**ATOMIC-LEVEL IMAGING OF CO₂ DISPOSAL AS A CARBONATE MINERAL:
OPTIMIZING REACTION PROCESS DESIGN**

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ABSTRACT

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Permanent and safe methods for CO₂ capture and disposal/storage need to be developed. Mineralization of stationary-source CO₂ emissions as carbonates can provide such safe capture and long-term sequestration. Mg-rich lamellar-hydroxide based minerals (e.g., brucite and serpentine) offer a class of widely available, low-cost materials, with intriguing mineral carbonation potential. Carbonation of such materials inherently involves dehydroxylation, which can disrupt the material down to the atomic level. As such, controlled dehydroxylation, before and/or during carbonation, may provide an important parameter for enhancing carbonation reaction processes. Mg(OH)₂ was chosen as the model material for investigating lamellar hydroxide mineral dehydroxylation/carbonation mechanisms due to (i) its structural and chemical simplicity, (ii) interest in Mg(OH)₂ gas-solid carbonation as a potentially cost-effective CO₂ mineral sequestration process component, and (iii) its structural and chemical similarity to other lamellar-hydroxide-based minerals (e.g., serpentine-based minerals) whose carbonation reaction processes are being explored due to their low-cost CO₂ sequestration potential. Fundamental understanding of the mechanisms that govern dehydroxylation/carbonation processes is essential for minimizing the cost of any lamellar-hydroxide-based mineral carbonation sequestration process. This final report covers the overall progress of this grant.

In the first project year, we used environmental-cell (E-cell), dynamic high-resolution transmission electron microscopy (DHRTEM) to directly observe the Mg(OH)₂ dehydroxylation process at the atomic-level for the first time. We also carried out exploratory semi-empirical modeling studies of the intermediate materials formed. *Dehydroxylation was discovered to be a lamellar nucleation and growth process, which includes intermediate lamellar oxyhydroxide formation. These intermediates offer a series of new carbonation reaction pathways, which may be able to enhance carbonation reactivity.* We also initiated studies to probe dehydroxylation/carbonation reaction mechanisms via C and H elemental analysis, optical microscopy and SIMS.

In the second year, we expanded our studies to better understand the mechanisms that govern Mg(OH)₂ carbonation reactivity. These investigations incorporated a range of techniques, including E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, TGA, XRD, and elemental analysis. In collaboration with DOE/NETL grant DE-FG26-99FT40580, we integrated advanced computational modeling studies with our experimental observations. *We found intermediate (e.g., oxyhydroxide) formation is a key component of both rehydroxylation-carbonation and dehydroxylation-carbonation processes, which, if controlled, can dramatically enhance carbonation reactivity, even at ambient temperature and CO₂ pressure.* Critical to optimizing this enhanced reactivity is the ability of Mg(OH)₂ to form nanostructured materials during controlled dehydroxylation, providing access to high surface area, carbonation reactive intermediate materials. Mechanisms that can inhibit carbonation include passivating carbonate layer formation and MgO crystal growth during dehydroxylation. These mechanisms combine

with delamination, cracking and nanostructured materials formation to control carbonation reactivity.

In the third year of the project, we primarily focused on developing a deeper understanding of nanostructure and oxyhydroxide formation and their impact on carbonation reactivity, due to their dramatic ability to enhance carbonation reaction rates and potential application to other Mg-rich lamellar hydroxide minerals of interest (e.g., serpentine-based minerals). These investigations included E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and elemental analysis. Highlights include: 1) *in situ* atomic-level observations of the dramatically enhanced ambient-temperature carbonation reactivity of dehydroxylated $\text{Mg}(\text{OH})_2$ under humid conditions, which produces an amorphous hydroxycarbonate; 2) the discovery of rapid Mg diffusion during dehydroxylated- $\text{Mg}(\text{OH})_2$ rehydroxylation, via *in situ* atomic-level E-cell DHRTEM, which appears to be key to the above enhanced carbonation reactivity; and (iii) developing an integrated overview of the impact of $\text{Mg}(\text{OH})_2$ cracking, delamination, nanoreconstruction, oxide crystal growth, and passivating carbonate layer formation on carbonation intermediate formation and carbonation reactivity based on macroscopic, microscopic, and nanoscopic dehydroxylation/rehydroxylation/carbonation mechanistic observations.

During our no-cost extension, our primary focus was on publishing our results (two peer-reviewed papers appeared in print during this time). We also repeated a couple of our previous experiments to confirm select prior results, which were confirmed.

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EXECUTIVE SUMMARY

OBJECTIVE

The objective of this project was to develop an atomic-level understanding of the mechanisms that govern the carbonation kinetics of the prototypical Mg-rich lamellar-hydroxide-based mineral $\text{Mg}(\text{OH})_2$, to facilitate engineering of improved carbonation materials and processes for CO_2 disposal. The chemical and structural simplicity of $\text{Mg}(\text{OH})_2$ provides a model system to develop a deeper fundamental understanding of Mg-rich lamellar-hydroxide-based mineral carbonation reaction mechanisms. The potential for these mineral carbonation processes to be economically viable has helped generate substantial interest in CO_2 mineral sequestration as a possible carbon management option (e.g., carbonation of the chemically and structurally more complex Mg-rich lamellar hydroxide serpentine-based minerals). Environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM) was used to probe the associated reaction processes down to the atomic level. A battery of complementary techniques was used to further elucidate key reaction mechanisms at the macroscopic and microscopic levels (via *in-situ* and *ex-situ* studies). As carbonation involves dehydroxylation, carbonation and potential competition between them, this project focused on developing an atomic-level understanding of dehydroxylation and carbonation reaction mechanisms and their impact on carbonation reactivity. Particular emphasis was placed on the mechanisms that have the greatest impact on carbonation reactivity.

