Hydration and Hydroxylation of MgO in Solution: NMR Identification of Proton-Containing Intermediate Phases

Jessica M. Rimsza, Eric G. Sorte, and Todd M. Alam

1Department of Geochemistry, 2Department of Organic Materials Science, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States

ABSTRACT: Magnesium oxide (MgO)-engineered barriers used in subsurface applications will be exposed to high concentration brine environments and may form stable intermediate phases that can alter the effectiveness of the barrier. To explore the formation of these secondary intermediate phases, MgO was aged in water and three different brine solutions and characterized with X-ray diffraction (XRD) and 1H magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. After aging, there is ~4% molar equivalent of a hydrogen-containing species formed. The 1H MAS NMR spectra resolved multiple minor phases not visible in XRD, indicating that diverse disordered proton-containing environments are present in addition to crystalline Mg(OH)2 brucite. Density functional theory (DFT) simulations for the proposed Mg−O−H−, Mg−Cl−O−H−, and Na−O−H−containing phases were performed to index resonances observed in the experimental 1H MAS NMR spectra. Although the intermediate crystal structures exhibited overlapping 1H NMR resonances in the spectra, Mg−O−H intermediates were attributed to the growth of resonances in the δ +1.0 to 0.0 ppm region, and Mg−Cl−O−H structures produced the increasing contributions of the δ = +2.5 to 5.0 ppm resonances in the chloride-containing brines. Overall, 1H NMR analysis of aged MgO indicates the formation of a wide range of possible intermediate structures that cannot be observed or resolved in the XRD analysis.

1. INTRODUCTION

Hydration processes of MgO and dehydration of Mg(OH)2 have been extensively investigated because of the wide application of MgO phases as refractories, catalysts, and cements. In addition, MgO has been approved for use as an engineered barrier for carbon remediation at the DOE waste isolation pilot plant (WIPP) located near Carlsbad, New Mexico, which is currently the only repository for transuranic waste in the United States. This has resulted in an increased interest in MgO hydration, particularly when these materials are in contact with aggressive subsurface brine environments. MgO was selected primarily to consume CO2 gas byproducts generated from degradation of organic materials in waste packages. In its application as a carbon remediator at the WIPP facility, the MgO barrier will be exposed to a high-salt aqueous environment as WIPP is located inside the geological Salado Salt Formation. How MgO converts to Mg(OH)2 in the presence of high concentration brines, and the presence and stability of any intermediate phases, is critical to describing the effectiveness of the engineered barrier.

Generally, the conversion of MgO to Mg(OH)2 is expected to occur in distinct steps, based on the dissolution and precipitation of MgO particles. Amaral et al. described a four-step process for hydration of MgO resulting in direct conversion of MgO to Mg(OH)2:

\[
\begin{align*}
\text{MgO}_\text{(s)} + \text{H}_2\text{O}_\text{(l)} &\rightarrow \text{MgOH}^+\text{(surface)} + \text{OH}^-\text{(aq)} \\
\text{MgOH}^+\text{(surface)} + \text{OH}^-\text{(aq)} &\rightarrow \text{MgOH}^+\text{OH}^-\text{(surface)} \\
\text{MgOH}^+\text{OH}^-\text{(surface)} &\rightarrow \text{Mg}^{2+}\text{(aq)} + 2\text{OH}^-\text{(aq)} \\
\text{Mg}^{2+}\text{(aq)} + 2\text{OH}^-\text{(aq)} &\rightarrow \text{Mg(OH)}_2\text{(s)}
\end{align*}
\]

In addition, lamellar intermediate hydration phases have been identified through Mg(OH)2 dehydration experiments and transmission electron microscopy (TEM) characterization. The stability of these different proposed phases was investigated through density functional theory (DFT) simulations, which indicated that a solid solution of oxyhydroxide intermediates with a Mg\textsubscript{x+x}O\textsubscript{x}OH\textsubscript{2y} composition may exist between MgO and Mg(OH)\textsubscript{2}. Therefore, it is

Received: October 8, 2018
Accepted: December 28, 2018
Published: January 14, 2019
expected that some secondary phases will form during aqueous aging of MgO because of incomplete hydration processes.

The identification of these intermediate phases becomes increasingly complicated when complex solution chemistries are present. Previous work on the impact of several salts (CaCl₂, KOH, MgCl₂, and MgSO₄) on the hydration process found that both the kinetics and thermodynamics of the hydration reaction were altered.¹¹ For example, the Mg⁺⁺ cations accelerated hydration, whereas Cl⁻ anions hindered it.¹ Interestingly, this effect was only seen at high salt concentrations (~10 wt %), a condition consistent with the high-salt-content brines present at WIPP.¹⁰ Long-term carbonation and aging studies of MgO have been performed for evaluation of MgO for use at WIPP. These studies used solutions that approximated the brines present at WIPP.¹⁰ The initial hydration of MgO was evaluated in di water and ERDA-6 brine.⁶ X-ray diffraction (XRD) analysis identified the formation of Mg(OH)₂ (brucite), CaCO₃ (calcite), Mg₆(PO₄)₄(OH)₂ (hydromagnesite), NaCl (halite), MgCl₂·H₂O (magnesium chloride hydroxide hydrate), Mg(HCO₃)OH·2H₂O (nesquehonite), and CaSO₄ (anhydrite) during brine + MgO + CO₂ interactions over many years. In addition, the formation of Mg₂SiO₄·8H₂O and Phase 5 (5Mg(OH)₂·H₂O) and Phase 5 (5Mg(OH)₂·H₂O) magnesium chloride hydroxide hydrates, termed for the ratio of OH/Cl, in hydrated MgO. The Phase 3 species has long-standing geological interest as a proposed pH buffer in saline environments since the 1970s.¹¹ More recently, evaluation of the solubility constant of the Phase 5 species has suggested that it is stable in GWB solutions and therefore is likely to be present in aged MgO engineered barriers. Additionally, in engineered materials, Phase 3 and Phase 5 both have been observed to impact the properties of Sorel cement.³,12 Therefore, a detailed understanding of how MgO reacts with brine solutions, and what hydroxylated and hydrated phases are produced in those interactions, is valuable in both geological and engineered material fields.

In addition to the crystalline structures discussed above, intermediate phases or structures formed during hydration may be highly disordered and present in relatively small concentrations, making identification of all secondary phases by common diffraction-based techniques challenging. Here, we demonstrate the use of nuclear magnetic resonance (NMR) spectroscopy as a tool to explore these hydrated intermediate MgO phases. NMR has proven to be a powerful tool in the study of disordered phases in the solid state,¹³ including ceramics, oxides, glasses, and polymers. As NMR is nucleus specific (e.g., ¹H, ²Li, ³¹O, ²³Si, and so forth), the local atomic structures can be directly probed and the technique does not depend on the retention of a periodic ordered structure. Recent advances in using first-principle computational methods¹⁴–¹⁵ to predict NMR parameters for different structural models (including disordered and amorphous structures) have proven critical in the interpretation of solid-state NMR results in disordered materials.

