4.1 Carbonation of Magnesium Oxide[1]

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Abstract

Sandia National Laboratories' (SNL's) Carlsbad Programs Group is currently investigating several issues with respect to the efficacy of magnesium oxide (MgO) under expected repository conditions. Characterization of Premier Chemicals MgO, with respect to both mineralogy and composition, and its ability to absorb water (H_2O) and carbon dioxide (CO_2) under repository conditions continues. Previous work has been described in SNL's (2001a, 2001b, 2002) progress reports to the US Department of Energy (DOE). This section of the status report concentrates on the ability of MgO to sequester CO_2.

MgO carbonation rates are being measured at a CO_2 partial pressure (P_{CO_2}) of about $10^{-3.5}$ atm (ambient atmospheric P_{CO_2}) and at 5% CO_2 (5×10^{-2} atm). In experiments using Premier MgO as the starting material at atmospheric P_{CO_2}, carbonation continues at a slow rate. After 264 days hydromagnesite was identified. (Hydromagnesite can have various compositions; the composition of hydromagnesite formed in these experiments has not been determined yet.) At 5% CO_2, carbonation occurs at a faster rate. Several different carbonation pathways have been identified.

In experiments started with brucite ($Mg(OH)_2$), the hydration product of periclase (MgO), and carried out at $P_{CO_2} = 10^{-3.5}$ atm and 25°C, hydromagnesite was formed about 1100 hours after initiation of the runs. Chemical speciation modeling based on experimentally determined solution compositions indicates that solutions are supersaturated with respect to hydromagnesite soon after initiation (after about 500 hours). The modeling also indicates that the tendency to precipitate nesquehonite ($MgCO_3 \cdot 3H_2O$) is not favored, especially in high ionic strength solutions. Therefore, the reaction path, periclase → brucite → nesquehonite → hydromagnesite, proposed before based upon the previous experimental results at a relatively high P_{CO_2} of 1 atm, should not be applicable to more realistic levels of P_{CO_2} (i.e., $P_{CO_2} = 10^{-3.5}$ atm or lower). Instead, the reaction path should be periclase → (magnesium chloride hydroxide hydrate) → brucite → hydromagnesite at low P_{CO_2}. This reaction path is well supported by field observations on the carbonation of magnesian lime owing to the exposure to atmospheric CO_2.

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[1] This work is covered by WBS #1.3.5.4.3.1

The conversion rate from brucite to hydromagnesite in de-ionized (DI) water is tentatively determined to be on the order of 10^{-5} hour^{-1}. Based upon this tentative conversion rate, the time required for the full carbonation of brucite in DI water would be expected to be on the order of a few decades. When more data become available, this conversion rate will be refined, and conversion rates in other solutions will also be obtained. When such conversion rates are available, these in combination with hydration rates of MgO established previously in various solutions (SNL, 2001a; 2001b; 2002) will allow estimation of the time required for the full carbonation of MgO in various solutions.

Introduction and Objectives

In the Compliance Certification Application (CCA), the DOE asserted (US DOE, 1996) that MgO, along with panel closures, shaft seals, and borehole plugs, would help meet the requirement for multiple natural and engineered barriers, one of the assurance requirements in the regulations for the radioactive constituents of transuranic waste (US EPA, 1993). In May 1998, the EPA certified that the WIPP complies with these regulations (US EPA, 1998). In its certification, the EPA ruled that MgO is the only engineered barrier in the WIPP disposal system, and that MgO will prevent or delay the movement of radionuclides toward the accessible environment by consuming the CO_2 generated by possible microbial degradation of organic materials in the waste. Furthermore, hydration of MgO will reduce the amount of brine in the repository. Finally, the reaction products of MgO will maintain the CO_2 fugacity (f_{CO_2}) and pH in the repository within optimal ranges, in which actinide solubilities in brine are at a minimum.

Experimental work carried out previously at Sandia has shown that MgO is effective at absorbing H_2O and CO_2 (Papenguth et al., 1997; 1999). Currently, more MgO will be emplaced in the WIPP than calculations suggest will be necessary to absorb CO_2 generated through microbial degradation of organic materials. At low pressures, the partial pressure of CO_2 equals to the fugacity of CO_2. At high pressures, the partial pressure of CO_2 needs to be corrected by fugacity coefficients to give the fugacity of CO_2, similar to correcting concentrations by activity coefficients to give activities in high ionic strength solutions. In total, about 70,000 metric tons of MgO will be emplaced in the WIPP to absorb CO_2.

Although the work done to date on MgO is sufficient to show that it will be an effective engineered barrier by consuming CO_2, buffering repository conditions, and limiting actinide solubilities, Sandia is currently examining several additional issues, as discussed in SNL (2001a). Experimental programs are evaluating the ability of MgO obtained from a new vendor (Premier Chemicals) to consume H_2O and CO_2, and are determining the hydration and carbonation pathways that Premier MgO will follow under WIPP-relevant conditions. The f_{CO_2} predicted by chemical speciation calculations performed for the CCA results from the assumption of equilibrium with brucite and magnetite ($MgCO_3$). However, during its evaluation of the CCA, the EPA asserted that metastable hydromagnesite is more likely than magnesite to form and persist throughout the 10,000-year period of performance of the WIPP and will have higher solubilities than magnesite. Furthermore, the EPA assumed that hydromagnesite will buffer f_{CO_2} at values higher than those calculated for the CCA. Previous work with MgO has been criticized for failing to consider the potential effect of metastable hydroxycarbonates such as hydromagnesite on repository chemistry. Sandia is currently working to identify the hydroxycarbonate phase(s) that might form.

To our knowledge, there are no previous experimental studies on the carbonation rates of MgO or its hydration product brucite under conditions relevant to the WIPP. Most of the previous experiments on the carbonation of periclase or brucite were conducted by engineers because hydromagnesite, one of the carbonation products of periclase or brucite, has several useful applications, including its use in pharmaceuticals as an inert vehicle and an adsorbent (Botha and Strydom, 2001). In these previous carbonation experiments, the partial pressures of CO_2 were at least 0.5 atm and as high as 7 atm (Fernandez et al., 1999; Botha and Strydom, 2001; and references therein). In addition, these experiments were conducted in solutions with low ionic strength (DI water, $I \approx 0$ M) (Fernandez et al., 1999; Botha and Strydom, 2001; and references therein). Clearly, such experimental conditions are irrelevant to the WIPP, in which very low partial pressures of CO_2 (at least as low as $10^{-3.5}$ atm) and solutions with high ionic strengths ($I = 7.2$ M for GWB, or 5.2 M for ERDA-6) are expected. Consequently, the results from such experiments conducted under conditions irrelevant to the WIPP cannot be used for the performance assessment of the WIPP. Therefore, carbonation experiments under conditions relevant to the WIPP must be conducted. Although there were preliminary carbonation experiments conducted at Sandia in Albuquerque (Papenguth et al., 1997), these experiments were also conducted at relatively high P_{CO_2} (1 atm).

The objectives of current experiments are multifold: (1) continued characterization of a new batch of Premier Chemicals MgO; (2) determination of hydration rates and pathways; (3) quantification of carbonation rates and identification of the metastable mineral(s) produced; (4) quantification of the effect(s) of possible lithification on hydration and carbonation rates and pathways. These experiments are described by Wang et al. (2001). All of these experiments are being run using MgO from Premier Chemicals, the new vendor supplying the repository, and pure MgO and brucite purchased from Fisher Scientific.

MgO Hydration Experiments

All hydration experiments are continuing. Since January 2002, a large amount of data has been collected. New inundated hydration experiments have been initiated to determine possible phases of magnesium chloride hydroxide hydrate forms at higher temperatures in GWB. However, samples collected to date have not been thoroughly analyzed yet. The results of the hydration experiments have been submitted as an abstract to the Material Research Society for the Fall 2002 conference.

Little space has been dedicated to the status of these experiments since the results to date have not brought forth interpretations fundamentally different than before. Instead it is the goal of this status report to concentrate primarily on what has been occurring with respect to carbonation experiments, for there is a great deal of new data to report.

Carbonation Rate Experiments

Reaction of MgO with CO_2 can produce a series of Mg-carbonate minerals with magnesite as the most stable phase (Königsberger et al., 1999). Different Mg-carbonate and hydroxycarbonate minerals impose different values of the CO_2 fugacity and possibly on brine pH. In the WIPP CCA, it was assumed that metastable Mg-carbonate minerals would ultimately be converted to magnesite. However, the EPA assumed that hydromagnesite would persist throughout the 10,000-year period of performance. The objectives of current experiments are to gain a more mechanistic understanding of MgO carbonation and determine which Mg-carbonate phase will control the f_{CO_2}. These experiments will help determine: (1) how solution chemistry affects Mg-carbonate formation; which in turn will control brine f_{CO_2} and possibly pH; (2) the carbonation rates of Premier Chemicals MgO and brucite under various conditions.

The design of carbonation experiments has been described in detail by Wang et al. (2001). Therefore, only a brief summary of these experimental designs is presented here.

Prior to carbonation, periclase hydrates to brucite or (in the case of inundated experiments with GWB) magnesium chloride hydroxide followed by brucite (SNL, 2002) as follows:

$$MgO\ (s) + H_2O\ \ (aq.\ or\ gas) = Mg(OH)_2\ (s) \qquad (1)$$

Hydration rates can be obtained from hydration experiments described in detail by SNL (2002). The carbonation experiments will provide rates of conversion of brucite to Mg-carbonate in various solutions. Using hydromagnesite as an example, the carbonation of brucite can be expressed as the following reaction,

$$5Mg(OH)_2\ (s) + 4CO_2\ (aq.\ or\ gas) = Mg_5(CO_3)_4(OH)_2{:}4H_2O \qquad (2)$$

In order to investigate the overall carbonation rates (MgO conversion to Mg-carbonate), additional experiments are being conducted using periclase as a starting material. The net reaction corresponds to the combination of Reactions 1 and 2.

As suggested by Reaction 2, carbonation can take place in both aqueous (inundated) and gaseous (humid) media. In carbonation experiments using brucite as starting material, experiments are designed to investigate carbonation rates in both aqueous and gaseous media. Most inundated experiments are conducted at $P_{CO_2} = 10^{-3.5}$

atm. Some inundated experiments are conducted at lower P_{CO_2} by utilizing the diffusivity of CO_2 dissolved in aqueous medium into polyethylene bottles containing brucite and solutions of interest. The amounts of dissolved CO_2 diffused into these polyethylene bottles are dictated by the saturation equilibrium of the carbonate phase that is forming. Then, from Henry's Law, the partial pressure of CO_2 can be obtained according to the concentration of the dissolved CO_2. In the carbonation experiments started with MgO, experiments are designed to investigate the carbonation rates in aqueous media only (inundated experiments) at P_{CO_2} of $5x10^{-2}$ and $10^{-3.5}$ atm.