ACCOMPLISHMENTS

We used environmental-cell (E-cell), dynamic high-resolution transmission electron microscopy (DHRTEM) to directly observe the $\text{Mg}(\text{OH})_2$ dehydroxylation process at the atomic-level for the first time. We integrated these observations with exploratory semi-empirical modeling studies of the intermediate materials formed. *Dehydroxylation was discovered to be a lamellar nucleation and growth process, which includes intermediate lamellar oxyhydroxide formation. These intermediates offer a series of new carbonation reaction pathways.*

After discovering intermediate oxyhydroxide formation is a key component of $\text{Mg}(\text{OH})_2$ dehydroxylation, we expanded our studies to better understand the mechanisms that govern $\text{Mg}(\text{OH})_2$ carbonation reactivity. These investigations incorporated a range of techniques, including E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, Raman, TGA, XRD, and elemental analysis. In collaboration with DOE/NETL grant DE-FG26-99FT40580, we integrated advanced computational modeling studies with our experimental observations. *We found intermediate (e.g., oxyhydroxide) formation is a key component of both rehydroxylation-carbonation and dehydroxylation-carbonation processes, which, if controlled, can dramatically enhance carbonation reactivity, even at ambient temperature and CO_2 pressure.* Critical to optimizing this enhanced reactivity is the ability of $\text{Mg}(\text{OH})_2$ to form nanostructured materials during controlled dehydroxylation, providing access to high surface area, carbonation reactive intermediate materials. Mechanisms that can inhibit carbonation include passivating carbonate layer formation and MgO crystal growth during dehydroxylation.

These mechanisms combine with delamination, cracking and nanostructured materials formation to control carbonation reactivity.

We also discovered the lamellar nucleation and growth process that governs $\text{Mg}(\text{OH})_2$ dehydroxylation may offer a level of control over the intermediate materials that form, as slow nucleation/rapid growth and rapid nucleation/slow growth should favor oxyhydroxide and $\text{MgO} + \text{Mg}(\text{OH})_2$ intermediate formation, respectively. This process can also result in extensive nanoscale crystal fracture, resulting in a morphological evolution of the reaction matrix involving internal blister formation, lattice cracking and morphological reconstruction, which has the ability to form nanoporous materials. Blister formation occurs internally, before lattice cracking can connect these regions with the exterior reaction atmosphere. Matrix cracking proceeds inward from the lamellar crystal edge and basal plane surfaces, connecting with the internal blisters that have formed to create high-surface-area intermediate materials with enhanced carbonation reactivity. Together with the potential to form carbonation reactive oxyhydroxide intermediate materials, these mechanisms provide exciting potential for engineering feedstock materials and processes with enhanced carbonation reactivity.

Although, the high-surface-area materials that result from low-temperature dehydroxylation were found to have a limited number of carbonation reactive sites, their controlled rehydroxylation can create/expose many more reactive sites resulting in *a dramatic increase in carbonation reactivity at ambient temperature*. *In situ* E-cell DHRTM combined with parallel electron energy loss spectroscopy has shown an amorphous magnesium carbonate containing material is formed in the process. Analogous atomic-level observations of the rehydroxylation process have discovered dramatic Mg mobility leads to the reformation of $\text{Mg}(\text{OH})_2$. Such high Mg mobility is apparently key to the greatly enhanced carbonation reactivity of dehydroxylated $\text{Mg}(\text{OH})_2$ observed under humid conditions.

The $\text{Mg}(\text{OH})_2$ dehydroxylation mechanisms discussed above and their ability to create nanoporous reaction matrices also impacts direct gas-phase $\text{Mg}(\text{OH})_2$ carbonation, including providing mechanistic avenues that can bypass passivating carbonate layer formation and enhance carbonation reactivity. They are also associated with the novel observation that $\text{Mg}(\text{OH})_2$ carbonation reaction rates *increase* with *decreasing* $\text{CO}_2(\text{g})$ pressure above the critical pressure needed for carbonate formation. Hence, direct gas-phase $\text{Mg}(\text{OH})_2$ carbonation reactivity can be optimized at the lowest CO_2 pressure at which MgCO_3 is stable. Higher CO_2 pressures further inhibit $\text{H}_2\text{O}(\text{g})$ diffusion out of and $\text{CO}_2(\text{g})$ diffusion into the nanoporous reaction matrix that forms, slowing both dehydroxylation and carbonation. Investigations of the role of Fe impurities during dehydroxylation/carbonation suggest they can segregate into Fe-rich regions during dehydroxylation, possibly reducing their impact on carbonation reactivity in the process. Similar mechanisms may be more broadly applicable to Mg/Ca-rich lamellar-hydroxide-based mineral (e.g., serpentine) carbonation processes, offering substantial potential for reducing CO_2 mineral sequestration process costs.

INTRODUCTION

Mineral Carbonation: An Attractive Candidate Process for CO₂ Sequestration

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Mineralization of stationary-source CO₂ emissions as carbonates can provide safe capture and long-term sequestration. The resulting carbonates (e.g., magnesium and calcium carbonate, MgCO₃ and CaCO₃) occur in nature in quantities that far exceed those that could result from carbonating the world's known coal reserves. Furthermore, they have already proven stable over geological time, eliminating the safety and cost concerns associated with long-term storage of CO₂ in compressed form. Conversion of CO₂ into Mg/CaCO₃ effectively disposes of CO₂ by accelerating the natural processes that already occur in nature.

Mg-rich minerals and mineral derivatives are being investigated as low-cost mineral carbonation feedstock materials by the CO₂ Mineral Sequestration Working Group (comprised of members from the Albany Research Center, our CO₂ Mineral Sequestration Research Group at Arizona State University, Los Alamos National Laboratory, the National Energy Technology Laboratory and Science Applications International Corporation).¹ The primary focus of the Working Group, which is managed by the Department of Energy's Office of Fossil Energy, is to evaluate the economic viability of mineral carbonation processes as long-term options for reducing atmospheric CO₂ emissions. A major challenge in cost-competitive process development is to accelerate these carbonation reaction(s) to a high degree of completion on an industrial time scale. The associated reaction rates depend on many materials and process parameters, providing substantial potential for rate enhancement. However, the effects of many of these parameters are poorly understood, especially at the atomic level, severely limiting their effective use. A fundamental understanding of the mechanisms that govern key carbonation processes is needed to create the foundation for reaction process improvement via materials and process engineering.