Solid-state ¹H magic angle spinning (MAS) NMR has been used to determine low water concentrations in mantle silicates because of the relatively high sensitivity of protons.¹⁶–¹⁷ NMR has also been successful in identifying different hydroxylated and hydration phases in minerals, nominally anhydrous minerals, and clays with studies including multinuclear NMR characterization of montmorillonite¹⁸ and the identification of Mg-AlₙOH (n = 1, 2 and 3) environments in layered clays.²⁰ The ¹H MAS NMR results for these systems demonstrated that the chemical shift is impacted by both the strength of local hydrogen bonding and the nature and ratio of the neighboring cations present in the material.

Combined solid-state ¹H, ³¹O, and ²⁵Mg MAS NMR methods have been used to characterize Mg-containing minerals and phases, including wadsleyite (β-Mg₃SiO₄),²¹–²³ ringwoodites (γ-Mg₂SiO₄),²⁴,²⁵ Mg acetates (Mg(CH₃COO)₂·nH₂O),²⁶ Mg-containing double hydroxides,²⁷ and hydrous magnesium silicates.²⁸ ³¹C MAS NMR has been used to characterize magnesium carbonate minerals.²⁹ ¹H MAS NMR studies on MgO have been more limited but involve the identification of hydroxyls in solid oxide catalysts,³⁰,³¹ and MgOH thermal decomposition or the formation of hydroxyls following water adsorption on MgO surfaces.³²,³³ A more extensive study combining ¹H MAS NMR and DFT computations for hydroxylated MgO surfaces has been reported² and identified three major proton environment types on the MgO surface, whereas the DFT cluster calculations assisted in the assignment and spectral deconvolution of the different (overlapping) OH-group resonances.

Despite the extensive interest in MgO interactions with brine solutions, unanswered questions on the possible formation of stable or semistable magnesium oxychlorides during MgO hydration in brine conditions persist. The identification of such phases provides insight into the stability of the MgO engineered barrier and their effects on the transition kinetics of MgO to Mg(OH)₂. In this paper, we investigate the formation of these intermediate phases by hydrating two different MgO materials in three different high-salinity solutions including DI water and three salt solutions: GWB, and 1 M NaCl (additional details in Supporting Information). The formation of intermediate phases during hydration would be expected to depend on the starting characteristics of the MgO material, particularly if significant differences in surface reactivity, structure, or particle size exist. Even visually, the two starting materials (WIPP-MgO and Marinco-MgO) appear very different (details for the two MgO samples are given in the Materials and Methods section). Marinco-MgO is a soft, white, fine-grained powder, whereas WIPP-MgO is a gray or off-white powder with hard, granular, large (~1 mm) particles as seen in Figure 1. Scanning electron microscopy (SEM) also reveals marked differences in the particle shape and surface structure. The Marinco-MgO particles appear to be composed of irregular, plate-like structures (Figure 2a), which transform into a more featured surface following aqueous aging in water or brine solutions (Figure 2b). In comparison, the WIPP-MgO contains rounded, smooth surface particles (Figure 2c), which evolve into more plate-like phases after aqueous exposure.
Based on studies of MgO dissolution with controlled particle sizes, the particle dimensions are well known to impact diffusion rates. Therefore, we anticipate that the larger average particle size of the WIPP samples are impacting the conversion rate of MgO to Mg(OH)₂. The finer grains of the Marinco-MgO result in a larger surface area/volume ratio, suggesting that there will be a higher initial MgO to Mg(OH)₂ conversion rate in these samples compared to the WIPP-MgO. Generally, this work is focused on aging of MgO samples in their as-received bulk state, where additional refining of the material (controlling particle size or shape) was not performed. Therefore, the tested MgO materials have a mixture of particles sizes and different MgO surfaces present for reaction with the aqueous solutions. Previous investigations have noted differences in dissolution rates on the MgO(100), (110), and (111) surfaces. As the water pressure increases, it is predicted that the (100) surface becomes less stable, resulting in formation of hydroxylated (110) and (111) surfaces at 300 K and 1 atm partial pressure of water, through a Wulff plot construction. For a small cubic particle, it is predicted that the controlled conversion of the (100) to the (110) surface causes some passivating effects, decreasing dissolution rate for particles with diameters between 10 nm to 1 μm. Both of the MgO materials used here have highly disordered particle shape and sizes, and therefore are not expected to form any passivating layers from complete transformation of the (100) surface to (110) as might be expected for perfectly cubic samples. The formation of the plate-like structures noted in Figure 2 is consistent with a variety of published literature. SEM has identified thin nanosheets organized as lamellar structures of “micro/nanoflowers” with microstructures comparable with the SEM results included here.

2.1. Identification of Intermediate Phases. Intermediate phases formed during Mg(OH)₂ dehydration have been previously reported from TEM characterization of the surface during dehydration. Other reports of MgO hydration in brine solutions noted the development of a wide variety of mineral phases from XRD but did not indicate if intermediate phases were formed. Therefore, questions arise concerning the presence of secondary or intermediate phases and their relative concentration during MgO hydration. Typically, XRD has been the most common method for identifying the formation of crystalline intermediates, and here, XRD of the initial material and the hydrolyzed MgO are presented in Figure 3. For both Marinco−MgO and WIPP-MgO, the XRD reveals that the crystalline component contains primarily MgO (periclase, 2θ = 36.9, 42.9). The Marinco-MgO also has some concentration of slightly disordered Mg(OH)₂ (brucite, 2θ = 18.6, 32.8, 38.0, 50.8, 57.9, 58.6). The sharp diffraction observed near 2θ = 16.5° evident in some traces is an instrumental sampling configuration artifact unrelated to MgO. The observation of the Mg(OH)₂ phase could represent a species initially in the material or represent a hydrated phase possibly forming during the long-time shelf storage of the material (~15 years). Analysis shows that 33 wt % of the crystalline phases in the starting Marinco-MgO material is Mg(OH)₂, whereas WIPP-MgO shows ~100% MgO phase.
After aqueous aging in DI water for 16 weeks, the crystalline MgO peaks in the XRD of Marinco-MgO (Figure 3a) disappear almost completely because of either conversion of all MgO to the Mg(OH)$_2$ hydroxide phase or disordering of the initially crystalline MgO solid into very small crystallites or a highly disordered amorphous phase for which scattering does not occur. This disordering of the MgO phase is supported by the $^1$H MAS NMR (see below) where the total proton molar concentration of the hydrated phase is only a few percent with respect to Mg. Conversely, the XRD of WIPP-MgO retains measurable (though significantly reduced) crystalline MgO scattering intensity after equivalent aging. This difference in behavior between the two MgO starting materials is attributed to the initial physical properties and surface structure of the samples (Figures 1 and 2), with the hard, large grains of WIPP-MgO being less impacted during the short hydration period (16 weeks) in comparison to Marinco-MgO. Following aging in NaCl solutions, the XRD also reveals formation of a crystalline NaCl phase in both MgO samples (Figure 3) with no other crystalline phases being detected in the XRD.