In the following, preliminary results from inundated experiments using both Premier MgO and Fisher brucite as starting materials are reported.

EXPERIMENTS USING MGO AS STARTING MATERIAL

The first set of carbonation rate experiments are run at two different partial pressures of CO_2, under atmospheric conditions (~$10^{-3.5}$ atm) and 5% CO_2 ($5x10^{-2}$). In the future experiments may be run under other partial pressures, such as 1/10th atmospheric CO_2.

Experiments At Atmospheric P_{co_2} ($10^{-3.5}$atm)

Experimental Setup

The experiment running under atmospheric P_{CO_2} conditions is using four different solutions: DI water, 4 M NaCl, ERDA-6, and GWB. Each sample bottle includes 5 g 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.

Samples were collected at weekly intervals and are now collected on a monthly to bimonthly interval. Samples are measured for pH, filtered, and the solid dried and crushed. Carbonate identification and conversion rates are ascertained by using a UIC carbon coulometer, x-ray diffractometer (XRD), and scanning electron microscope (SEM) to analyze the solid phase, and an inductively coupled plasma optical emission spectrometer (ICP-OES) to analyze the filtrate. The carbon coulometer determines the percent C in the solid, whereas the XRD identifies the carbonate phase present. The SEM qualifies what elements constitute the mineral phases and shows the physical attributes of each mineral. The ICP-OES quantifies concentrations of elements of interest in sampled brines to help in the interpretation of the carbonation pathway(s).

Experimental Results

Carbonate conversion. Carbon coulometer results (corrected for mole percent carbonation) from atmospheric P_{CO_2} conditions are displayed in Figure 1. The data points represent a minimum mole percent carbonation. Calculations used a one to one ratio of moles of C to moles of Mg. If the Mg-carbonate phase were solely hydromagnesite, then the maximum value calculated would be approximately 20% higher than the results reported below. These results show that carbonation is proceeding slowly in both of the WIPP brines (ERDA-6 and GWB). Analysis of samples from ERDA-6 indicates over 7 mol % conversion, whereas samples with GWB have converted approximately 5 mol % Mg. However, these results are not surprising in view of the fact that this experiment is being run at a low P_{CO_2} in order to simulate the very slow rates at which microbial activity will produce CO_2 in the repository. (Experiments carried out at high CO_2 pressures result in faster carbonation rates, but could produce metastable Mg-hydroxycarbonates different from those that will form in the repository. These phases could in turn buffer the P_{CO_2} and pH at a value different from that expected in the repository.) In view of the uncertainties associated with these data (see error bars in Figure 1), it is not believed that the decrease in the C content of the ERDA-6 samples from 264 to 327 days represents de-carbonation, or even a cessation of carbonation, of these samples. Rather, it is likely that the overall upward trend exhibited by the ERDA-6 samples - and the samples from the other three solutions - will continue, albeit slowly.

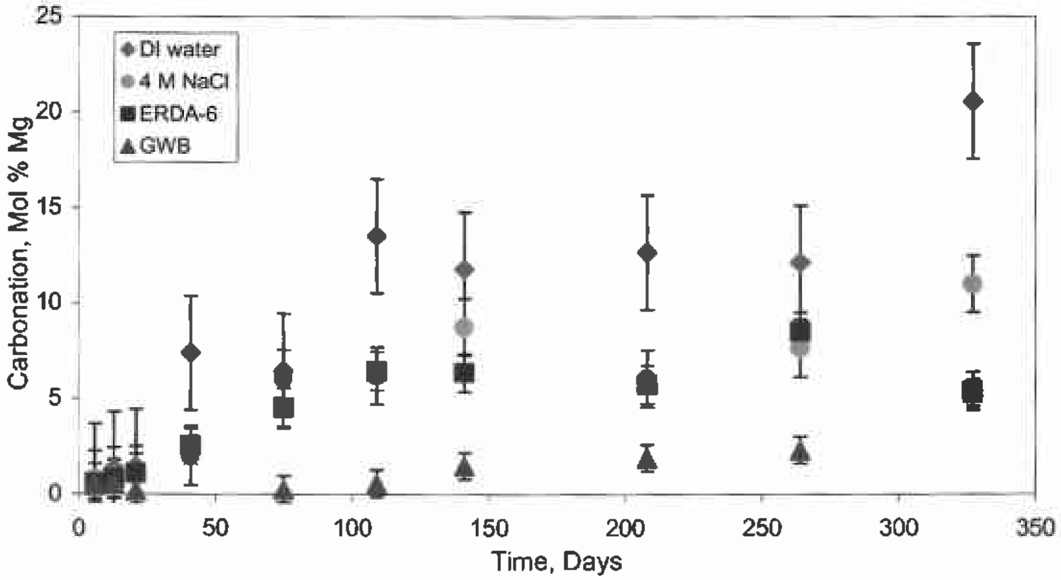

Figure 1. Results from the atmospheric P_{CO_2} experiment.

XRD results. Carbonates were not detected by XRD analysis until 264 days after the experiment had been initiated. The XRD has a detection limit of several percent. If carbonates were present before, they would constitute only a few percent of the total sample. At 264 days, 4 M NaCl was the only sample to display peaks representative of hydromagnesite and calcite ($CaCO_3$). After 327 days all four samples (DI water, 4 M NaCl, ERDA-6, and GWB) exhibited hydromagnesite and calcite peaks (Figure 2).

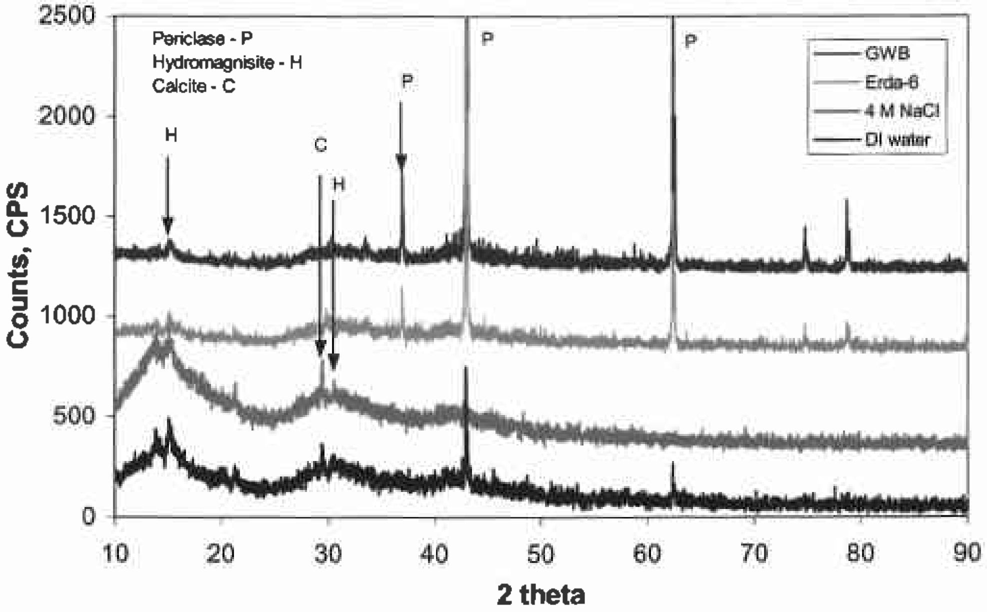

Figure 2. XRD patterns from atmospheric P_{CO2} experiments after 327 days. Note hydromagnesite (5:4:2:4; H) peaks. Hydromagnesite was confirmed using Rietveld refinement.

SEM results. After 141 days, the SEM showed the first evidence of carbonates. Ca-rich carbonates, determined using energy-dispersive x-ray spectrometry (EDS), were seen in both samples that had reacted in DI water and ERDA-6 (Figure 3). An SEM phase identification program was used to identify the carbonate phase(s) present. To identify a mineral, it must have a flat crystal surface that faces towards the detector. A pattern can then be produced as seen in Figure 4. The pattern produced did not have an exact phase ID match. The pattern most closely corresponded to a monoclinic Ca carbonate and, to a lesser degree, a Ca-Mg carbonate.

Although SEM analysis did not provide direct evidence for the conversion of brucite to a Mg carbonate, carbonate conversion calculations provided indirect evidence for carbonation of brucite. Calculations show that 1.7 mol % conversion of the total solid (ERDA-6 at 141 days) is equivalent to the conversion of ~5.7 mol % of Mg or ~7.9 mol % of Ca. However, as stated in SNL (2001), Premier Chemicals MgO contains < 1 wt % CaO. Therefore, there is not enough CaO in this material to have reacted with all of the CO_2 consumed by 141 days in ERDA-6. Assuming that there were 1 wt % CaO in the Premier Chemicals MgO, there would only be enough CaO to react with 12.7 % of the CO_2 in the ERDA-6 sample after 141 days. This calculation suggests that other carbonate-bearing minerals must be present, most likely Mg-carbonate minerals.

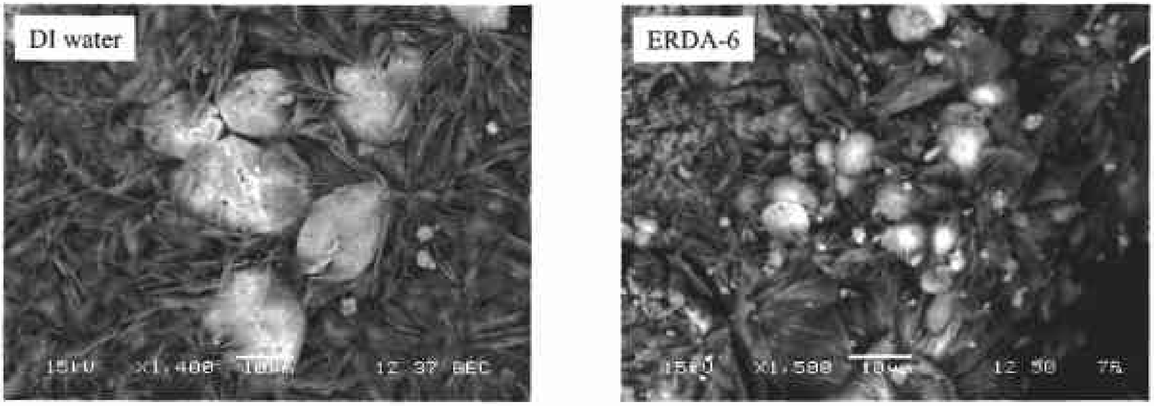

Figure 3. SEM images of Ca-carbonates (white) surrounded by brucite (gray) after 141 days.

