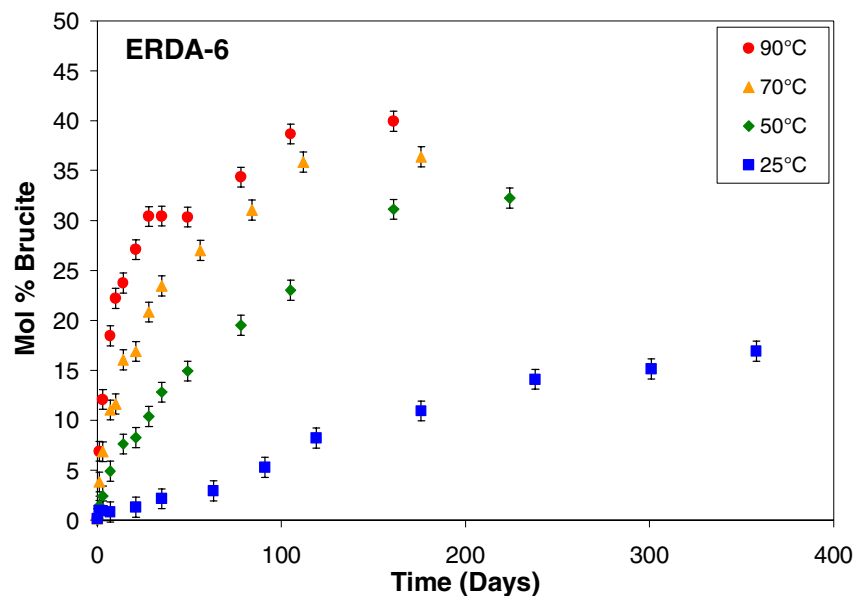


Figure 1. Hydration as a function of time of samples from ERDA-6.

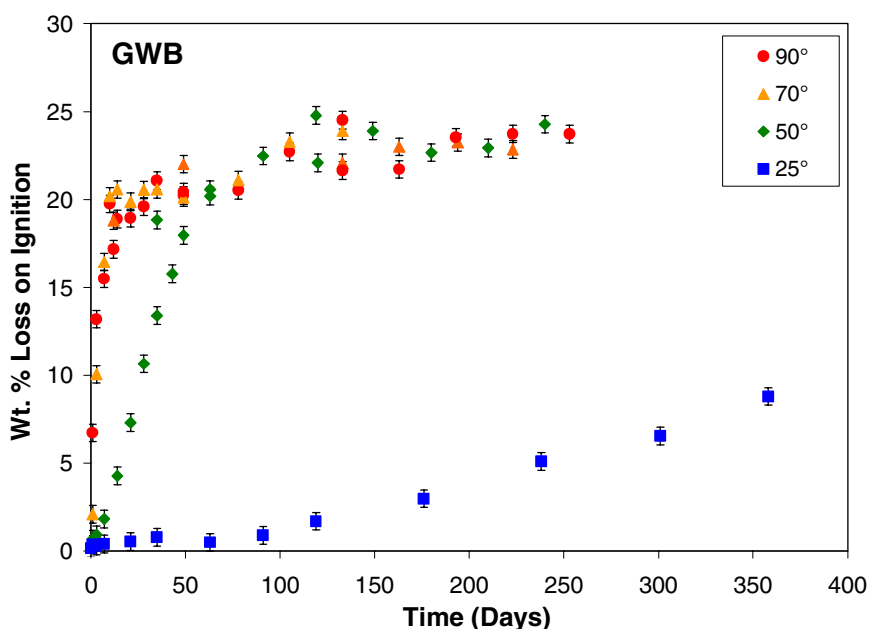


Figure 2. Hydration as a function of time of samples from GWB.

Hydration proceeded to completion in DI water at 90 and 70 °C and in 4 M NaCl at 90 °C. After 14 days, 90 °C samples in DI water reached 82–85 mol % hydration. After 14 days periclase was below detection by the XRD. After 160 days, ERDA-6 samples at 90 °C hydrated to 40 mol % (Figure 1). GWB behave somewhat differently than the others (Figure 2). The 70 and 90 °C samples in GWB behave similarly to one another. The data rise rapidly initially, and after 10 days the rate of hydration slows and appears to flatten to approximately 23 wt % LOI. The samples at 50 °C initially hydrate at a slower rate than the 70 and 90 °C samples. After 50 days the 50 °C data points converge with the higher temperatures and continue to follow the

same trend at approximately 23 wt % LOI. If the GWB hydration product was entirely brucite then 23 wt % LOI would be equivalent to approximately 80 mol % hydration. If magnesium chloride hydroxide hydrate was the only hydration product then 23 wt % LOI would be equivalent to approximately 33 mol %.