Figure 4 shows the $^1$H MAS NMR spectra of each MgO material following aging at 80 °C in the different water and brine solutions. The most prominent hydrogen-containing phases generated ($\delta = -0.3$ to 0.8 ppm) are assigned to isolated MgOH proton environments that are not strongly hydrogen bonded to nearby atoms; this is consistent with Mg(OH)$_2$ observed in the XRD (Figure 3). The $^1$H NMR also reveals resonances between $\delta = +3.0$ and +4.8 ppm consistent with different H$_2$O hydration environments, whereas the resonances between $\delta = +6.0$ and +7.0 ppm result from the proton in either OH or H$_2$O that is in hydrogen-bonded environments.\(^{42}\) Note that the $^1$H MAS NMR spectra resolve multiple proton-containing phases that are not visible in XRD, including the 4–10 different MgOH-type phases. Except for the MgO materials aged in the GWB brine, these multiple MgOH phases are the dominant intermediate species produced during aging (73–76%) for DI, NaCl and ERDA M$^6$. In the GWB-aged materials, the MgOH phases constitute only $\sim 39$ to 42% of the total proton concentration. The proton-containing phases and relative concentration resulting from aging in DI water and 1 M NaCl brine are very similar, with the WIPP-MgO and Marinco-MgO materials giving equivalent results except for the minor increase in sharpness (lower disorder) of the NMR resonances in the Marinco-MgO samples. The Marinco-MgO material from the DI and NaCl brine aging also had a minor increase in the $\delta = +0.3$ ppm environment concentration. For the ERDA-6 brine-aged materials, the WIPP-MgO has a higher concentration of the OH environments (90%) in comparison to the aged Marinco-MgO (76%, see Figure 4).

The complexity of the high number of different proton-containing MgOH phases can be realized by analyzing the double quantum (DQ)-filtered $^1$H MAS spectra shown in Figure 5. In these types of filtered experiments, only resonances that have significant $^1$H–$^1$H dipolar coupling will be retained. Increasing the length of the DQ excitation period ($N_2 =$ number of rotor periods during excitation) will also modulate the relative intensity and type of resonances observed. For example, at $N_2 = 1$, only proton environments having the strongest dipolar coupling contribute to the signal and produce the broad resonances that are hidden under the sharper resonances in the Hahn echo spectra (Figure 5, top). As the dipolar coupling strength scales with the $^1$H–$^1$H distance as $r^{-3}$, these broad resonances arise from environments with smaller distances or higher number of $^1$H–$^1$H contacts. With increasing $N_2$, $^1$H environments with slightly weaker dipolar coupling begin to appear until the sharper resonances begin to dominate the NMR spectra ($N_2 = 4$, Figure 5, bottom). Spectral filtering can also be obtained based on spin relaxation, including spin–spin relaxation time ($T_2$)-filtered experiments (see Figure S3 in Supporting Information). In the $T_2$-filtered experiments, the broad resonances with short $T_2$ values are suppressed, whereas those proton environments with long $T_2$ times are retained, producing spectra that are dominated by the narrow resonances. These distinct types of filtering experiments allow us to identify the multiple proton-containing phases (\(\sim 15\)) present in the aged MgO materials and were used to fix variables during the deconvolution process.

Additional details about the multiple $^1$H environments can be obtained by looking at the 2D DQ–SQ (single quantum) $^1$H MAS NMR correlation spectra as shown in Figure 6. In these 2D NMR experiments, correlations (peaks) are observed for protons that are spatially near each other and thus experience significant $^1$H–$^1$H dipolar coupling. Peaks that are observed on the diagonal (dashed line) are auto-correlation resonances and arise from equivalent $^1$H environments that are spatially near each other (solid circles designate distinct $^1$H species). The resonances between $\delta = +2$ and $-2$ ppm are all MgOH-type environments with the presence of auto-correlation peaks demonstrating that they interact mainly with $^1$H that are in the same environment (same chemical shift) and are in the same proton-containing phase. The exception to this is the missing autocorrelation peak for the $\delta = -2.5$ ppm resonance, which shows that this proton environment is not near other protons, which is consistent with the assignment as an isolated hydroxyl species based on the chemical shift range. Off-diagonal correlation peaks (colored boxes) reveal $^1$H–$^1$H dipolar coupling between different proton environments (chemical shifts) and are not very strong.
in the 2D DQ NMR experiments. There is some weak correlation between select MgOH ($\delta = +2$ to $-2$ ppm) and H$_2$O environments ($\delta = 2.5$ to $6$ ppm) and would be consistent with the different Mg(OH)$_2$·$n$H$_2$O phases discussed below. On the other hand, these 2D NMR experiments reveal that the majority of MgOH produced exists in a nonhydrated phase.

These resonance assignments are also supported by previous $^1$H MAS NMR investigations of Chizallet et al. on MgO surface hydration, where DFT calculations were used to identify unique OH sites on the MgO surface. They assigned different $^1$H NMR chemical shift ranges based on the local surface environments of the OH species and classified them into three distinct domains: (i) the larger chemical shifts (+$1.2 > \delta > -0.7$ ppm) were assigned to hydrogen bond donor OH groups, (ii) hydrogen bond acceptor or isolated OH groups were assigned to the more negative chemical shifts ($< -0.7$ ppm) and have been related to catalytically active surface sites such as steps or corners, and (iii) resonances near $\delta \approx -0.7$ ppm resulting from OH species near kinks and divacancies in the MgO surface. Although their NMR spectra are similar to the results reported here (Figure 4), it is important to note that the study utilized clean MgO surfaces produced by high temperature treatment ($\approx 1023$ K), thus eliminating the presence of carbonates, water, and excess hydroxyl concentrations. Our MgO samples obtained after aqueous aging are expected to contain both waters of hydration and possibly carbonate species sequestered from the atmosphere.