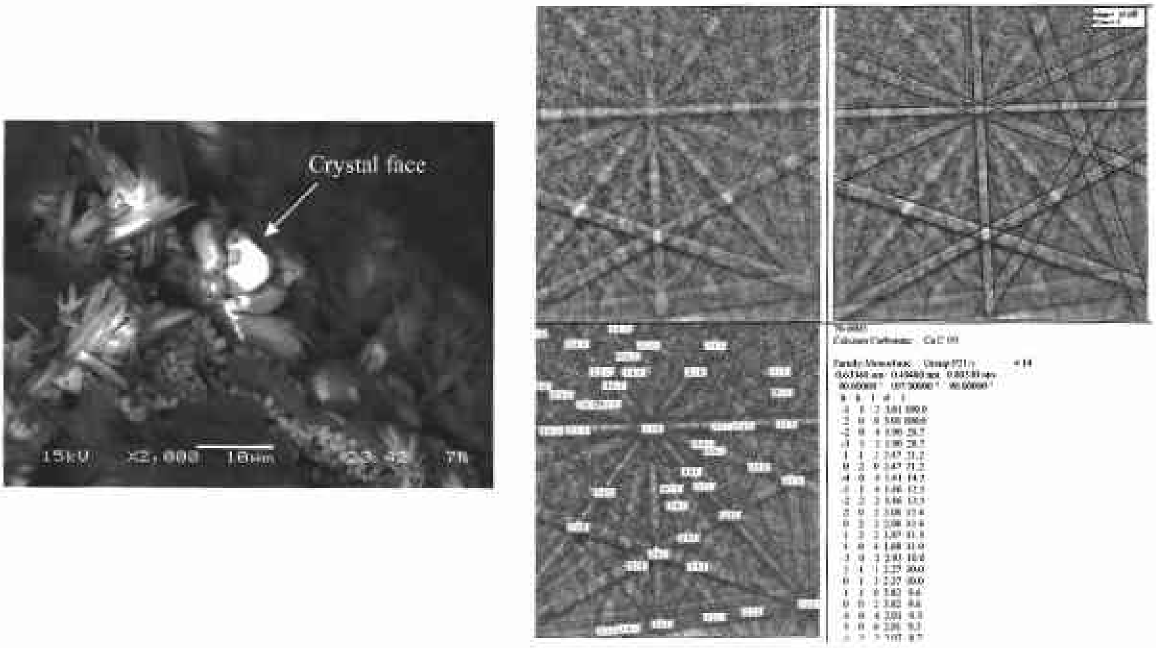

Figure 4. SEM image showing the crystal face (from a DI water sample) that was analyzed to find the accompanying pattern (right) using a SEM Phase ID program. The red lines superimposed on the pattern are a match that the computer found, identifying the mineral as a monoclinic calcium carbonate.

As suspected, after 264 days samples examined under the SEM using EDS confirmed the presence of Mg carbonates in all four solutions (Figure 5). The gray reaction mineral is most likely the Mg-carbonate mineral identified by the XRD as hydromagnesite.

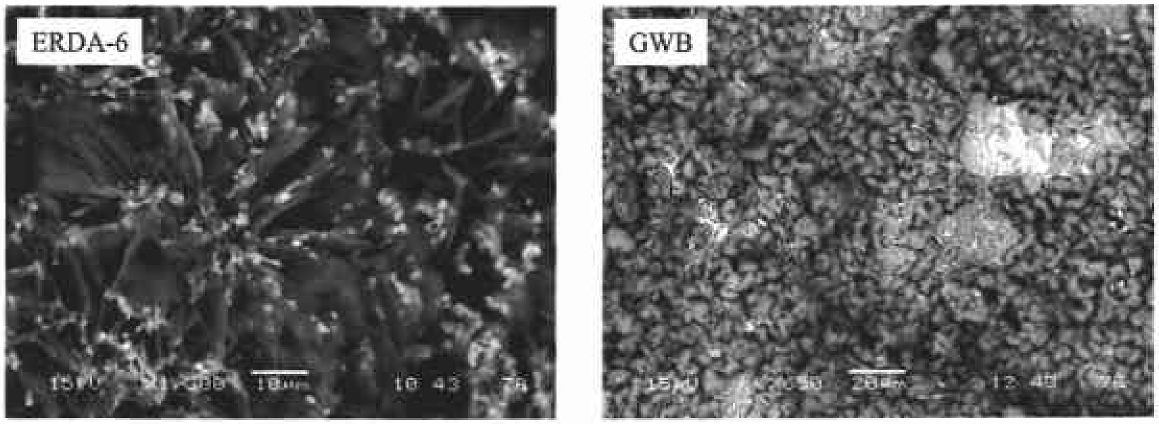

Figure 5. SEM images of Mg-carbonate minerals (gray) covered with halite (white) after 264 days.

ICP-OES results. Brine has been collected at each sampling from the atmospheric CO_2 experiments since the ninth sampling (264 days after experiment was initiated). The ICP-OES will be used to analyze the concentrations of Mg and Ca in each sample. The results will hopefully give additional information into deciphering the carbonate reaction pathway(s). To date only one set of samples has been analyzed. Consequently not enough data have been collected to make an interpretive statement. The other sets will be analyzed in the near future.

Summary

After 264 days, the SEM coupled with the XRD demonstrated that all solutions were forming a Mg-carbonate under atmospheric P_{CO_2} conditions. To date samples are continuing to carbonate, although slowly. MgO carbonates in ERDA-6 at a faster rate than GWB. The carbonates have been identified as calcite and hydromagnesite. Due to the high reactivity of lime (CaO), calcite forms first followed by hydromagnesite, a product from the reaction of periclase with CO_2. There has been no evidence to support the formation of nesquehonite.

Experiments at 5% CO_2 ($5x10^{-2.0}$atm)

Experimental Setup

The 5% CO_2 experiment will quantify carbonation in two brines, GWB and ERDA-6. The matrix of this experiment differs from that used for the atmospheric P_{CO_2} experiment. There are 64 samples (two brines x four solids x eight samples each). Each 125 ml polypropylene bottle contains 5 g of one of the following solids: Premier Chemicals MgO; Fisher Scientific MgO; "pre-hydrated", crushed Premier Chemicals MgO; and "pre-hydrated" Fisher MgO. Hydrated samples are prepared by adding 5 g of either crushed Premier Chemicals MgO, or Fisher MgO to 100 ml of brine. The bottles are placed in a 90°C oven for approximately three to four weeks. Before the "pre-hydrated" samples are added to the manifold, a small portion of the sample was analyzed for brucite. The experiment with 5% CO_2 is sampled at a higher frequency than the experiment with atmospheric P_{CO_2} due to the anticipated accelerated reactions. New sets of samples will be added periodically to extend the life of the experiment. Samples are subject to the same analyses as the atmospheric P_{CO_2} samples.

All 5% CO_2 samples are placed in a glovebox with a controlled atmosphere. The 5% CO_2 is controlled by pumping pre-mixed 5% CO_2 mixed with N_2 into the glovebox at 500 ml/min. To bring the glovebox up to 5% CO_2 in a timely manner after the box is opened for sampling, dilute sulfuric acid is mixed with sodium bicarbonate within the glovebox, which releases a pre-determined amount of CO_2 to the atmosphere. The atmosphere is monitored frequently with a Bacharach CO_2 analyzer.

Experimental Results

Carbonate Conversion. Carbon coulometer results (corrected for conversion of moles of Mg) for all four solids in both ERDA-6 and GWB are shown in Figures 6 and 7. Note that the data points represent a minimum mole percent carbonation. As expected all samples are reacting at a much faster rate than samples subjected to atmospheric partial pressures of CO_2. After only 91 days, ERDA-6 Fisher MgO has converted over 27 mol % of Mg to carbonate, and Fisher "pre-hydrated" MgO, Premier MgO, and Premier "pre-hydrated" MgO have not yet reached over 19% carbonation.

Data collected from GWB samples display more scatter. This may result from the difficulty in keeping all samples bubbling continuously. A cessation in bubbling may cause a CO_2 stratification within the liquid, thus preventing the sample from continuously being in full contact with 5% CO_2. "Pre-hydrated Fisher MgO shows the most scatter. What can be determined is that some hydrated Fisher MgO samples have converted over 18 mol % of Mg to carbonate, Fisher MgO has converted over 14 mol %, and the Premier products have converted between 6 and 11 mol %.

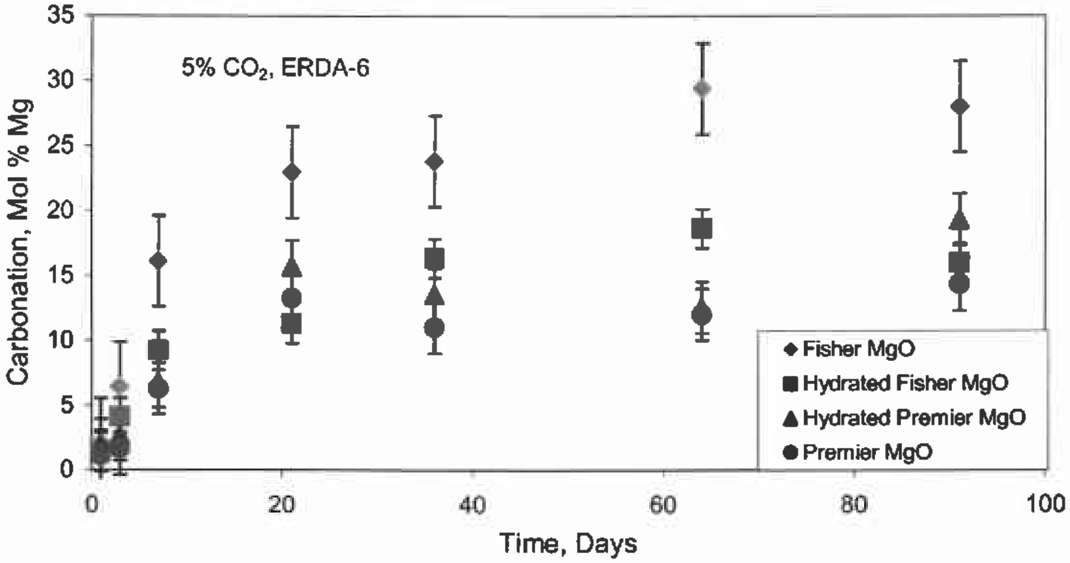

Figure 6. Results from 5% CO_2 samples inundated in ERDA-6 brine.