Mg-Rich Lamellar-Hydroxide-Based Minerals: Candidate Feedstock Materials for Cost Competitive CO₂ Mineral Sequestration

Carbonation of Mg-rich lamellar-hydroxide-based minerals (e.g., the serpentine-based minerals and brucite: Mg(OH)₂) is a leading CO₂-mineral-sequestration, process candidate. Increasing the carbonation reaction rate and its degree of completion is key to lowering process cost. Mg(OH)₂ was chosen as the model material for investigating lamellar hydroxide mineral dehydroxylation/carbonation mechanisms due to (i) its structural and chemical simplicity,² (ii) the interest in Mg(OH)₂ gas-solid carbonation as a potentially cost-effective CO₂ mineral sequestration process component,³⁻⁵ and (iii) its structural and chemical similarity to other lamellar-hydroxide-based minerals (e.g., serpentine, see Figure 1), whose carbonation reaction processes are being explored due to their low-cost CO₂ sequestration potential.¹ This project focuses on developing an atomic-level understanding of the reaction mechanisms that govern dehydroxylation/rehydroxylation-carbonation processes for this model lamellar hydroxide feedstock material. The long-term goal is to develop the necessary atomic-level mechanistic

Figure 1. A lamellar view of the Mg-rich lamellar hydroxide minerals (a) brucite, $\text{Mg}(\text{OH})_2$, and (b) serpentine (lizardite). Note the close structural similarities, with both structures containing Mg lamella and hydroxide lamella. The green, red and white spheres correspond to the Mg, O, and H atom positions, respectively. The grey tetrahedra with small red spheres at the corners correspond to the silica (SiO_4) groups connected in lamellar sheets, which also contain hydroxyl groups.

understanding to engineer improved carbonation materials and processes for Mg-rich lamellar-hydroxide-based minerals.

EXPERIMENTAL

MATERIALS: Natural single crystal brucite from Delora, Canada was used as the starting material. Elemental analysis by proton-induced X-ray emission and total carbon analysis showed the material to contain 0.16% Mn, 0.06% C, 0.01% Cl and 0.01% Si by weight. X-ray powder diffraction was used to structurally characterize the starting material [$a=3.147(1)$ Å and $c=4.765(1)$ Å], in good agreement with the known parameters for brucite [$a=3.147$ Å and $c=4.769$ Å].⁶ E-cell DHRTEM samples were prepared in a He glovebox by either cold crushing at -196°C or scraping the crystal with a razor blade. Crystals were then dry loaded on to holey-carbon-coated copper grids for DHRTEM analysis. Single crystal fragments for carbonation studies were cleaved from the crystal matrix. High pressure carbonation/dehydroxylation reactions were carried out in a sealed autoclave. The samples were introduced to the autoclave in vitreous silica boats. The autoclave was sealed, dry CO_2 introduced, and the autoclave brought quickly to reaction temperature. *In situ* $\text{Mg}(\text{OH})_2$ dehydroxylation/rehydroxylation-carbonation reaction processes were investigated using a Setaram TGS2 thermogravimetric analysis system, with 1 μ sensitivity.

E-Cell DHRTEM: The *in-situ* studies of $\text{Mg}(\text{OH})_2$ dehydroxylation/rehydroxylation/carbonation were performed using a Philips 430 HRTEM (300 kV; 2.3 Å pt. to pt. resolution) equipped with a Gatan Imaging energy Filter (GIF) and a 0-5 torr E-cell. Dehydroxylation was induced by electron beam heating and resistive heating using the sample holder, both with and without the presence of water vapor. Direct imaging of the reaction was recorded on videotape in real time (30 frame/sec). Water vapor (e.g., ~ 1 torr) was required to slow the dehydroxylation process sufficiently for direct imaging. Digital Micrograph was used to analyze the interlamellar

spacings in four-frame time-averaged images of the dehydroxylation process parallel to the brucite layers. Selected area diffraction of the reaction process was recorded as a function of time using internal gold island diffraction standards and photographic plates. *In situ* rehydroxylation-carbonation processes were followed by direct imaging, SAD and PEELS. $\text{Mg}(\text{OH})_2$ was first dehydroxylated *in situ* via resistive heating, followed by reaction at ambient temperature with ~ 800 mtorr of humid CO_2 .

GENERAL FACILITIES: The SIMS system used was a Cameca IMS 3f ion microscope. Base pressure in the sample chamber is 10^{-7} torr. Depth resolution can be better than 10 nm. Lateral resolution is $\sim 5\text{-}20\ \mu\text{m}$ in point analysis mode and lateral image resolution is $\sim 1\ \mu\text{m}$. The digital optical microscope system used was a Mitutoyo Ultraplan FS-110, with bright and dark field, polarized light, Nomarski, and reflected and transmitted illumination capabilities together with extra-long working distance objectives and fraction of a micron resolution. X-ray powder diffraction (XPD) studies were carried out using a Rigaku D/MAX-IIIB X-ray diffractometer with $\text{CuK}\alpha$ radiation, line focus, and graphite monochromator. Ion beam analyses of partially carbonated $\text{Mg}(\text{OH})_2$ single crystal samples were performed using a 1.7 MV General Ionex Tandetron system. Mg was analyzed via Rutherford backscattering spectroscopy (RBS) analysis using 2 MeV He^{++} ions. Carbon analysis used a $\text{C}(\alpha, \alpha)\text{C}$ reaction occurring at 4.63 MeV. Oxygen analysis used a similar reaction at 3.05 MeV. H analysis was performed by forward scattering using 2.8 MeV He^{++} ions. Total hydroxide, oxide and carbonate contents for the partially dehydroxylated/carbonated single crystal fragments were determined using a Perkin Elmer PE 2400 Series CHNS analysis system. Careful use of standards before and after sample analysis showed an absolute error of ± 0.2 wt%. The field emission scanning electron microscope (FESEM) system used was a Hitachi S-4100 equipped with an Oxford Instruments ISIS energy dispersive spectrometer.

MODELING: *Ab initio* density functional theory calculations and non-empirical electron-gas modeling based on the VIB method^{6,7} were used to investigate the relative stability, elastic behavior and structural trends of the intermediate oxyhydroxides as a function of composition. The methods used have been previously described in detail.^{6,7} Similar methods were used for the carbonation modeling studies. These are described in detail in the 2000 annual report for the DOE UCR Innovative Concepts project “Atomic-Level Modeling of CO_2 Disposal as a Carbonate Mineral: a Synergetic Approach to Optimizing Reaction Process Design,” (grant #DE-FG26-99FT40580), which fully collaborated with the project described herein.