Alternatively, the existence of Mg(OH)$_2$-based intermediate phases have been indicated by previous dehydration studies with a series of compounds containing different hydroxide compositions and packing densities proposed. As NMR is sensitive to local atomic-level proton environments, we explored the possibility of using DFT chemical shift calculations to separate or identify these different overlapping OH-group resonances ($\delta = 0.2$ to $-2.2$ ppm) observed in Figure 4. The $^1$H NMR chemical shifts and densities for seven different Mg–O–H structures were calculated and are summarized in Table 1. These intermediate MgOH-type structures result from a proposed lamellar decomposition path of Mg(OH)$_2$ based on layer-by-layer dehydroxylate covering 20–80% hydroxide content. Crystal structures were obtained from the crystallography open database (COD) and information on the creation of these different structure models has been described previously. The optimized, structurally relaxed structures are provided in the Supporting Information; the calculated $^1$H NMR chemical shifts (Table 1) range from $\delta = -0.18$ to $0.78$ ppm and reflect a narrow range of local proton environments. The spectral overlap in Figure 4, along with the ±$0.25$ ppm error between the experimentally observed NMR chemical and DFT-calculated chemical shifts (Sorte et al., unpublished), make it...
Table 1. Structure, Densities, and $^1$H NMR Chemical Shifts for Selected Magnesium Hydroxide Structures$^a$

| structure name | density (g/cm$^3$) | $\delta$ (ppm) | COD ID |
|----------------|-------------------|----------------|--------|
| Mg$_4$O$_9$(OH)$_8$2H$_2$O | 1.54 | 1.59 | 2.62, 3.09, 4.87, 4.89 |
| Mg$_5$O$_3$(OH)$_6$·H$_2$O | 1.58 | 1.65 | 4.30, 4.33, 4.40, 4.64 |
| Mg$_3$O(OH)$_2$·H$_2$O | 1.79 | 1.90 | 4.41 |
| Mg$_3$O(OH)$_2$·H$_2$O | 1.97 | 2.02 | 4.05, 4.28 |
| Mg(OH)$_2$·H$_2$O | 1.86 | 1.94 | 3.07, 4.39 |
| 2Mg(OH)$_2$·MgCl$_2$·8H$_2$O | 2.06 | 2.22 | 3.33 |
| 3Mg(OH)$_2$·MgCl$_2$·8H$_2$O | 1.67 | 1.86 | −0.13, 0.15, 0.26, 3.47, 3.60, 3.87, 4.32, 5.78, 6.08, 6.38, 11.61 |
| 5Mg(OH)$_2$·MgCl$_2$·8H$_2$O | 1.82 | 1.91 | −2.32, 0.64, 1.21, 1.56, 1.75, 1.92, 4.71, 4.80, 5.03, 8.24 |

$^a$Multiple chemical shifts indicate multiple H environments in the crystal structure.

Table 2. Chemical Structures, Densities, and $^1$H NMR Chemical Shifts for Selected Magnesium Chloride Hydroxide Structures$^a$

| structure name | density (g/cm$^3$) | $\delta$ (ppm) | COD ID |
|----------------|-------------------|----------------|--------|
| MgCl$_2$·6H$_2$O | 1.54 | 1.59 | 2.62, 3.09, 4.87, 4.89 |
| MgCl$_2$·4H$_2$O | 1.58 | 1.65 | 4.30, 4.33, 4.40, 4.64 |
| MgCl$_2$·2H$_2$O | 1.79 | 1.90 | 4.41 |
| MgCl$_2$·H$_2$O | 1.97 | 2.02 | 4.05, 4.28 |
| Mg(ClO$_4$)$_2$·4H$_2$O | 1.86 | 1.94 | 3.07, 4.39 |
| Mg(ClO$_4$)$_2$·2H$_2$O | 2.06 | 2.22 | 3.33 |
| 3Mg(OH)$_2$·MgCl$_2$·8H$_2$O | 1.67 | 1.86 | −0.13, 0.15, 0.26, 3.47, 3.60, 3.87, 4.32, 5.78, 6.08, 6.38, 11.61 |
| 5Mg(OH)$_2$·MgCl$_2$·8H$_2$O | 1.82 | 1.91 | −2.32, 0.64, 1.21, 1.56, 1.75, 1.92, 4.71, 4.80, 5.03, 8.24 |

$^a$Multiple chemical shifts indicate multiple H environments in the crystal structure.
hydrogen-containing phase formation occurred in the samples aged either at 20°C converted to hydrated or hydroxyl phases. For the sets of means of quantifying the extent to which MgO has been determine the total proton concentration (Figure 9) as a sa From the integration of these NMR spectra, it is possible to determine the total proton concentration (Figure 9) as a means of quantifying the extent to which MgO has been converted to hydrated or hydroxyl phases. For the sets of samples aged either at 20°C or at 80°C, the majority of hydrogen-containing phase formation occurred in the first four weeks, with less significant changes in proton concentration occurring in the subsequent aging time. Of course, 16 weeks is a brief time period on geological time scales, but these initial formed phases represent the most reactive MgO sites available for hydration and hydroxide formation. These results show that the hydrogen concentration is ~4% of the original MgO concentration. Marinco-MgO exhibits a consistently higher hydrogen concentration than WIPP-MgO, with the highest hydrogen concentration occurring for the DI-aged samples, followed by NaCl, GWB, and ERDA6 brine solutions.

Table 3. Chemical Structure, Densities, and 1H NMR Chemical Shifts for Selected Sodium Hydroxide Structures

| structure name | density (g/cm³) | comp. | exper. | δ (ppm) | COD ID | notes |
|---------------|----------------|-------|--------|---------|--------|-------|
| NaOH·H₂O     | 1.63           | 1.69  | 2.69, 7.78, 8.15  |         | 1532133 | layered hydrated NaOH structure |
| NaOH·3H₂O    | 1.40           | 1.45  | ~0.16, 2.17, 2.70, 3.37, 4.14, 4.48, 4.73, 4.90, 5.23, 5.91, 6.18, 6.36, 6.48, 6.68, 6.80, 8.84 |         | 1532134 | |
| α-NaOH·4H₂O  | 1.27           | 1.29  | 0.74, 2.27, 3.89, 4.14, 6.97, 7.56, 7.71, 9.86, 11.57 |         | 1532135 | |
| β-NaOH·4H₂O  | 1.33           | 1.31  | 0.16, 2.60, 3.00, 4.69, 5.13, 6.45, 7.24, 9.29 |         | 1532136 | |
| Na₂O₂·8H₂O   | 1.49           | 1.57  | 1.41, 3.70, 4.44, 6.08, 6.59, 7.69, 8.30, 9.68 |         | 2003594 | sodium peroxide oxyhydrate |
| NaOH         | 1.83           | 2.02  | ~3.09 |         | 2310820 | crystalline NaOH |

“Multiple chemical shifts indicate multiple H environments in the crystal structure.

Figure 7. 1H MAS NMR for (a) WIPP-MgO and (b) Marinco-MgO aged at 80°C in DI water with varying exposure time. Deconvolutions of the (c) WIPP-MgO and (d) Marinco-MgO 1H MAS NMR spectra.

Although proton density for Marinco-MgO indicates that there is only ~4% hydrogen equivalent in this phase, XRD revealed that nearly all of the MgO crystallinity has been lost. It is hypothesized that the disappearance of the MgO scattering arises primarily from disordering within the MgO phase and not complete conversion to Mg(OH)₂. Generally, this supports the existence of MgO-containing disordered phases, particularly when MgO has a high surface area available for hydration.