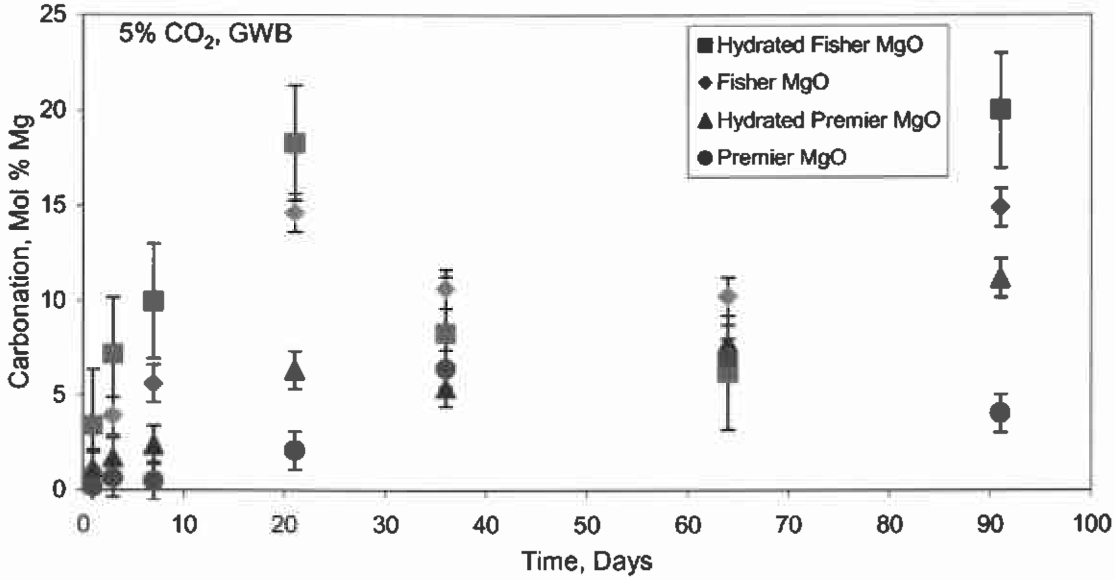

Figure 7. Results from 5% CO_2 samples inundated in GWB.

XRD Results. The XRD results within the 5% CO2 experiment suggest carbonation reaction pathways are dependent on the combination of solids, and/or brine used. ERDA-6 samples with Fisher Scientific products converted to nesquehonite first. Between seven and 21 days, Fisher "pre-hydrated" MgO converted to hydromagnesite (Figure 8). After 91 days Fisher MgO still has strong nesquehonite peaks with a possible, poorly developed hydromagnesite peak starting to form. ERDA-6 samples with Premier Chemicals MgO behave somewhat differently. Premier "pre-hydrated" MgO forms 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 (Figure 9). 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.

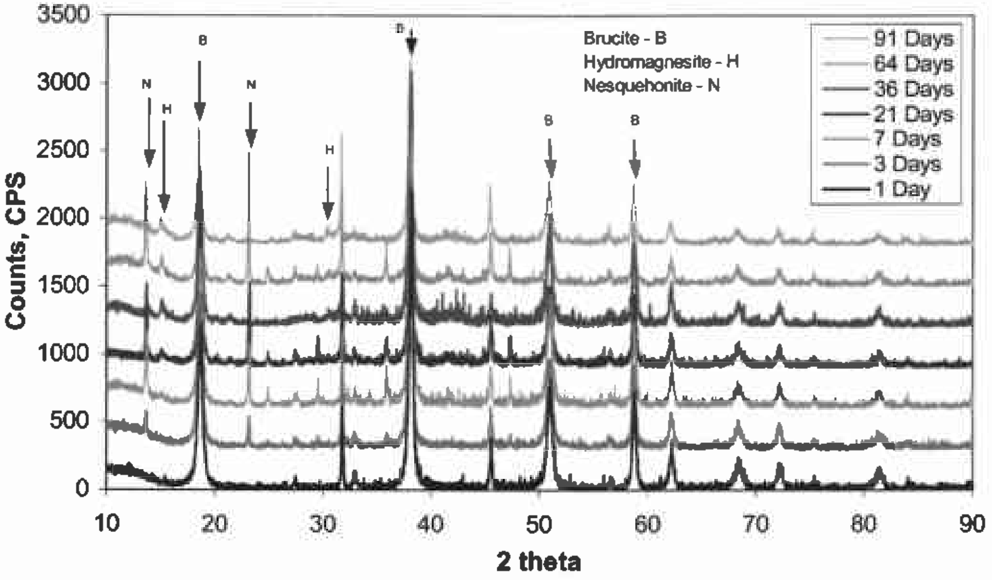

Figure 8. XRD patterns of Fisher pre-hydrated MgO inundated in ERDA-6 brine displayed sequentially through time. Note the nesquehonite (N) and hydromagnesite (5:4:2:4; H) peaks. Hydromagnesite was confirmed using Reitveld refinement. CPS- counts per second.

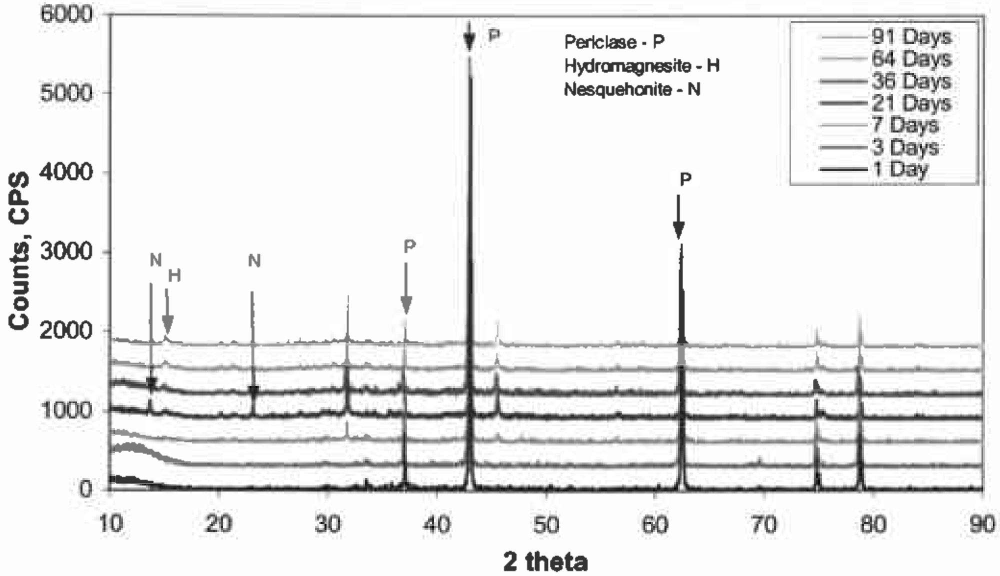

Figure 9. XRD patterns of Premier Chemicals MgO inundated in ERDA-6 displayed sequentially through time. Note hydromagnesite (5:4:2:4; H) peaks. Hydromagnesite was confirmed using Reitveld refinement.

Additionally, the GWB samples appear to skip the step of nesquehonite formation and instead form hydromagnesite. However, the hydromagnesite peak is not well developed, even after 91 days. In the Fisher products the small peak begins to appear after 21 days, whereas the hydromagnesite peak is first noted at 91 days in the samples that contained Premier Chemicals' products (Figure 10).

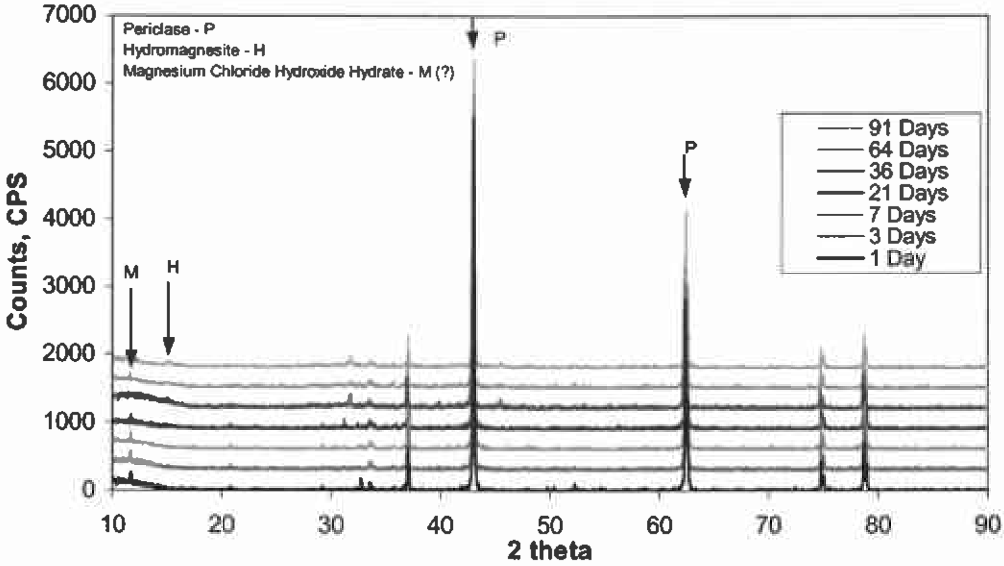

Figure 10. XRD patterns of Premier Chemicals MgO inundated in GWB displayed sequentially through time. Note hydromagnesite (5:4:2:4, H) peaks. Hydromagnesite was confirmed using Reitveld refinement.

SEM Results. The 5 % CO_2 samples taken after 91 days were analyzed on the SEM. With the aid of EDS, all samples show evidence of carbonation. The reaction products are Ca- and Mg-carbonates. All samples, except Fisher MgO in ERDA-6 brine, appear to have formed similar carbonate minerals (Figure 11), the reaction products most likely being Ca-carbonate and hydromagnesite. Fisher MgO in ERDA-6 shows a Mg-carbonate mineral, which exhibits a different crystal structure (Figure 12). Based on the data from XRD, the mineral is nesquehonite.

ICP-OES Results. Brine has been collected from every 5% CO_2 sampling. The ICP-OES will be used to analyze the dissolved concentration of Mg and Ca in each sample. The results will give additional information regarding the carbonate reaction pathway(s). To date the brine has not been analyzed.

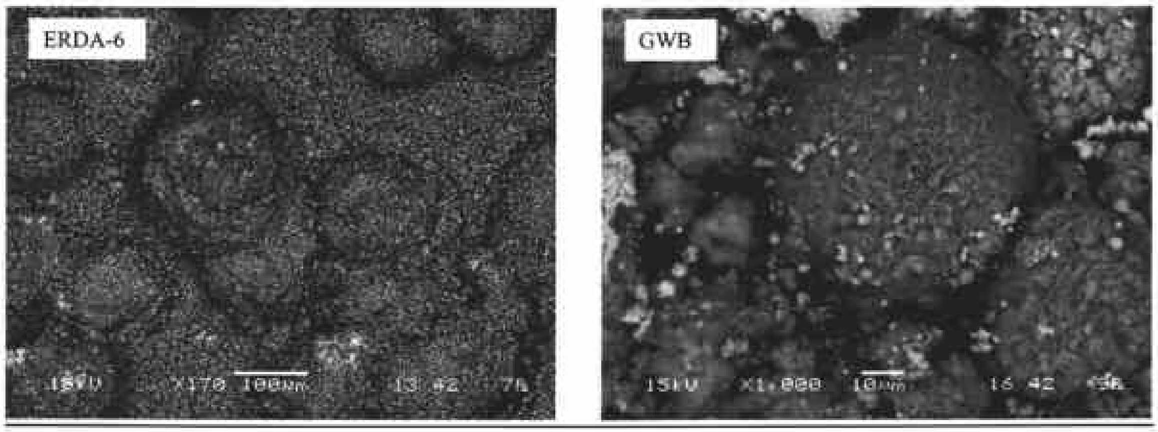

Figure 11. SEM images of Mg-carbonates (gray) found in ERDA-6 and GWB samples containing pre-hydrated Premier Chemicals MgO after 91 days.