RESULTS AND DISCUSSION

$\text{Mg}(\text{OH})_2$ Dehydroxylation: The First Step in Carbonation

As $\text{Mg}(\text{OH})_2$ dehydroxylation (reaction 1), is intimately associated with carbonation (reaction 2),

its mechanisms are of direct interest in understanding and optimizing the carbonation process. Although Mg(OH)_2 dehydroxylation has been extensively studied, relatively little was known about the atomic-level nature of the process, especially in the early stages of dehydroxylation, prior to this project. The early stages of the process are of particular interest, since carbon dioxide may react to form magnesite (MgCO_3) locally as soon as dehydroxylation begins in that region. During the first year of this project (Appendix I), we discovered that Mg(OH)_2 dehydroxylation is governed by a lamellar nucleation and growth process. Environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM) was used to directly observe the *in-situ* process at the atomic-level for the first time. These observations were combined with preliminary advanced computational modeling studies using a non-empirical density functional theory (DFT) approach to better elucidate the atomic-level dehydroxylation process. During the second project year (Appendix II), we developed a deeper understanding of the lamellar nucleation and growth process, including (i) analysis of the interrelationship between oxyhydroxide intermediate and nanostructure formation and (ii) advanced modeling studies of the oxyhydroxide intermediate materials formed in collaboration with DOE/NETL grant DE-FG26-99FT40580. During the third project year (Appendix III) and the no-cost extension, we extended this understanding to direct atomic level observations of dehydroxylated Mg(OH)_2 rehydroxylation. These studies have discovered very high Mg mobility during gas-phase rehydroxylation, which leads to rapid Mg(OH)_2 crystal growth. Such Mg mobility is very likely key to the dramatically enhanced carbonation reactivity observed for dehydroxylated Mg(OH)_2 at ambient temperature under the humid conditions discussed below.

Mg(OH)_2 Dehydroxylation/Rehydroxylation-Carbonation Processes

During the first project year (Appendix I), we combined our initial dehydroxylation studies with preliminary dehydroxylation-carbonation studies of single crystal Mg(OH)_2 fragments to better elucidate dehydroxylation-carbonation reaction mechanisms. We found dehydroxylation generally occurred in advance of carbonation during Mg(OH)_2 carbonation, suggesting intermediate formation may be important to carbonation reactivity during simultaneous dehydroxylation-carbonation. We also discovered initial evidence for passivating carbonate layer formation and substantial delamination and cracking of the Mg(OH)_2 feedstock material during dehydroxylation-carbonation.

During the second project year (Appendix II), we discovered dehydroxylation/rehydroxylation intermediate (e.g., oxyhydroxide) formation is a key component of both dehydroxylation-carbonation and rehydroxylation-carbonation processes, with essentially the entire lamellar oxyhydroxide solid solution series ($\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$) accessible during Mg(OH)_2 dehydroxylation/rehydroxylation. The ability of Mg(OH)_2 to form nanostructured materials during controlled dehydroxylation is another key component affecting carbonation reactivity. Together with delamination and cracking, these factors enhance carbonation by increasing the reactive carbonation surface area. On the other hand, carbonation can slow high-surface-area reactive intermediate formation via the formation of passivating carbonate layers. MgO crystal

growth during dehydroxylation can also inhibit carbonation. In addition, $\text{Mg}(\text{OH})_2$ feedstock impurities may also play important roles in carbonation reactivity. However, initial studies indicate Fe impurities at low concentrations can phase separate during $\text{Mg}(\text{OH})_2$ dehydroxylation, suggesting they do not substantially inhibit carbonation, at least locally. All of the above factors must be adroitly balanced to enhance carbonation reactivity. Our efforts to combine oxyhydroxide intermediate formation with controlled nanostructure formation to probe their ability to enhance carbonation reactivity proved quite promising, as we *achieved carbonation reaction rates at ambient temperature and CO_2 pressure similar to those previously reported for optimum ambient CO_2 pressure $\text{Mg}(\text{OH})_2$ carbonation (at 375 °C).*

During the third project year (see Appendix III), we primarily focused on developing a deeper understanding of the reaction matrix morphology, nanostructure and oxyhydroxide formation and their impact on carbonation reactivity, due to their dramatic ability to enhance carbonation reaction rates and potential application to other Mg-rich lamellar hydroxide minerals of interest (e.g., serpentine-based minerals). These investigations include E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and elemental analysis. Highlights include: 1) *in situ* atomic-level observations of the dramatically enhanced ambient-temperature carbonation reactivity of dehydroxylated $\text{Mg}(\text{OH})_2$ under humid conditions, which produces an amorphous hydroxycarbonate; 2) the discovery (via *in situ* atomic-level E-cell DHRTEM) of dramatically enhanced Mg diffusion during dehydroxylated- $\text{Mg}(\text{OH})_2$ rehydroxylation, which appears to be a key mechanistic tool for enhancing carbonation reactivity; and (iii) developing an integrated overview of the impact of $\text{Mg}(\text{OH})_2$ cracking, delamination, nanoreconstruction, oxide crystal growth, and passivating carbonate layer formation on carbonation intermediate formation and carbonation reactivity based on macroscopic, microscopic, and nanoscopic dehydroxylation/rehydroxylation/carbonation mechanistic observations.

CONCLUSIONS

$\text{Mg}(\text{OH})_2$ gas-phase carbonation reactivity is intimately associated with dehydroxylation/rehydroxylation processes. The extent of dehydroxylation is consistently observed to exceed the extent of carbonation for direct $\text{Mg}(\text{OH})_2$ carbonation reactions, indicating that dehydroxylation and carbonation are separate but intimately interrelated reaction processes. $\text{Mg}(\text{OH})_2$ dehydroxylation is a more complicated process than the simple two-phase process previously assumed and is best described as a lamellar nucleation and growth process that can lead to a solid solution series of lamellar oxyhydroxide intermediate materials with potentially enhanced carbonation reactivity, as shown in Figure 2. These intermediates may also form during rehydroxylation, providing similar new reaction pathways for rehydroxylation-carbonation. Relatively low-temperature dehydroxylation also induces a range of morphological changes that can serve to enhance carbonation reactivity, including translamellar cracking, delamination, and morphological reconstruction into nanostructured materials. Importantly, these phenomena can mitigate the ability of passivating carbonate layer formation to slow carbonation reaction rates.