Overall, the measured proton concentrations are relatively low, with only a maximum of 0.04 mol of protons per mole of MgO observed at 16 weeks. If one assumes that only hydroxyl and hydration waters are present (limiting value), then the overall composition of the sample is estimated as MgO·[Mg(OH)₂]ₓ·(H₂O)ₙ, where (2x + 2y) is equal to the total relative proton concentration with respect to MgO (i.e., ~0.04 from Figure 9). Using the relative fraction of OH to the total number of protons (~0.75) for the aged samples, this corresponds to a MgO·[Mg(OH)₂]₀ₓ·(H₂O)ₙₓ average overall composition. You can also think of the phase created in terms of the average composition of just the hydrated phase, which is given by the ratio of the hydroxyl and water protons, as approximately Mg(OH)₂·(H₂O)ₓ. This approximation of

ACS Omega 2019, 4, 1033−1044
DOI: 10.1021/acsomega.8b02705
the proton-containing hydrated phase does not consider any phases containing carbonate or other cations/anions that may have formed, where the impact of these different constituents would require additional methods to determine the existence, concentration, and composition of the additional speciation. The $^1$H NMR chemical shifts for a range of carbonate phases have been calculated (Sorte et al., unpublished) and are consistent with the $^1$H NMR chemical shifts observed here. These carbonate chemical shifts are not included in the current discussion because of the inability to prove the formation of carbonate phases in the aged MgO, especially at these low amorphous phase concentrations but will be the target of future efforts.

3. CONCLUSIONS

As a carbon remediatior at the WIPP facility, the MgO engineered barrier will be exposed to a high-salt aqueous environment and may form stable intermediate phases that can alter the effectiveness of the barrier. Here, two different MgO materials (WIPP-MgO and Marinco-MgO) were aged in water and brine solutions (NaCl, GWB, and ERDA6) for up to 16 weeks, with XRD and NMR analysis performed to identify changes in the structure and the possible formation of secondary phases. After aging, there is the formation of ~4% molar equivalent of a hydrogen-containing phase. The concentration and formation rate for this hydrogen-containing phase is a function of the initial MgO particle structure, with the fine-grained Marinco-MgO powders resulting in more extensive loss of crystallinity and a higher proton-containing phase concentration than the harder, larger particle size of WIPP-MgO (Figure 1). $^1$H MAS NMR spectra can resolve low concentration of the minor phases not visible in XRD and has revealed a diverse set of $^1$H NMR environments. DFT simulations for twenty-one proposed Mg-OH-, Mg-Cl-OH-, and Na-OH-containing phases were performed to index the different resonances which appear in the experimental $^1$H MAS NMR spectra. Although the different proposed crystal structures exhibited overlapping $^1$H NMR resonances, Mg-Cl-OH intermediates were attributed to the growth of resonances in the $\delta = +1.0$ to 0 ppm range, whereas the proposed Mg-Cl-OH structures most likely contributed to the $\delta = +2.5$ to 5.0 ppm peak in the chloride-containing brines (Figure 4). Overall, NMR analysis of aged MgO indicates the formation of a range of possible intermediate structures that cannot be resolved with XRD analysis alone. Further documentation of secondary phases will require additional characterization based not just on protons but also other nuclei such as $^{23}$Na, $^{25}$Mg, or $^{17}$O NMR for separation of overlapping resonances and identification of nonproton-containing phases (e.g., calcite, halite, anhydrite).

4. MATERIALS AND METHODS

4.1. Hydrated MgO Materials. It should be noted that the MgO materials from different manufacturers have significant variation in appearance, particle size, and color. We therefore investigated two different unaged MgO materials. The first was MagChem 10 WTS-60 obtained from Martin Marietta Specialties (Baltimore, MD), which is a hard-burned MgO produced from magnesium-rich brine and dolomitic lime, giving low reactivity and coarse particle size material. This sample was equivalent to the material used in previous WIPP facility studies and was designated as WIPP-MgO. The other material is Marinco OL MgO (this material was...
Aqueous aging of the MgO materials was carried out by immersing 200 mg of the sample in 500 mL of different brine solutions or DI water. The salt solutions investigated included GWB, castile brine (ERDA-6), and a 1 M NaCl solution. Recipes for the synthetic Salado brines are given in Table S1 (Supporting Information). Samples were sealed during exposure but opened briefly for sample extraction every several weeks. No effort was made to remove atmospheric CO₂ from the aging test chambers. Each MgO material was aged in the different solutions unagitated at room temperature (25 °C) for up to 16 weeks exposure. Additional samples were also prepared by aging at 80 °C in an agitated water bath (oscillating at ~1 Hz). Small sample aliquots were extracted periodically by removing ~20 mg of saturated MgO material from the test chamber, then dried overnight (25 °C) under vacuum in the presence of P₂O₅, before packing and sealing in NMR MAS rotors.

**4.2. Solid-State NMR.** All solid state ¹H MAS NMR spectra were obtained on a Bruker AVANCE III spectrometer at a proton observe frequency of 600.1 MHz using a 2.5 mm broadband MAS probe spinning between 25 and 30 kHz. The nominal set temperature was 295 K but because of fractional heating under MAS, the sample temperature was 329 K (30 kHz). The sample temperature was calibrated with the 2²⁰Pb chemical shift change of the secondary Pb(NO₃)₂ standard.¹⁴,²⁵ ¹H spectra were obtained using a rotor-synchronized Hahn echo with 2 s recycle delays and 16 scan averages. The experimental ¹H MAS NMR chemical shifts were referenced to the secondary standard adamantane (δ = +0.8 ppm) with respect to tetramethylsilane (TMS, δ = 0 ppm). The NMR spectral deconvolutions were obtained using the DMFIT software package.³⁰ ¹H concentrations in the aged MgO samples were obtained by direct comparison of signal intensity to the intensity of a secondary external standard of adamantane under the same experimental conditions. The 2D DQSQ ¹H MAS correlation experiments and the DQ-filtered spectra utilized the chemical shift and offset compensated back-to-back multiple pulse sequence for excitation and reversion of the multiple quantum coherences.⁵⁷ The 2D experiment used phase-sensitive detection in the F₁ dimension via the States time-proportional phase incrementation method.

Powder XRD patterns were obtained by placing 40–50 mg of each sample in a mortar and pestle, adding acetone, and grinding the wetted powder. An aliquot of this suspension was transferred onto a 25 mm diameter, off axis, zero background quartz planchette to give an ~1 mm thick sample. Diffraction was obtained on a Siemens Kristalloflex DS500 diffractometer, using Cu Kα radiation (λ = 1.54178 Å) at 40 kV and 30 mA; analysis was performed using MDI Jade v9.6 with ICDD PDF-4 2018.

**4.3. Chemical Shift Calculations.** The initial Mg-containing crystal structures were imported from the COD.⁴³ These structures were then relaxed using DFT periodic calculations as implemented in the Quantum ESPRESSO open-source electronic structure code.²⁸ Norm-conserving pseudopotentials,⁴⁹ with the generalized gradient approximation in the form of Perdew, Burke, and Ernzerhof,⁵⁰ were used. An energy cut-off of 90 Ry was used with a 6 × 6 × 6 k-point matrix. High convergence levels were used: total energy convergence threshold = 4.0 × 10⁻⁵ Ry, force convergence threshold = 2.0 × 10⁻⁵ Ry, and self-consistent energy threshold = 1.0 × 10⁻¹⁰ Ry. For initial identification of low-energy crystal structures, the lattice parameters were changed iteratively to identify the lowest energy structure, which was then used as the starting point for a variable cell relaxation calculation. Optimized structures are provided in Supporting Information.