XRD analysis of GWB samples, corresponding to GWB data points plotted across the apparent plateau, indicates that periclase is continuing to decrease, while brucite peaks are increasing in intensity. The rate of MgO hydration is most likely linked to mineral phase changes between magnesium chloride hydroxide hydrate and brucite, which are caused by the change in Mg concentration in solution. It is not evident how magnesium chloride hydroxide hydrate behaves over time. The compound is thought to be amorphous at higher temperatures and may explain why it was not detected by XRD. However, its existence is inferred from SEM images coupled with Energy Dispersive System (EDS, that identify Mg-Cl phases) at all temperatures and XRD patterns from 25 °C samples. GWB contains high concentrations of Mg (1 M). MgO dissolves and reprecipitates as magnesium chloride hydroxide hydrate. This reaction, which consumes excess Mg in the brine, continues until the Mg concentration drops to ~0.7 M, according to EQ6 calculations. At this point, brucite becomes the stable hydroxide phase.

Mol % conversion plots for humid hydration data show that hydration is relatively slow at lower temperatures and humidities, but occurs readily at elevated temperatures. After four weeks, the degree of hydration reached over 80% in 95 and 75% relative humidity samples at 80 °C (Figure 3). XRD patterns from 80 °C and 95% relative humidity after 30 days confirm that brucite is the only hydration product detected. No periclase peaks are evident. At 60 °C, the rate of hydration at higher humidities slowed around 70 mol % conversion. There is evidence of hydration at 25 °C and 50% and 75% relative humidity, a range that includes the expected relative humidity in WIPP disposal rooms after filling and sealing, about 70%. The experiments at 35% relative humidity have not shown any evidence of hydration at 25, 40, 60, or even 80°C. An interesting point to note is that MgO in DI water at 90 °C and MgO exposed to high relative humidities at 80 °C behave similarly. They both are completely hydrated by 37 days.

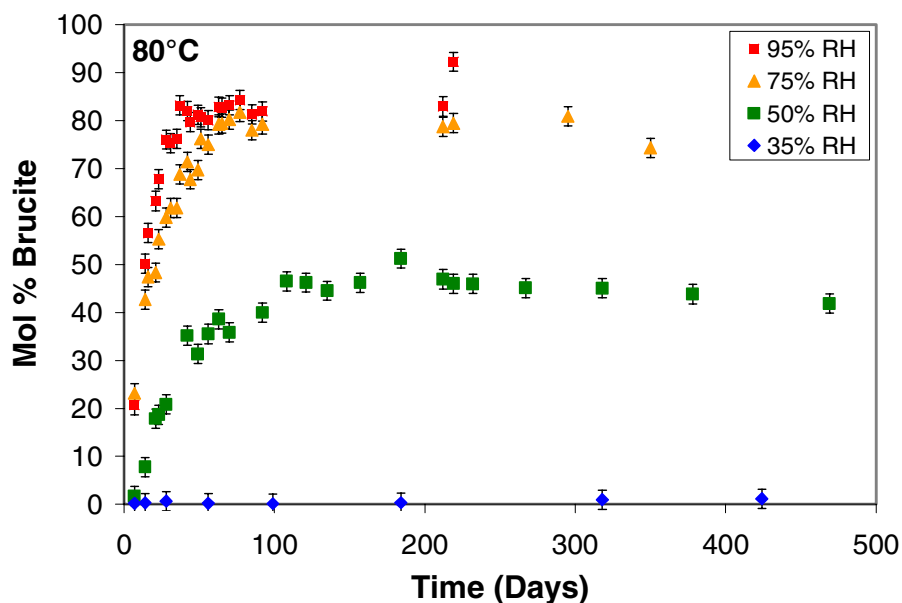


Figure 3. Hydration as a function of time for humid experiments at 80 °C.

CONCLUSION

Premier Chemicals MgO comprises of approximately 90 wt % periclase and 10 wt % silicates, aluminates, and lime. Premier MgO hydrates under inundated environments relevant to predicted WIPP conditions (28 °C). Brucite is the reaction product formed in DI water, 4 M NaCl and ERDA-6 systems. In GWB, magnesium chloride hydroxide hydrate forms initially. Magnesium chloride hydroxide hydrate has been identified by XRD at 25 °C and inferred at higher temperatures by SEM and LOI. Brucite becomes the stable hydration phase, once the concentration of Mg in solution drops below ~0.7 M. ERDA-6 and GWB experiments continue to hydrate as testing progresses. Humid hydration samples exposed to higher relative humidities behave in a manner similar to samples inundated in DI water.

ACKNOWLEDGEMENTS

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