Figure 2. Possible $\text{Mg}(\text{OH})_2$ carbonation reaction pathways during dehydroxylation and/or rehydroxylation. The intermediate lamellar oxyhydroxide solid solution series, $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$, is represented by nominal compositions of $\text{Mg}_3\text{O}(\text{OH})_4$ and $\text{Mg}_3\text{O}_2(\text{OH})_2$.⁶⁻⁸ The green, red, white, and black spheres correspond to the Mg, O, H, and C atom positions, respectively. Whereas MgO and $\text{Mg}(\text{OH})_2$ can form by dehydroxylation and rehydroxylation, respectively (potentially cycling back and forth at low temperatures), carbonate formation is thermodynamically dictated as a one way reaction (below the MgCO_3 decomposition temperature).

The above mechanistic understanding leads to general approaches to enhance carbonation reaction rates. Highlights include, first, reaction rates for direct $\text{Mg}(\text{OH})_2$ carbonation are optimized at CO_2 reaction pressures that just exceed the minimum pressure needed to stabilize MgCO_3 formation. Progressively higher reaction pressures increasingly inhibit dehydroxylation and carbonation by slowing H_2O diffusion away from and CO_2 diffusion to the reaction sites, respectively. Second, dramatically enhanced carbonation reactivity can be achieved via rehydroxylation-carbonation for low-temperature dehydroxylated $\text{Mg}(\text{OH})_2$, even at ambient temperature. We have observed this process at the atomic-level/nanoscale via DHRTEM and parallel energy loss spectroscopy for the first time. Advanced computational modeling corroborates that the ambient temperature carbonation process yields an amorphous carbonate containing material during rehydroxylation-carbonation. We have also observed the rehydroxylation of partially dehydroxylated $\text{Mg}(\text{OH})_2$ via E-cell DHRTEM and found $\text{Mg}(\text{OH})_2$ recrystallization exhibits rapid Mg diffusion, which likely contributes to the dramatic increase in carbonation reactivity observed during rehydroxylation-carbonation. As $\text{Mg}(\text{OH})_2$ is a prototypical Mg-rich lamellar hydroxide based mineral, some of the above reaction mechanisms may also apply more generally (in whole or in part) to Mg-rich lamellar hydroxide based mineral (e.g., serpentine) dehydroxylation/rehydroxylation-carbonation reaction processes.

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ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Articles

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Conference Presentations

- “Developing a Mechanistic Understanding of Lamellar Hydroxide Mineral Carbonation Reaction Processes,” Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, R.W. Carpenter, Jason Diefenbacher, and George Wolf, presented at the U.S. Department of Energy Workshop on CO₂ Mineral Sequestration, Pittsburgh, Pennsylvania, August 8, 2001.
- “Atomic-Level Imaging of CO₂ Disposal as a Carbonate Mineral: Optimizing Reaction Process Design,” Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, presented at the University Coal Research Contractors Review Conference, Pittsburgh, Pennsylvania, June 5-6, 2001.
- “Developing a Mechanistic Understanding of Lamellar Hydroxide Mineral Carbonation Reaction Processes to Reduce CO₂ Mineral Sequestration Process Cost,” Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, an oral presentation at the First National Conference on Carbon Sequestration, Washington, D.C., May 14-17, 2001.
- “Developing a Mechanistic Understanding of Lamellar Hydroxide Mineral Carbonation Reaction Processes to Reduce CO₂ Mineral Sequestration Process Cost,” Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, a poster presentation at the First National Conference on Carbon Sequestration, Washington, D.C., May 14-17, 2001.
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- “Methods for Developing an Atomic-Level Understanding of Carbon Dioxide Mineral Sequestration Reaction Processes,” Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, presented at the 2001 SME Meeting, Denver, Colorado, February 26-28, 2001.
- “Developing an Atomic-Level Understanding to Enhance CO₂ Mineral Sequestration Reaction Processes via Materials and Reaction Engineering,” Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, presented at Summit 2000, the Annual Meeting of the Geological Society of America, Reno, Nevada, November 9-18, 2000.

- “Developing an Atomic-Level Understanding to Enhance CO₂ Mineral Sequestration Reaction Processes via Materials and Reaction Engineering,” Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, presented at the 17th Annual International Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September 11-14, 2000.
- “Atomic-Level Imaging of CO₂ Mineral Sequestration: Optimizing Reaction Process Design,” Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, Hamdallah Bearat, and R.W. Carpenter, presented at the University Coal Research Contractors Review Conference, Pittsburgh, Pennsylvania, June 6-7, 2000.
- “Atomic-Level Modeling of Mineral Carbonation Reaction Processes: Integrating Experiment with Theory,” Andrew V.G. Chizmeshya, Renee Olsen, and Michael J. McKelvy, presented at the University Coal Research Contractors Review Conference, Pittsburgh, Pennsylvania, June 6-7, 2000.
- “Atomic-Level Modeling of CO₂ Disposal as a Carbonate Mineral: A Synergetic Approach to Optimizing Reaction Process Design,” Andrew V.G. Chizmeshya, Renee Olsen, and Michael J. McKelvy, presented at the DOE Basic Energy Sciences Combustion Research Meeting, Chantilly, Virginia, May 30 - June 2, 2000.
- “Atomic-Level Imaging of CO₂ Disposal as a Carbonate Mineral: Optimizing Reaction Process Design,” Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, Hamdallah Bearat, and R.W. Carpenter, presented at the DOE Basic Energy Sciences Combustion Research Meeting, Chantilly, Virginia, May 30 - June 2, 2000.
- “Mg(OH)₂ Dehydroxylation: Implications for Enhancing CO₂ Mineral Sequestration Reaction Processes,” Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, Hamdallah Bearat, and R.W. Carpenter, presented at the 25th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, 2000.
- “The Role of Dehydroxylation in Mg(OH)₂ Carbonation: Implications for Lamellar Hydroxide Mineral Carbonation,” M.J. McKelvy, H. Bearat, A.V.G. Chizmeshya, R. Sharma, R.W. Carpenter, and K. Streib, presented at the Fourth CO₂ Mineral Sequestration Forum, Tempe, Arizona, 1999.
- “Advanced Simulation and Modeling of Lamellar Hydroxide Minerals: Dehydroxylation and Carbonation,” A.V.G. Chizmeshya and M.J. McKelvy, presented at the Fourth CO₂ Mineral Sequestration Forum, Tempe, Arizona, 1999.