Computational ¹H NMR chemical shifts were calculated using the gauge-including projector augmented-wave (GIPAW) methods as implemented in Quantum ESPRESSO with a cut off energy of 1225 eV. Readers are encouraged to see a recent review for a more thorough description of the GIPAW method and its application to oxide and ceramic systems. GIPAW methods have already proven successful in calculating proton NMR shielding in MgO phases.¹⁴,²¹ Generally, the GIPAW method is used for the calculation of both electric field gradient and absolute shielding tensors (δ¹H). The advantage of the GIPAW method is that it uses a plane-wave basis set, which is suitable for simulation of infinite periodic systems such as bulk solids. Previously, most NMR calculations had been limited to quantum mechanical calculations, which used localized atom-centered basis sets that are computationally expensive to extend to bulk systems or surfaces. Plane-wave codes use an approximation, called a pseudopotential, for the corevalence interactions of an atom that freezes the core electrons in place and which simplifies the calculation and reduces the computational cost. The projector augmented wave (PAW) portion of the GIPAW method is used to reconstruct the true all-electron wave function in the atomic core, so that the response of the system to a uniform external magnetic field can be calculated. The gauge-including (GI) portion refers to the fact that with a finite basis set, the results may vary with the distance between the wave function and the gauge origin, making results inconsistent depending on where the origin is set (commonly the center of mass). Additionally, the paramagnetic and diamagnetic terms of the magnetic field, calculated through the current density, are both individually dependent on the gauge origin. Therefore, by advancing the PAW methodology to include gauge invariance, the accuracy and transferability of the methodology was substantially improved for a wide variety of systems.

In our simulations, the absolute chemical shielding tensors for the computationally-relaxed crystalline systems were obtained from fully converged all-electron calculations. The experimental (δ¹Hexp) and calculated (δ¹Hcalc) ¹H NMR chemical shifts are related to the isotropic component of the chemical shielding tensor, σiso using,

\[ \delta_\text{exp} = \sigma_\text{iso}^{\text{calc}} - \sigma_\text{iso}^{\text{Ref}} \]

\[ \delta_\text{calc} = \sigma_\text{iso}^{\text{calc}} - \sigma_\text{iso}^{\text{Ref}} \]

where σisoRef is the isotropic component of the reference chemical shielding tensor. It has been argued that the variation in the experimental chemical shift (or chemical shielding) is proportional to the variation in the chemical shift obtained from DFT calculations.

\[ \Delta \delta_\text{exp} = a \Delta \delta_\text{calc} \]

\[ \sigma_{\text{iso}}^{\text{exp}} = a \sigma_{\text{iso}}^{\text{calc}} \]

Experimentally, the reference standard for ¹H NMR is TMS (tetramethylsilane), but in general σisoRef or σisoCalc are not required.
to be equivalent. The proportionality between $\alpha$ and $\sigma_{\text{calc}}^{\text{Mg}}$ was determined by correlating experimental chemical shifts to calculated chemical shieldings via.

$$\delta^{\text{exp}} = \beta - \alpha\sigma^{\text{calc}}_{\text{Mg}}$$  \hfill (3)

where $\beta = \alpha\sigma^{\text{calc}}_{\text{Mg}}$ (see Supporting Information for additional details). Using a series of Mg-containing mineral structures, including Mg(OH)$_2$ (brucite), MgCl$_2$·6H$_2$O (bischofite), MgSO$_4$·7H$_2$O (epsomite), and Mg(NO$_3$)$_2$·6H$_2$O (nitromagnesite), the correlation between the experimental chemical shift and calculated shielding tensor it was found that $\alpha = 0.701$ and that $\sigma_{\text{Mg}}^{\text{calc}} = 30.7$ ppm (Sorte et al., unpublished results) and is shown in Figure S4 for completeness. This $\sigma_{\text{Mg}}^{\text{calc}}$ is similar to the 30.8 ppm recently reported for uranyl hydroxide phases$^{64}$ but is slightly higher than that reported for organic compounds$^{65}$. These results allowed a direct comparison between the experimental and calculated chemical shifts using eq 1.

## ASSOCIATED CONTENT

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02705.

$^1$H MAS NMR and DFT-predicted chemical shifts; chemical shift referencing equation used for comparing computational and experimental NMR shielding data; correlation between experimental $^1$H MAS NMR chemical shift and calculated chemical shielding for selected Mg-containing crystalline structures, methodology for MgO aging in different brine solutions; protocol for preparing GWB and ERDA-6 brines, and the energy-relaxed structures for the intermediate phases reported (PDF).

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: tmalam@sandia.gov* (T.M.A.).

**ORCID**

Jessica M. Rimsza: 0000-0003-0492-852X

Todd M. Alam: 0000-0002-1047-1231

**Notes**

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors would like to thank David X. Redmacher and Mark A. Rodrigue (Sandia National Laboratories) for providing the XRD spectra and Gema J. Alas (NSF Science, Technology, Engineering, and Mathematics Talent Expansion Program (STEP), University of New Mexico) for preliminary DFT simulations. This work was fully supported by the Laboratory Directed Research and Development (LDRD) program of Sandia National Laboratories. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003552S. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

## REFERENCES

(1) Amaral, L. F.; Oliveira, I. R.; Salomão, R.; Frollini, E.; Pandolfelli, V. C. Temperature and Common-Ion Effect on Magnesium Oxide (MgO) Hydration. *Ceram. Int.* 2010, 36, 1047–1054.

(2) Chizallet, C.; Costentin, G.; Lauron-Pernot, H.; Che, M.; Bonhomme, C.; Maquet, J.; Delbecq, F.; Sautet, P. Study of the Structure of OH Groups on MgO by 1D and 2D $^1$H MAS NMR Combined with DFT Cluster Calculations. *J. Phys. Chem. C* 2007, **111**, 18279–18287.

(3) Sugimoto, K.; Dinnebier, R. E.; Schlecht, T. Structure determination of Mg(OH)$_2$Cl$^\cdot$4H$_2$O (F5 phase) from laboratory powder diffraction data and its impact on the analysis of problematic magnesia flours. *Acta Crystallogr., Sect. B: Struct. Sci.* 2007, **63**, 805–811.

(4) Helton, J. C.; Anderson, D. B.; Jow, H.-N.; Marietta, M. G.; Basabivazoo, G. Performance Assessment in Support of the 1996 Compliance Certification Application for the Waste Isolation Pilot Plant. *Risk Anal.* 1999, **19**, 959–968.