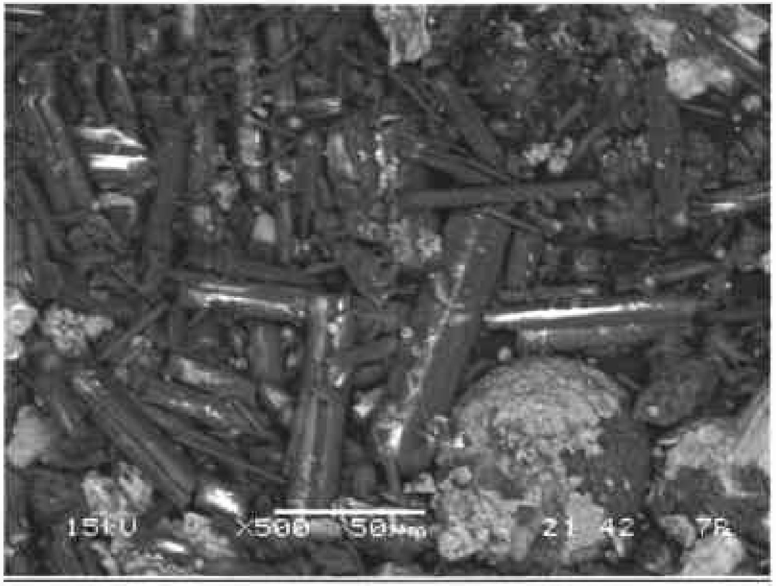

Figure 12. SEM image of nesquehonite (elongate gray crystals) present in the sample that contained Fisher MgO inundated in ERDA-6 brine after 91 days.Summary

Samples from the 5% CO_2 experiment show that carbonation is occurring at a faster rate than in the atmospheric P_{CO_2} experiment. Data exhibit more scatter in GWB, but all solids are continuing to carbonate. Carbonation pathways seem to be dependent on the solution and solid used. All solids in ERDA-6, except Fisher MgO, were converted to nesquehonite before eventually forming hydromagnesite. After 91 days, Fisher MgO has produced only nesquehonite. Solids inundated in GWB appear to have converted directly to hydromagnesite; however, the XRD peaks are not well developed.

EXPERIMENTS USING BRUCITE AS STARTING MATERIAL

In the following, results from inundated carbonation experiments using Fisher brucite in powder form as the starting material are presented in two parts. The first part covers the solution chemistry owing to carbonation processes. The second part describes the amounts of carbon incorporated in solid phases. Analysis of solution chemistry has been conducted on samples from DI H_2O and 4 M NaCl experiments. Analysis of solid phase chemistry has been conducted on samples from DI H_2O, 4 M NaCl, ERDA-6, and GWB experiments. Runs using brucite as starting material are compared to runs using uncrushed Premier MgO directly from the vender and Fisher MgO in powder form as starting material.

Solution Chemistry

In inundated experiments, solutions are sampled periodically and analyzed for Mg, Ca, K, Na, and pH. After the termination of runs, reaction products are filtered, dried and analyzed by a carbon coulometer for the amounts of C that have been incorporated into solid phase(s), and the carbonate phase(s) is determined by XRD and SEM. The advantage in analyzing dissolved chemical elements is that the carbonation processes can also be documented by changes in solution chemistry.

Figure 13 shows the change in pH with time at ionic strength close to zero (DI water) in runs using Premier MgO, Fisher MgO, and brucite. The decrease in pH in all three runs prior to 1500 hours suggests carbonation of starting materials, because it has been well established that carbonation decreases the pH (Butler, 1982). The initial pH in the run with Premier MgO is higher than initial pH in runs with Fisher MgO and brucite. After about 1500 hours, the pH values from these three runs are similar to each other and become stable. The initially higher pH in the run using Premier MgO is related to the buffering capacity of $Ca(OH)_2$, produced by the hydration of CaO:

$$CaO\ (s) + H_2O\ (l) = Ca(OH)_2\ (s) \quad (3)$$

Comparison of the initial pH in the experiment using Fisher MgO with that in the run using brucite also indicates that the initially higher pH in the run using Fisher MgO is initial dissolution of periclase. The pH values in the runs using Fisher MgO and brucite are very close to each other after about 800 hours, implying the solution in the run using Fisher MgO as starting material reaches saturation with brucite. This will be quantitatively demonstrated in the following saturation calculations.

The negative logarithm of hydrogen ion concentration (pcH) is plotted versus time for 4 M NaCl experiments in Figure 14. It can be seen from Figure 14 that changes in pcH with time in 4 M NaCl solutions have the same trends as in the runs in DI water. Accordingly, explanations for the behavior in DI water should also be true for behavior in 4 M NaCl solution. Notice that pcH instead of pH is used in these runs in 4 M NaCl solution. The relation between the pH electrode reading (pH_{ob}) and pcH can be expressed as (Rai et al., 1995):

$$pcH = pH_{ob} + A \qquad (4)$$

In Eq. (4), A is defined as:

$$A = \log \gamma_{H+} + (F/2.303RT)\, \Delta E_j, \qquad (5)$$

in which γ_{H+} is the conventional activity coefficient of H^+, and ΔE_j is the difference in liquid junction potential between standards and solution. Both terms on the right-hand side of Equation 5 are not individually measurable, but the combination can be measured. Rai et al. (1995) have already obtained A values for NaCl solutions up to 6.0 m. Therefore, the experimentally measured pH values in this study (pH_{ob}) are corrected with the A value at the corresponding ionic strength to obtain pcH.

In Figures 15 and 16, concentrations of Ca in DI water and 4 M NaCl started with Premier MgO are shown. The steady-state concentrations of Ca are attained after about 1800 hours. The initial concentrations of Ca in these two runs are close. However, the steady state concentrations in 4 M NaCl solution ($\sim 2\times10^{-5}$ m) are about four times as high as those in DI water ($\sim 5\times10^{-6}$ m).

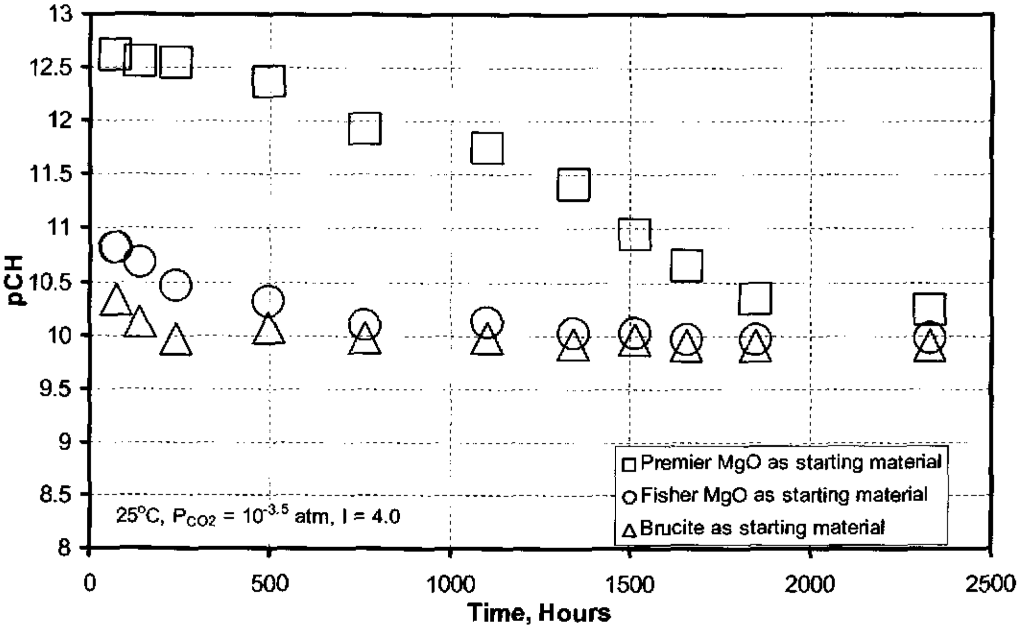

Figure 13. pH as a function of run time in DI water. The uncertainty is less than the size of symbols.

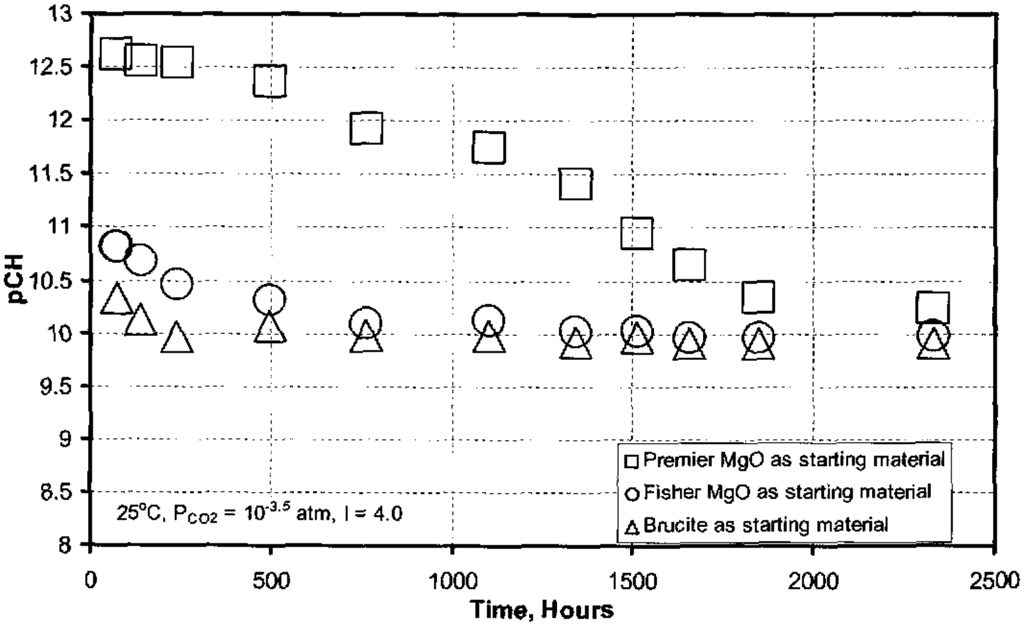

Figure 14. Hydrogen ion concentration (pcH) as a function of run time in 4 M NaCl solution. The uncertainty is less than the size of symbols.