- “Mg(OH)₂ Dehydroxylation/Carbonation: A Microscopic View,” H. Bearat, M. Schade, A.V.G. Chizmeshya, C. Redmacher, and M.J. McKelvy, presented at the Fourth CO₂ Mineral Sequestration Forum, Tempe, Arizona, 1999.
- “Mg(OH)₂ Dehydroxylation: A Lamellar Nucleation and Growth Process,” M.J. McKelvy, R. Sharma, A.V.G. Chizmeshya, R.W. Carpenter and K. Streib, presented in Symposium Q of the Materials Research Society Meeting, Boston, Massachusetts, 1999.
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- “Mg(OH)₂ Dehydroxylation: The Path to Brucite CO₂ Mineral Sequestration,” M.J. McKelvy, R. Sharma, A.V.G. Chizmeshya, H. Bearat, R.W. Carpenter, and K. Streib, presented at the Third CO₂ Mineral Sequestration Forum, Pittsburgh, Pennsylvania, 1999.
- “Mg(OH)₂ Dehydroxylation: A Lamellar Nucleation and Growth Process,” M.J. McKelvy, R. Sharma, A.V.G. Chizmeshya, R.W. Carpenter and K. Streib, presented at the University Coal Research Contractors Review Conference, Pittsburgh, Pennsylvania, 1999.
- “Atomic-Level Imaging of CO₂ Disposal as a Carbonate Mineral: Optimizing Mg(OH)₂ Carbonation,” M.J. McKelvy, R.W. Carpenter, R. Sharma, and Ken Streib, presented at the Second CO₂ Mineral Sequestration Forum, Albany, Oregon, 1998.
- “Atomic-Level Imaging Of CO₂ Disposal as a Carbonate Mineral: Optimizing Reaction Process Design,” M.J. McKelvy, R.W. Carpenter, and R. Sharma, presented at the First CO₂ Mineral Sequestration Forum, Los Alamos, New Mexico, 1998.

Students Supported under this Grant

- Hamdallah Bearat, graduate (Ph.D.) student in the Science and Engineering of Materials Graduate Program, Arizona State University.
- Kenneth Streib, graduate (Ph.D.) student in the Science and Engineering of Materials Graduate Program, Arizona State University.

APPENDIX I: Year 1 Technical Progress Report

ATOMIC-LEVEL IMAGING OF CO₂ DISPOSAL AS A CARBONATE MINERAL: OPTIMIZING REACTION PROCESS DESIGN

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ABSTRACT

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Permanent and safe methods for CO₂ capture and disposal/storage need to be developed. Mineralization of stationary-source CO₂ emissions as carbonates can provide such safe capture and long-term sequestration. Mg(OH)₂ carbonation is a leading process candidate, which generates the stable naturally occurring mineral magnesite (MgCO₃) and water. Key to process cost and viability are the carbonation reaction rate and its degree of completion. This process, which involves simultaneous dehydroxylation and carbonation is very promising, but far from optimized. In order to optimize the dehydroxylation/carbonation process, an atomic-level understanding of the mechanisms involved is needed. Since Mg(OH)₂ dehydroxylation is intimately associated with the carbonation process, its mechanisms are also of direct interest in understanding and optimizing the process.

In the first project year, our investigations have focused on developing an atomic-level understanding of the dehydroxylation/carbonation reaction mechanisms that govern the overall carbonation reaction process in well crystallized material. In years two and three, we will also explore the roles of crystalline defects and impurities. Environmental-cell, dynamic high-resolution transmission electron microscopy has been used to directly observe the dehydroxylation process at the atomic-level for the first time. These observations were combined with advanced computational modeling studies to better elucidate the atomic-level process. These studies were combined with direct carbonation studies to better elucidate dehydroxylation/carbonation reaction mechanisms.

Dehydroxylation follows a lamellar nucleation and growth process involving oxide layer formation. These layers form lamellar oxyhydroxide regions, which can grow both parallel and perpendicular to the Mg(OH)₂ lamella. The number of oxide layers within the regions increases as they grow during dehydroxylation. Selected area diffraction suggests a novel two-dimensional variant of Vegard's law can describe the oxyhydroxide regions, with intralamellar Mg-Mg packing distances observed between those known for Mg(OH)₂ and MgO. Intralamellar and interlamellar elastic stress induced during dehydroxylation can contribute to crystallite cracking and MgO surface reconstruction, which may serve to enhance carbonation reactivity. The observed dehydroxylation process indicates a range of candidate materials for carbonation may be present during the carbonation process (i) the hydroxide, (ii) a range of intermediate oxyhydroxides, and (iii) the oxide, potentially in more-reactive, very small particle size form. Partial carbonation of single-crystal Mg(OH)₂ fragments over a wide range of reaction conditions (varying CO₂ pressure and temperature) shows a linear or near-linear correlation between carbonation and dehydroxylation, with the extent of dehydroxylation substantially greater than the extent of carbonation. This suggests carbonation primarily occurs via intermediate oxyhydroxide or oxide formation. The range and type of intermediate oxyhydroxides/oxides that can form in advance of carbonation should provide a degree of control over both their formation and the overall reactivity observed for the carbonation process.

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INTRODUCTION

Mg(OH)₂ Carbonation: A Leading CO₂ Mineral Sequestration Process Candidate

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Permanent and safe methods for CO₂ capture and disposal/storage need to be developed. Mineralization of stationary-source CO₂ emissions as carbonates can provide such safe capture and long-term sequestration. Mg(OH)₂ carbonation is a leading process candidate, which generates the stable naturally occurring mineral magnesite (MgCO₃) and water according to reaction (1). The long

term stability of magnesite has already proven effective over geological time, allowing permanent disposal of anthropogenic CO₂, a distinct advantage over proposed storage technologies. Other advantages of this process include (i) the broad availability of magnesium minerals which can be economically converted to Mg(OH)₂, (ii) it is exothermic, allowing the complete process to be energy self-sufficient, and (iii) apparent economic feasibility. Key to process cost and viability are the carbonation reaction rate and its degree of completion. The few available (macroscopic) studies of this complex process, which involves simultaneous dehydroxylation and carbonation, show it to be very promising, but far from optimized.¹ Optimizing the carbonation reaction rate and its degree of completion are key to minimizing process cost, providing motivation to develop an understanding of the mechanism(s) that govern the carbonation process.