(5) Xiong, Y.; Deng, H.; Nemer, M.; Johnsen, S. Experimental determination of the solubility constant for magnesium chloride hydride hydrate (Mg$_3$Cl(OH)$_4$$^\cdot$4H$_2$O, phase S) at room temperature, and its importance to nuclear waste isolation in geological repositories in salt formations. *Geochim. Cosmochim. Acta* 2010, **74**, 4605–4611.

(6) Xiong, Y.; Lord, A. S. Experimental investigation of the reaction path in the MgO–CO$_2$–H$_2$O system in solutions with various ionic strengths, and their applications to nuclear waste isolation. *Appl. Geochem.* 2008, **23**, 1634–1659.

(7) Rocha, S. D.; Mansur, M. B.; Ciminelli, V. S. Kinetics and Mechanistic Analysis of Caustic Magnesia Hydration. *J. Chem. Technol. Biotechnol.* 2004, **79**, 816–821.

(8) McKelvy, M. J.; Sharma, R.; Chizmeshya, A. V. G.; Carpenter, R. W.; Streib, K. Magnesium Hydroxide Dehydroxylation: in situ Nanoscale Observations of Lamellae Nucleation and Growth. *Chem. Mater.* 2001, **13**, 921–926.

(9) Chizmeshya, A. V. G.; McKelvy, M. J.; Sharma, R.; Carpenter, R. W.; Beraat, H. Density functional theory study of the decomposition of Mg(OH)$_2$: a lamellar dehydroxylation model. *Mater. Chem. Phys.* 2003, **77**, 416–425.

(10) Stein, C. L. Mineralogy in the Waste Isolation Pilot Plant (WIPP) Facility Stratigraphic Horizon; Sandia National Labs.: Albuquerque, NM (USA), 1985.

(11) Bodine, M. W., Jr. Magnesium Hydroxychloride: A Possible pH Buffer in Marine Evaporite Brines. *Geology* 1976, **4**, 76–80.

(12) Dehua, D.; Chuanmei, Z. The formation mechanism of the hydrate phases in magnesium oxide hydrate cement. This paper was originally submitted to Advanced Cement Based Materials. It was received at the Editorial Office of Cement and Concrete Research on 20 August 1998 and accepted in final form on 16 December 1998. *Cem. Concr. Res.* 1999, **29**, 1365–1371.

(13) Moran, R. E.; Dawson, D. M.; Ashbrook, S. E. Exploiting NMR Spectroscopy for the Study of Disorder in Solids. *Int. Rev. Phys. Chem.* 2003, **22**, 36–115.

(14) Pedone, A.; Palazzetti, F.; Barone, V. Models of Aged Magnesium-Silicate-Hydrate Cements Based on the Lizardite and Hafnia Silica Glass. *Miner.* 2003, **46**, 1634–1659.

(15) G. Performance Assessment in Support of the 1996 Compliance Certification Application for the Waste Isolation Pilot Plant. *Risk Anal.* 1999, **19**, 959–968.

(16) Girard, G.; Vasconcelos, F.; Montagne, L.; Delevoye, L. 31P MAS NMR spectroscopy with $^{9}$Nb decoupling and DFT calculations: A structural characterization of defects in a niobium-phosphate phase. *Solid State Nucl. Magn. Reson.* 2017, **84**, 210–215.

(17) Eckert, H.; Yesinowski, J. P.; Silver, L. A.; Stolper, E. M. Water in Silicate Glasses: Quantitation and Structural Studies by Proton Solid Echo and Magic Angle Spinning NMR Methods. *J. Phys. Chem.* 1988, **92**, 2055–2064.
Frost, D. J.; Senker, J. Hidden Oceans? Unraveling the Structure of Magnesium Silicates: Evidence for Proton Dynamics. *Environ. Sci. Technol.* 2008, *copy.

Study of Mixed Oxides Obtained by Calcination of Layered-Double Hydroxides. *ACS Omega* 2014, *copy.

Ashbrook, S. E. Hunting for Hydrogen: Random Structure Searching and Prediction of NMR Parameters of Hydrous Wadsleyite. *Phys. Chem. Chem. Phys.* 2016, *copy.

Griffin, J. M.; Senker, J.; Frost, D. J.; Slawski, A. E.; Wood, B. J. Ordering of hydroxyl defects in hydrous wadsleyite (β-Mg₈SiO₁₀). *Am. Mineral.* 2002, *copy.

Moran, R. F.; McKay, D.; Pickard, C. J.; Berry, A. J.; Griffin, J. M.; Ashbrook, S. E. H3 O+ and H+ in MgO: A Study of Proton Transfer and Kinetic Basicity on MgO Surfaces by 1H MAS NMR. *Phys. Chem. Chem. Phys.* 2014, *copy.

Chizallet, C.; Petitjean, H.; Costentin, G.; Lauron-Pernot, H.; Che, M. Identification of Mg-OH bonds in MgO by 1H MAS NMR spectroscopy. *Chem. Mater.* 2002, *copy.

Balunow, S. O.; Schneider, J.; Sterng, A.; Thomele, D.; Stankic, S.; Berger, T.; Grönbäck, H.; Dwindal, O. Size Effects in MgO Thin Films. *Langmuir* 2015, *copy.

Schwaiger, R.; Schneider, J.; Bourret, G. R.; Dwindal, O. Hydration of Magnesia Cubes: A Helium Ion Microscopy Study. *Beilstein J. Nanotechnol.* 2016, *copy.

Geysermans, P.; Finocchi, F.; Goniakowski, J.; Hacquart, R.; Jupille, J. Characterization of Various Crystal Shapes from Dry to Wet Environment. *Phys. Chem. Chem. Phys.* 2009, *copy.

Das, P. S.; Dey, A.; Mandal, A. K.; Dey, N.; Mukhopadhyay, A. K. Synthesis of Mg(OH)₂ micro/nano flowers at room temperature. *J. Adhes. Ceram.* 2013, *copy.

Gao, Y.; Wang, H.; Su, Y.; Shen, Q.; Wang, D. Influence of Temperature on the Hydration Behavior of Magnesium Hydroxide. *J. Cryst. Growth* 2009, *copy.

Limbach, H.-H.; Tolsky, P. M.; Pérez-Hernández, N.; Guo, J.; Shenderovich, I. G.; Denison, G. S. Hydrogen Bond Geometries and NMR Chemical Shifts: From Equilibrium Structures to Geometric H/D Isotope Effects, with Applications for Water, Protonated Water, and Compressed Ice. *Isr. J. Chem.* 2009, *copy.

Grüninger, H.; Armstrong, K.; Greim, D.; Boffa-Ballaran, T.; Frost, D. J.; Senker, J. Hidden Oceans? Unraveling the Structure of Hydrous Defects in the Earth’s Deep Interior. *J. Am. Chem. Soc.* 2017, *copy.

Seymour, V. R.; Day, S. P.; Scholz, G.; Scheurell, K.; Iuga, D.; Griffin, J. M.; Kemnitz, E.; Hanna, J. V.; Smith, M. E. A Combined 25Mg Solid-State NMR and Ab Initio DFT Approach to Probe the Local Structural Differences in Magnesium Acetate Phases Mg(CH₃COO)₂ and Na₂H₂O₁₂. *ChemPhysChem* 2018, *copy.