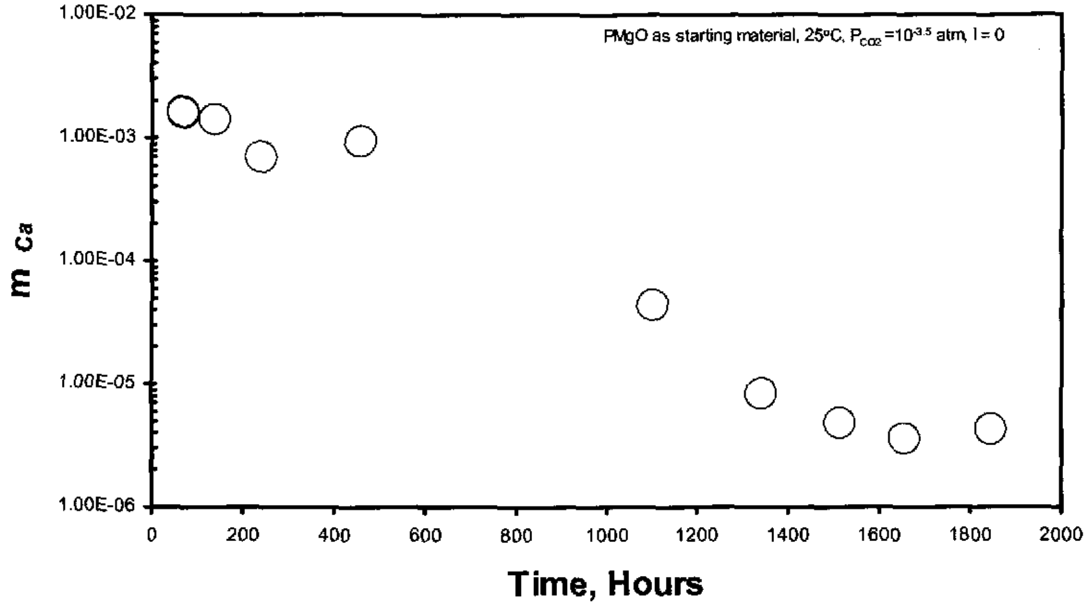

Figure 15. Ca concentration as a function of time in the DI water experiment using Premier MgO as starting material. The uncertainty is less than the size of symbols.

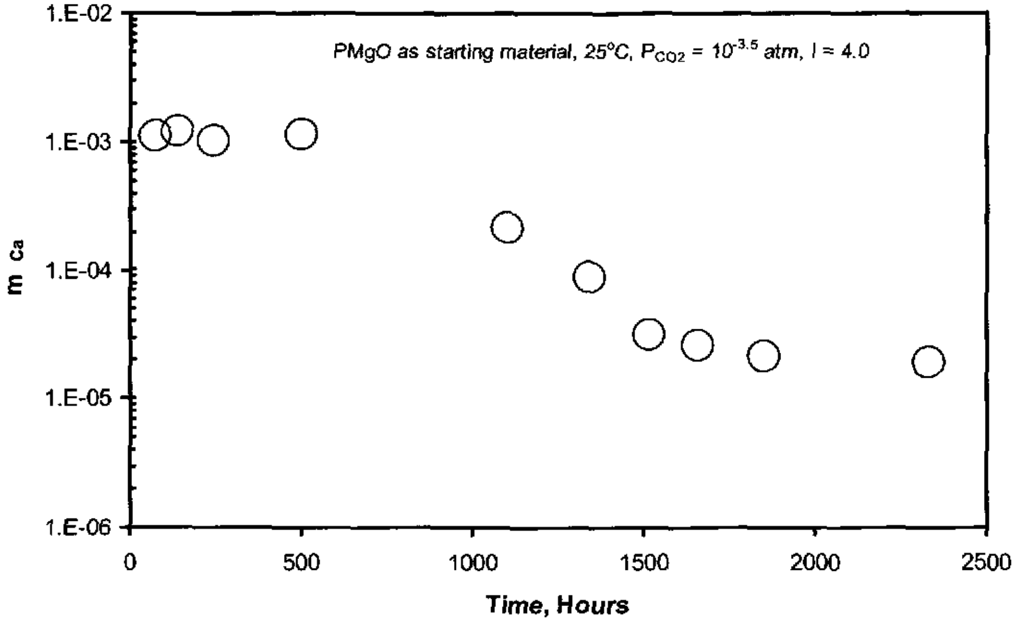

Figure 16. Ca concentration in 4 M NaCl as a function of time in the experiment using Premier MgO. Uncertainty is less than the size of symbols.

In Figure 17, concentrations of Mg in DI water are shown. The concentrations of Mg from the run started with uncrushed Premier MgO are lower than those from the runs using Fisher MgO and brucite in powder form. The lower concentrations in the run using uncrushed Premier MgO may be due to the larger size of MgO or the steady state concentrations have not been reached yet. In the runs using Fisher MgO and brucite as starting materials, the steady-state concentrations were attained after about 1100 hours, and the concentrations of Mg from these two runs using different starting materials are almost the same, implying the formation of the same solid phase(s).

In Figure 18, concentrations of Mg in 4 M NaCl solution are presented. Again, the Mg concentrations from the run using uncrushed Premier MgO are lower than those from the runs using Fisher MgO and brucite in powder form, which is consistent with the results in DI water (Figure 17). The steady-state Mg concentrations are attained after 1500 hours. The Mg concentrations from the runs using Fisher MgO and brucite are very close, implying the formation of the same solid phase(s).

On the basis of these results, the saturation states of various Mg-containing phases were calculated with the computer code EQ3NR, Version 7.2c (Wolery, 1992). Although XRD can determine whether the carbonation product(s) of interest is present when the amount of that phase exceeds a few percent, it cannot provide information regarding the onset of the formation of a particular phase. On the other hand, the saturation states would indicate the onset of the carbonation processes if the kinetics were favorable.

The saturation index (SI) is defined as:

$$SI = \log (Q/K_{sp}), \quad (6)$$

in which Q is ion activity product and K_{sp} is the solubility product for a phase of interest. When the SI of a solid phase of interest is positive in a solution, it means that the solution is supersaturated with that phase, implying that the phase has a tendency to precipitate. When the SI is negative, the solution is undersaturated with that phase, suggesting that the phase has a tendency to dissolve. When the SI is zero, the solution is in saturation equilibrium with that phase. Therefore, the SI for the following Mg-containing phases can be calculated for the following solubility reactions to infer their respective saturation states:

$$MgO\ (s) + H_2O = Mg^{+2} + 2OH^- \quad (7)$$

$$Mg(OH)_2\ (s) = Mg^{+2} + 2OH^- \quad (8)$$

$$Mg_5(CO_3)_4(OH)_2{:}4H_2O\ (s) = 5Mg^{+2} + 4CO_3^{-2} + 2OH^- + 4\ H_2O \quad (9)$$

$$Mg_4(CO_3)_3(OH)_2{:}3H_2O\ (s) = 4Mg^{+2} + 3CO_3^{-2} + 2OH^- + 3H_2O \quad (10)$$

$$MgCO_3{:}3H_2O\ (s) = Mg^{+2} + CO_3^{-2} + 3H_2O \quad (11)$$

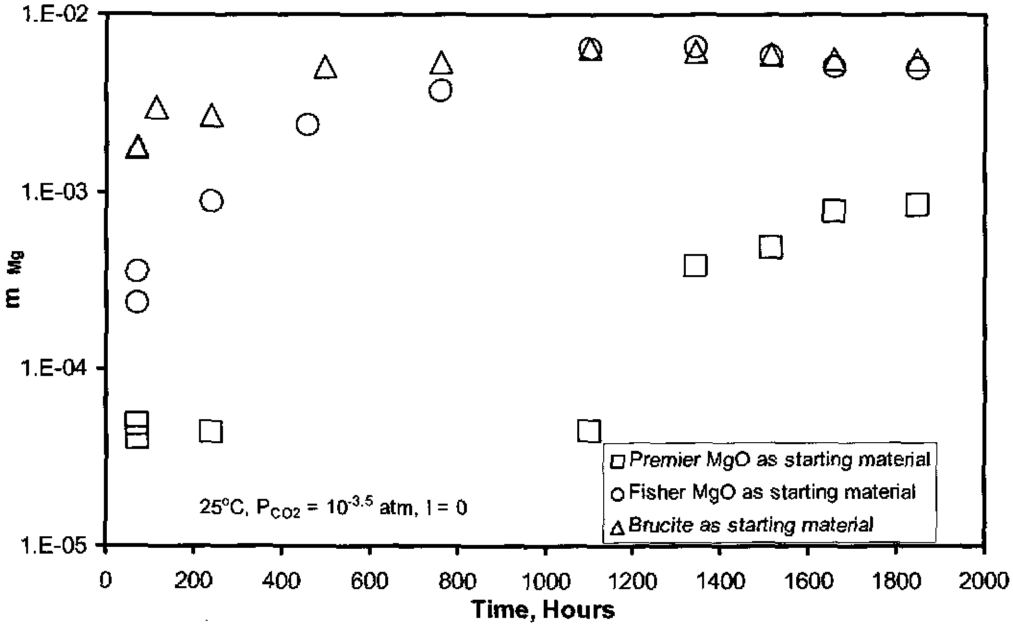

Figure 17. Mg concentration in DI water as a function of time. Uncertainty is less than the size of symbols.