Mg(OH)₂ Dehydroxylation: The First Step in Carbonation

As Mg(OH)₂ dehydroxylation, depicted in reaction (2), is intimately associated with the carbonation process, its mechanisms are of direct interest in understanding and optimizing the

carbonation process. Although Mg(OH)₂ dehydroxylation has been extensively studied, relatively little is known about the atomic-level nature of the process, especially in the early stages of dehydroxylation. The early stages of the process are of particular interest, since carbon dioxide may react to form magnesite (MgCO₃) locally as soon as dehydroxylation begins in that region. Herein, we report on our investigation of the Mg(OH)₂ dehydroxylation process using environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM) to directly observe the *in-situ* process at the atomic-level for the first time. Direct imaging observations are combined with *in-situ* selected area diffraction (SAD) of the dehydroxylation process. These observations are combined with advanced computational modeling studies using a non-empirical density functional theory (DFT) approach to better elucidate the atomic-level dehydroxylation process. We have combined these dehydroxylation studies with ongoing dehydroxylation/carbonation studies of single crystal Mg(OH)₂ fragments to better elucidate dehydroxylation/carbonation reaction mechanisms. Herein, we report on our studies of these processes using secondary ion mass spectrometry (SIMS), optical microscopy, and elemental analysis.

EXECUTIVE SUMMARY

OBJECTIVE

The goal of this project is to develop an atomic level understanding of the mechanisms that govern the kinetics of the complex $\text{Mg}(\text{OH})_2$ carbonation process to facilitate engineering of improved carbonation materials and processes for carbon dioxide disposal. This project utilizes environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM) to probe the reaction processes down to and at the atomic level. Other techniques are incorporated to optimally elucidate the overall reaction process (e.g., *in-situ* vs. *ex-situ* studies, advanced non-empirical computer modeling and studies based on reactant particle and crystalline grain size). As the overall carbonation process involves dehydroxylation, carbonation and the potential competition between them, developing an atomic-level understanding of the dehydroxylation process is first targeted to provide a foundation from which to explore the overall carbonation process. Process mechanisms are targeted for exploration as a function of potential feedstock material characteristics, which may be incorporated to enhance carbonation. In the first year the primary focus has been on high purity $\text{Mg}(\text{OH})_2$ single crystal fragments to elucidate basic reaction processes for highly crystalline material. In years two and three we will also explore (i) $\text{Mg}(\text{OH})_2$ materials containing crystalline defects to probe the effect of grain boundaries, crystallinity, etc. on reaction processes and (ii) $\text{Mg}(\text{OH})_2$ materials containing known impurities to investigate the effects of impurities (e.g., Ca) on dehydroxylation/carbonation processes:

ACCOMPLISHMENTS TO DATE

During the initial project period, the materials and operational foundation for the project have been established, including (i) development of the $\text{CO}_2/\text{H}_2\text{O}$ gas mixing system for the E-cell DHRTEM studies, (ii) evaluation and characterization (morphological, structural and elemental) of a number of potential feedstock materials for reaction process studies, and (iii) development of appropriate sample preparation techniques for the E-cell DHRTEM studies.

DHRTEM observations of the *in situ* $\text{Mg}(\text{OH})_2$ dehydroxylation process together with advanced computational modeling indicate dehydroxylation proceeds by a lamellar nucleation and growth process. Lamellar oxide nuclei form via the dehydration of single double hydroxide layers or layer regions (e.g., $\cdots \text{OH}/\text{Mg}/\text{OH}/\text{OH}/\text{Mg}/\text{OH} \cdots \rightarrow \cdots \text{OH}/\text{Mg}/\text{O}/\text{Mg}/\text{OH} \cdots + \text{H}_2\text{O}$). Growth occurs by the formation of additional nearby oxide lamella, creating lamellar oxyhydroxide regions, which can grow both parallel and perpendicular to the $\text{Mg}(\text{OH})_2$ lamella in the host $\text{Mg}(\text{OH})_2$ matrix. The oxide lamella have a substantial theoretical in-plane close packing mismatch with the adjacent hydroxide lamella (the in-plane close-packing Mg-Mg distance of $2.98\text{\AA}$ for ideal MgO lamella is 5% smaller than that observed for $\text{Mg}(\text{OH})_2$ lamella: $3.15\text{\AA}$). Electron diffraction of the *in-situ* dehydroxylation process supports the general applicability of a novel two-dimensional variant of Vegard's law in the oxyhydroxide regions, with the regions exhibiting intermediate lamellar Mg-Mg packing distances. The associated stress within these regions is believed to strongly contribute to crystallite cracking during dehydroxylation and the (111) to (100) surface

reconstruction of the resulting MgO. Such a lamellar nucleation and growth process can take on homogeneous or biphasic character via slow nucleation/rapid growth and rapid nucleation/slow growth, respectively. This may have important implications for optimizing $\text{Mg}(\text{OH})_2$ carbonation, as controlled dehydroxylation before and/or during carbonation may have the potential to create intermediate interfaces with large areas and enhanced carbonation reactivity. A range of dehydroxylation control may be possible, as initial carbonation studies indicate dehydroxylation occurs in advance of carbonation locally.

Partial carbonation of single-crystal $\text{Mg}(\text{OH})_2$ fragments over a wide range of reaction conditions (varying CO_2 pressure and temperature) shows a strong relationship between the extent of carbonation and the extent of dehydroxylation, independent of the reaction conditions used. Chemical analysis found all partially carbonated samples contain hydroxide, oxide (and/or oxyhydroxide) together with carbonate. A strong correlation exists between the level of dehydroxylation and carbonation, as samples with higher levels of carbonation also have higher dehydroxylation levels. The linear or near-linear correlation between carbonation and dehydroxylation, with the extent of dehydroxylation being substantially greater than the extent of carbonation, suggests carbonation primarily occurs via intermediate oxyhydroxide or oxide formation. Thus, dehydroxylation (i) is occurring significantly in advance of carbonation and (ii) carbonation and dehydroxylation do not occur as a simple exchange reaction (i.e., carbon dioxide directly displacing two hydroxyl groups, with water evolution). Initial studies indicate increasing the partial pressure of water vapor during the carbonation process slows both the rate of dehydroxylation and the rate of carbonation, providing further support for dehydroxylation occurring in advance of carbonation locally. Importantly, the range and type of intermediate oxyhydroxides/oxides that can form in advance of carbonation should provide a degree of control over both their formation and potential carbonation reactivity.