Aramendía, M. a. a.; Borau, V.; Jiménez, C.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. J. XRD and 1H MAS NMR Spectroscopic Study of Mixed Oxides Obtained by Calcination of Layered-Doubly Hydroxides. *Mater. Lett.* 2000, *copy.

Griffin, J. M.; Wimperis, S.; Berry, A. J.; Pickard, C. J.; Ashbrook, S. E. Solid-State 17O NMR Spectroscopy of Hydrous Magnesium Silicates: Evidence for Proton Dynamics. *J. Phys. Chem. C* 2008, *copy.

Moore, J. K.; Surface, J. A.; Brenner, A.; Skemer, P.; Conradi, M. S.; Hayes, S. E. Quantitative Identification of Metastable Magnesium Carbonate Minerals by Solid-State 13C NMR Spectroscopy. *Environ. Sci. Technol.* 2014, *copy.

Aramendía, M. a. a.; Benitez, J. A.; Borau, V.; Jiménez, C.; Marinas, J. M. a.; Ruiz, J. R.; Urbano, F. Characterization of Various Magnesium Oxides by XRD and 1H MAS NMR Spectroscopy. *J. Solid State Chem.* 1999, *copy.

Chizallet, C.; Petitjean, H.; Costentin, G.; Lappo-Pernot, H.; Maquet, J.; Bonhomme, C.; Che, M. Identification of the OH groups responsible for kinetic basicity on MgO surfaces by 1H MAS NMR. *J. Catal.* 2009, *copy.

Aramendía, M.; Benitez, J. A.; Borau, V.; Jiménez, C.; Marinas, J. M. a.; Ruiz, J. R.; Urbano, F. Characterization of Various Magnesium Oxides by XRD and 1H MAS NMR Spectroscopy. *J. Catal.* 1999, *copy.

Chizallet, C.; Petitjean, H.; Costentin, G.; Lappo-Pernot, H.; Maquet, J.; Che, M. Identification of Mg(OH)₂ micro/nano flowers at room temperature. *Beilstein J. Nanotechnol.* 2016, *copy.

Saldi, G. D.; Jordan, G.; Schott, J.; Oelkers, E. H. Magnesite Growth Rates as a Function of Temperature and Saturation State. *Geochim. Cosmochim. Acta* 2009, *copy.

Raucher, P.; Fedorovčik, A. Study of Inhibiting Effect of Acid Concentration on the Dissolution Rate of Magnesium Oxide During the Leaching of Dead-Burned Magnesite. *Hydrometallurgy* 2004, *copy.

Baumann, S. O.; Schneider, J.; Sterng, A.; Thomele, D.; Stankic, S.; Berger, T.; Grönbäck, H.; Dwindal, O. Size Effects in MgO Thin Films. *Langmuir* 2015, *copy.

Marinas, J. M.; Ruiz, J. R.; Urbano, F. Study of MgO and Pt/MgO Systems by XRD, TPR, and 1H MAS NMR. *Langmuir* 1999, *copy.

Kohn, S. C.; Brooker, R. A.; Frost, D. J.; Slesinger, A. E.; Wood, B. J. Ordering of hydroxyl defects in hydrous wadsleyite (β-Mg₈SiO₁₀). *Am. Mineral.* 2011, *copy.

Moran, R. F.; McKay, D.; Pickard, C. J.; Berry, A. J.; Griffin, J. M.; Ashbrook, S. E. Hunting for Hydrogen: Random Structure Searching and Prediction of NMR Parameters of Hydrous Wadsleyite. *Phys. Chem. Chem. Phys.* 2016, *copy.

Kohn, S. C.; Brooker, R. A.; Frost, D. J.; Slesinger, A. E.; Wood, B. J. Ordering of hydroxyl defects in hydrous wadsleyite (β-Mg₈SiO₁₀). *Am. Mineral.* 2011, *copy.

216.
(55) Takahashi, T.; Kawashima, H.; Sugisawa, H.; Toshihide, B. Chemical Shift Thermometer at High Temperature for Magic Angle Spinning Experiments. *Solid State Nucl. Magn. Reson.* 1999, 15, 119–123.

(56) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvë, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gian, Z.; Hoatson, G. Modelling one- and two-dimensional solid-state NMR spectra. *Magn. Reson. Chem.* 2001, 40, 70–76.

(57) Schnell, I.; Spiess, H. W. High-Resolution $^1$H NMR Spectroscopy in the Solid State: Very Fast Sample Rotation and Multiple-Quantum Coherences. *J. Magn. Reson.* 2001, 151, 153–227.

(58) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; Dal Corso, A.; de Gironcoli, S.; Fabris, S.; Fratesi, G.; Gebauer, R.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-Samos, L.; Marzari, N.; Mauri, F.; Mazzarello, R.; Paolini, S.; Pasquarello, A.; Paulatto, L.; Sbraccia, C.; Scandolo, S.; Sclauzero, G.; Seitsonen, A. P.; Smogunov, A.; Umari, P.; Wentzcovitch, R. M. QUANTUM ESPRESSO: a Modular and Open-Source Software Project for Quantum Simulations of Materials. *J. Phys.: Condens. Matter* 2009, 21, 395502.

(59) Kresse, G.; Hafner, J. Norm-Conserving and Ultrasoft Pseudopotentials for First-Row and Transition Elements. *J. Phys.: Condens. Matter* 1999, 6, 8245–8257.

(60) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868.

(61) Pickard, C. J.; Mauri, F. All-Electron Magnetic Response with Pseudopotentials: NMR Chemical Shifts. *Phys. Rev. B* 2001, 63, 245101.

(62) Charpentier, T. The PAW/GIPAW Approach for Computing NMR Parameters: A New Dimension Added to NMR Study of Solids. *Solid State Nucl. Magn. Reson.* 2011, 40, 1–20.

(63) Vasconcelos, F.; Cristol, S.; Paul, J.-F.; Montagne, L.; Mauri, F.; Delevoye, L. First-Principles Calculations of NMR Parameters for Phosphate Materials. *Magn. Reson. Chem.* 2010, 48, S142–S150.

(64) Alam, T. M.; Liao, Z.; Nyman, M.; Yates, J. Insight into Hydrogen Bonding of Uranyl Hydroxide Layers and Capsules by Use of $^1$H Magic-Angle Spinning NMR Spectroscopy. *J. Phys. Chem. C* 2016, 120, 10675–10685.

(65) Asakura, T.; Suzuki, Y.; Yazawa, K.; Aoki, A.; Nishiyama, Y.; Nishimura, K.; Suzuki, F.; Kaji, H. Determination of Accurate $^1$H Positions of (Ala-Gly)n as a Sequential Peptide Model of Bombyx mori Silk Fibroin before Spinning (Silk I). *Macromolecules* 2013, 46, 8046–8050.