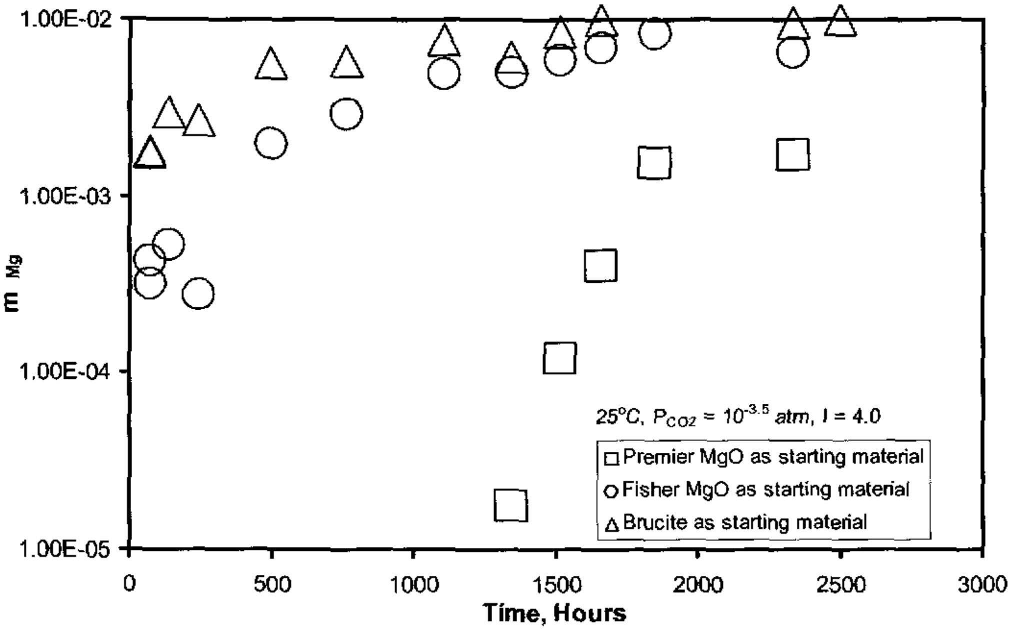

Figure 18. Mg concentration in 4 M NaCl as a function of time. Uncertainty is less than the size of symbols.

Reactions 7, 8, 9, 10, and 11 depict the solubility equilibria for periclase, brucite, hydromagnesite (5:4:2:4), hydromagnesite (4:3:2:3), and nesquehonite, respectively.

In Figure 19, SIs for the above Mg-containing phases are calculated for the results from the run in DI water started with Fisher MgO. It is shown that brucite reaches saturation after about 250 hours. This is in excellent agreement with previous hydration experiments of MgO in which hydration rates of MgO in DI water are found to be very fast (SNL, 2002). After about 500 hours, the solution becomes supersaturated with hydromagnesite (both 5:4:2:4 and 4:3:2:3), implying that hydromagnesite could precipitate because hydromagnesite is supersaturated by a few orders of magnitude. The inference that hydromagnesite is forming from the solution according to the SI of hydromagnesite is further supported by the identification of hydromagnesite in similar experiments described below. It appears from Figure 19 that the precipitation of nesquehonite is not favored. In other words, nesquehonite would not be formed under the experimental condition ($P_{CO_2} = 10^{-3.5}$ atm).

In Figure 20, SIs are shown for a run using brucite as starting material in DI water (Fisher $Mg(OH)_2$-0Cl). In contrast to the SIs described above, hydromagnesite reaches supersaturation very early in the run (after about 100 hours), suggesting that hydromagnesite could form from the solution soon after the start of the run. That hydromagnesite forms is supported by results from an almost identical run ($Mg(OH)_2$-25/AQ-1) in which hydromagnesite was positively identified using XRD (Figure 21). The run $Mg(OH)_2$-25/AQ-1 was terminated after about 1100 hours.

Figures 22 and 23 illustrate SIs for experiments in 4 M NaCl solution starting with Fisher MgO and brucite. In the run using pure MgO, hydromagnesite (5:4:2:4) reaches saturation after about 1100 hours. In contrast, in the run using brucite as starting material, hydromagnesite (both varieties) reaches saturation after about 500 hours. In both runs, nesquehonite is more clearly undersaturated (SI less than or equal to -1) than in the DI water runs. Another difference between the experimental runs in DI water and those in 4 M NaCl is that brucite seems slightly undersaturated in the latter.

An important conclusion from these results and EQ3NR modeling of experiments started with brucite is that the tendency to form nesquehonite is not thermodynamically favored in the DI water runs, and especially in 4 M NaCl runs, at $P_{CO_2} = 10^{-3.5}$ atm. Therefore, we are confident that the reaction path periclase → brucite → nesquehonite → hydromagnesite, inferred from previous experimental results at high P_{CO_2} (1 atm) at SNL in Albuquerque (Papenguth et al., 1997), is not applicable to the WIPP, in which low P_{CO_2} is expected. Instead, the reaction path in the repository and other low P_{CO_2} environments will be periclase → (magnesium chloride hydroxide hydrate) → brucite → hydromagnesite. The reaction path from periclase to brucite and from magnesium chloride hydroxide hydrate to brucite has been well documented in Papenguth et al. (1997) and SNL (2002). The reaction path from brucite to hydromagnesite is clearly demonstrated in the runs using brucite as starting material.

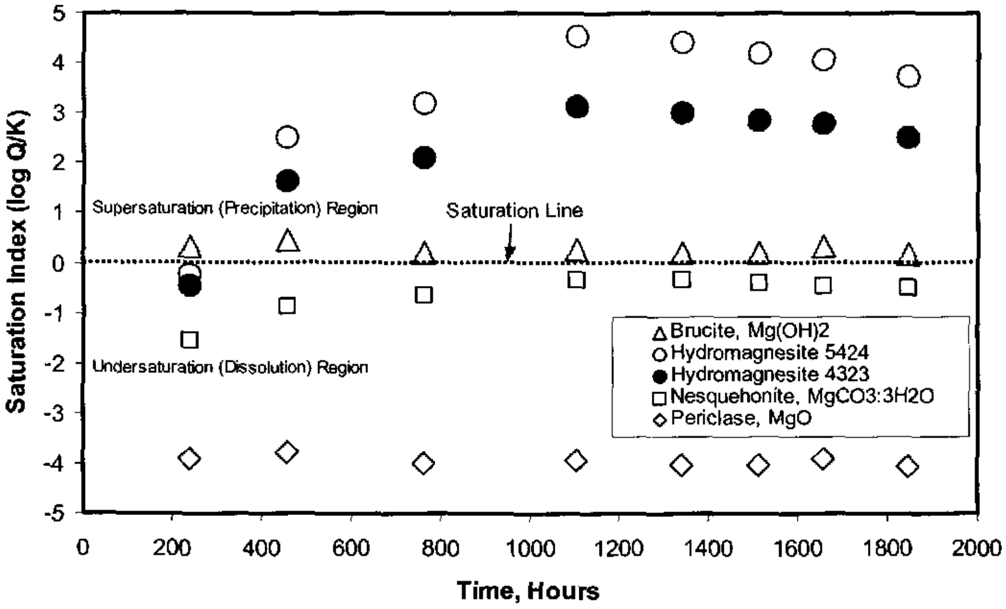

Figure 19. Saturation indexes for Mg-containing phases in the experiment containing Fisher MgO as the starting material in DI water.

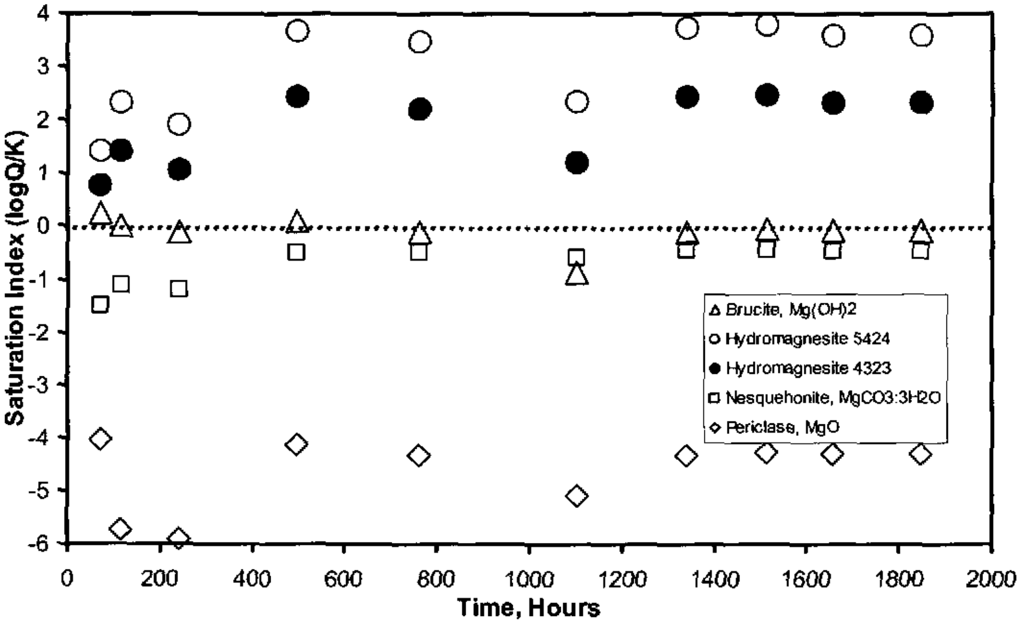

Figure 20. Saturation indexes for Mg-containing phases in the experiment using brucite as the starting material in DI water.

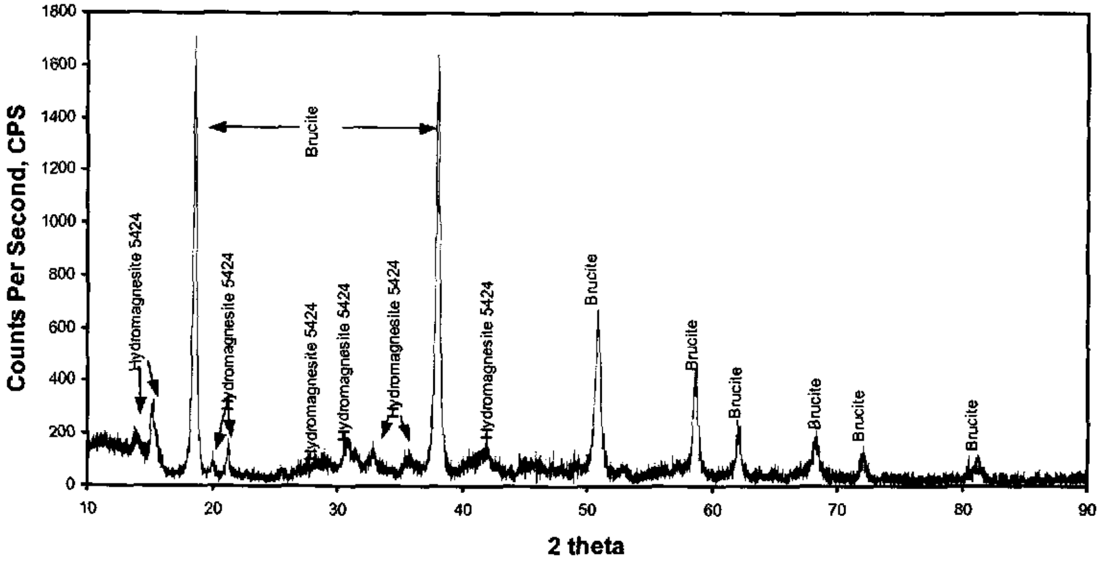

Figure 21. XRD pattern for the reaction product of the experimental run Mg(OH)2-25/AQ-1 using brucite as starting material. The experiment was conducted in DI water at $P_{CO_2} = 10^{-3.5}$ atm and 25°C. The experiment was terminated after about 1100 hours of the initiation of the experiment.

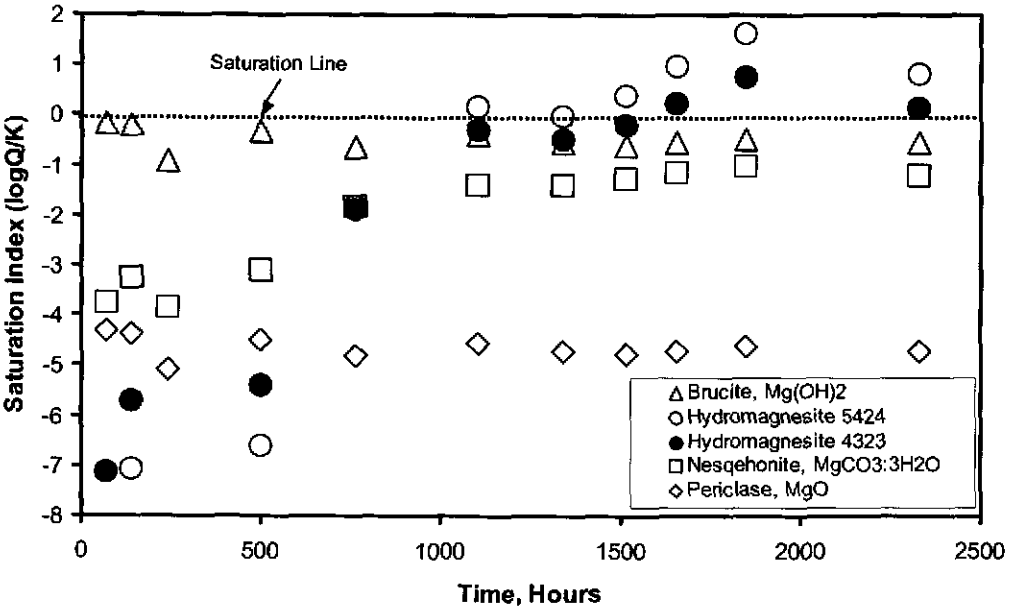

Figure 22. Saturation indexes for Mg-containing phases in the experiment using Fisher MgO as the starting material in 4 M NaCl solution.

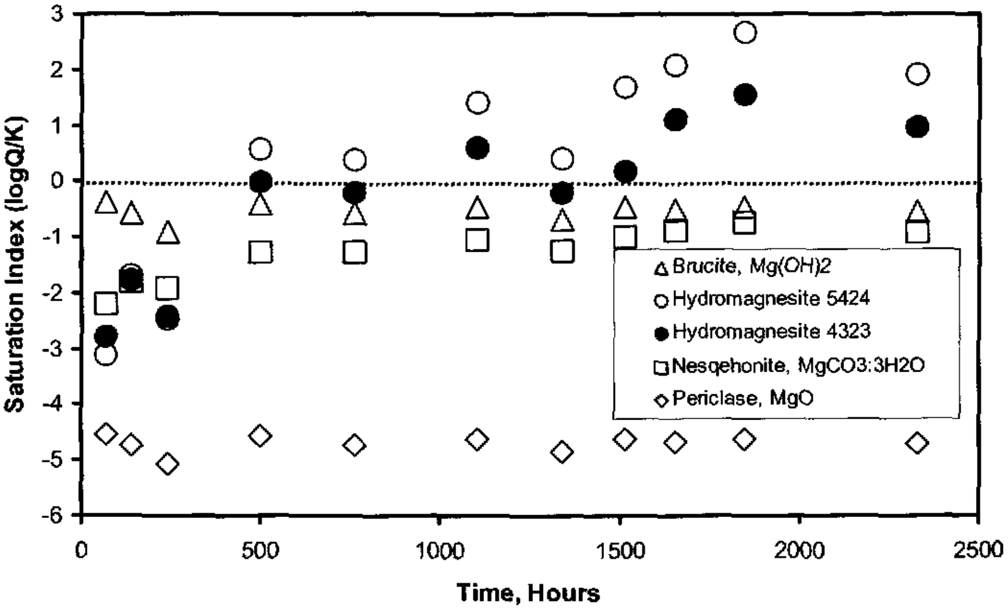

Figure 23. Saturation indexes for Mg-containing phases in the experiment using brucite as the starting material in 4 M NaCl solution.

In fact, Papenguth et al. (1997) were aware that nesquehonite would not be formed in low P_{CO_2} environments and favored the metastable phase hydromagnesite in these environments.

The above reaction path periclase → (magnesium chloride hydroxide hydrate) → brucite → hydromagnesite is well supported by field observations on the carbonation of magnesian lime exposed to atmospheric CO_2 (Bruni et al. 1998; Dheilly et al., 1999). For example, the carbonation products of historical mortars containing magnesian lime in the northern Italy exposed to air have hydromagnesite but no nesquehonite (Bruni et al., 1998).

Solid Phase Chemistry

After filtration and drying, reaction products in inundated experiments are analyzed for C using a carbon coulometer. Then, the quantities of brucite converted to hydromagnesite are calculated. In Figure 24, preliminary data for the conversion of brucite to hydromagnesite are plotted against run time. Based on preliminary data, the carbonation rate in DI water is faster than those in 4 M NaCl and ERDA-6. The carbonation rates in 4 M NaCl and ERDA-6 are similar, which may be due to the ionic strength effect. (The ionic strength of 4 M NaCl is similar to that of ERDA-6.) The C contents in the runs in GWB terminated so far are below the detection limit of the carbon coulometer. In the future, when more data, especially the data in 0.01 M, 0.1 M and

1.0 M NaCl solutions, become available, the effect of the ionic strength on the carbonation rate will be quantitatively addressed.

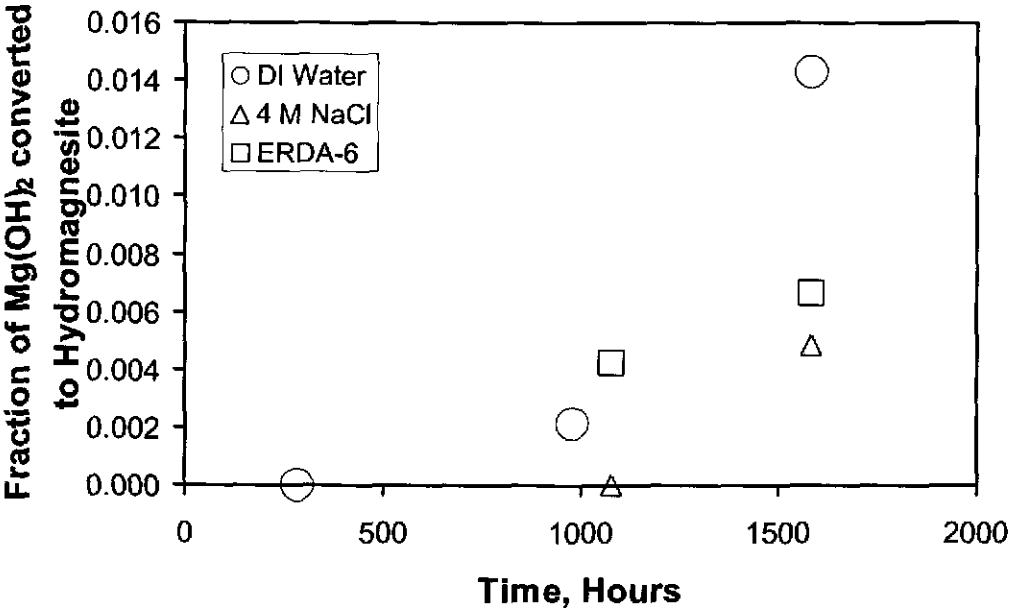

Figure 24. Brucite converted to hydromagnesite as a function of time.

The conversion rate for the experimental data in DI water obtained so far is tentatively determined to be 1.1x10^{-5} $hour^{-1}$. Using this rate, the time required for the full carbonation of brucite (i.e., 100% conversion) in DI water is on the order of 10^5 hours. Therefore, brucite should carbonate completely in a few decades. When more data become available, this rate constant of carbonation in DI water will be refined, and rate constants of carbonation in other solutions will also be determined. Then, we will be able to quantify the time required for the full carbonation of the engineered barrier.

Summary

In runs using Premier MgO as starting material at $P_{CO_2} = 10^{-3.5}$ atm (atmospheric CO_2), hydromagnesite has been positively identified in the experiment in 4 M NaCl after 264 days. After 327 days of run time, hydromagnesite has been identified in all experiments in DI water, 4 M NaCl, ERDA-6 and GWB. No nesquehonite has been observed in any experiments at $P_{CO_2} = 10^{-3.5}$ atm. However, nesquehonite is observed in the experiments at higher P_{CO_2} (5x10^{-2} atm), about 160 times the partial pressure of CO_2 in the atmosphere. In most experiments, nesquehonite was eventually converted to hydromagnesite, implying that hydromagnesite is more stable than nesquehonite even at $P_{CO_2} = 5\times10^{-2}$ atm.

In experiments using brucite (the hydration product of MgO) as starting material at $P_{CO_2} = 10^{-3.5}$ atm and 25°C, hydromagnesite was formed after about 1100 hours of the initiation of the runs. EQ3NR modeling using experimental results indicate that solutions are supersaturated with respect to hydromagnesite soon after the initiation (after about 500 hours). The modeling also indicates that nesquehonite remains undersaturated.

Based upon the above experimental results at $P_{CO_2} = 10^{-3.5}$ atm using Premier MgO and brucite as starting materials and corresponding EQ3NR modeling, it is concluded that the reaction path, periclase → brucite → nesquehonite → hydromagnesite, proposed before based upon the preliminary experimental results at high P_{CO_2} (1 atm) generated at SNL in Albuquerque (Papenguth et al., 1997), is not applicable to low P_{CO_2} environments such as the WIPP (i.e., $P_{CO_2} = 10^{-3.5}$ atm or lower). Instead, the reaction path in the repository and other low-P_{CO_2} environments will be periclase → (magnesium chloride hydroxide hydrate) → brucite → hydromagnesite. This reaction path is well supported by field observations on the carbonation of magnesian lime exposed to atmospheric CO_2.

The conversion rate of brucite to hydromagnesite in DI water was tentatively determined to be in the order of 10^{-5} $hour^{-1}$. Based on this rate, the time for the full carbonation of brucite in DI water will be in the order of a few decades. When more data become available, this conversion rate will be refined, and conversion rates in other solutions will be obtained. When such conversion rates are available, in conjunction with hydration rates of MgO already determined (SNL, 2001a; 2001b; and 2002), the time required for complete carbonation of MgO in various solutions will be estimated.

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