Secondary ion mass spectrometry observations of single crystal $\text{Mg}(\text{OH})_2$ fragments before and after partial carbonation suggest carbonation primarily occurs at the crystal-gas interface, likely passivating the carbonation process. Optical microscopy observations of similar fragments indicate substantial cracking and delamination of the crystals can occur during carbonation, providing an avenue to enhance their reactive surface area and overall carbonation reactivity. Maximizing the occurrence of such processes may be particularly important to optimizing carbonation reactivity, as they can provide a path around passivating layer formation.

EXPERIMENTAL

MATERIALS: Natural single crystal brucite from Delora, Canada was used as the starting material. Elemental analysis by proton-induced X-ray emission and total carbon analysis showed the material to contain 0.16% Mn, 0.06% C, 0.01% Cl and 0.01% Si by weight. X-ray powder diffraction was used to structurally characterize the starting material [$a=3.147(1)$ Å and $c=4.765(1)$ Å], in good agreement with the known parameters for brucite [$a=3.147$ Å and $c=4.769$ Å].² E-cell DHRTEM samples were prepared in a He glovebox by either cold crushing at -196°C or scraping the crystal with a razor blade. Crystals were then dry loaded on to holey-carbon-coated copper grids for DHRTEM analysis. Single crystal fragments for carbonation studies were cleaved from the crystal matrix. High pressure carbonation/dehydroxylation reactions were carried out in a sealed autoclave. The samples were introduced to the autoclave in vitreous silica boats. The autoclave was sealed, dry CO₂ introduced, and the autoclave brought quickly to reaction temperature. Samples reacted at one atmosphere of carbon dioxide (with and without water vapor present) were reacted in a Setaram TGS2 thermogravimetric analysis system, with 1 µ sensitivity.

E-Cell DHRTEM: The *in-situ* studies of Mg(OH)₂ dehydroxylation were performed using a Philips 430 HRTEM (300 kV; 2.3 Å pt. to pt. resolution) equipped with a Gatan Imaging energy Filter (GIF) and a 0-5 torr E-cell. Dehydroxylation was induced by electron beam heating and resistive heating using the sample holder, both with and without the presence of water vapor. Direct imaging of the reaction was recorded on videotape in real time (30 frame/sec). Water vapor (e.g., ~ 1 torr) was required to slow the dehydroxylation process sufficiently for direct imaging. Digital Micrograph was used to analyze the interlamellar spacings in four-frame time-averaged images of the dehydroxylation process parallel to the brucite layers. Selected area diffraction of the reaction process was recorded as a function of time using internal gold island diffraction standards and photographic plates.

GENERAL FACILITIES: The SIMS system used was a Cameca IMS 3f ion microscope. Base pressure in the sample chamber is 10⁻⁷ torr. Depth resolution can be better than 10 nm. Lateral resolution is ~5-20 µm in point analysis mode and lateral image resolution is ~1 µm. The digital optical microscope system used was a Mitutoyo Ultraplan FS-110, with bright and dark field, polarized light, Nomarski, and reflected and transmitted illumination capabilities together with extra-long working distance objectives and fraction of a micron resolution. Total hydroxide, oxide and carbonate contents for the partially dehydroxylated/carbonated single crystal fragments were determined using a Perkin Elmer PE 2400 Series CHNS analysis system. Careful use of standards before and after sample analysis showed an absolute error of ± 0.2 wt%.

MODELING: Non-empirical simulation was undertaken to elucidate the energetics of a number of systems of composition Mg_{x+y}O_x(OH)₂. The structural parameters and cohesive energies were obtained by directly minimizing the Gibbs free energy of the crystal with respect to structural and electronic degrees of freedom using density functional theory-based Variationally Induced

Breathing (VIB) and Potential Induced Breathing (PIB) methods. The crystal energy is estimated using a Gordon-Kim-like procedure for short-ranged forces and changes in the site energy due to charge deformation, while the Madelung energy is treated using the Ewald method. Thus, for a given deformation state, each atomic/ionic density is recalculated self-consistently using the Kohn-Sham procedure³ and the total short-ranged crystal energy is re-evaluated. The theoretical model described above is particularly well suited for compounds that exhibit strong ionic character. The more covalent O-H bonds are held fixed in our simulations. The average behavior of the bonding with the hydroxide/oxyhydroxide layers is reasonably described.

RESULTS AND DISCUSSION

Mg(OH)₂ DEHYDROXYLATION

DHRTM observations parallel to the Mg(OH)₂ lamella during dehydroxylation show the general lamellar nature of the process. Time averaged videotape sequences of the process show its distinct lamellar character (Figures 1-4). Digital Micrograph analysis of the sequences show the presence of lamellar oxyhydroxide regions containing discrete oxide, hydroxide, and oxyhydroxide interlamellar spacings, underscoring the lamellar nature of the dehydroxylation process (Figures 2 and 4). The oxyhydroxide regions create substantial in-plane close-packing mismatch between ideal adjacent oxide and hydroxide lamella (the in-plane closest-packing Mg-Mg distance of 2.98 Å for ideal MgO lamella is 5% smaller than the 3.15 Å observed for Mg(OH)₂ lamella).

SAD of the *in-situ* dehydroxylation process perpendicular to the Mg(OH)₂ lamella (Figure 5) supports the general applicability of a novel two-dimensional variant of Vegard's law in the oxyhydroxide regions, with the regions exhibiting lamellar Mg-Mg packing distances between those observed for Mg(OH)₂ and MgO (Figure 6). Initially, lamellar oxyhydroxide regions are observed with an in-plane Mg-Mg distance of 3.04 Å (suggesting a relatively high concentration of oxide lamella), which slowly decreases with continued dehydroxylation to the 2.98 Å observed for MgO.

Advanced non-empirical Variationally Induced Breathing and Potential Induced Breathing computer modeling of lamellar oxyhydroxide Mg_{x+y}O_x(OH)_{2y} reaction intermediate regions show them to be thermodynamically unstable with respect to isolated regions of Mg(OH)₂ and MgO for high concentrations of magnesium hydroxide layers (Figure 7). However, at lower hydroxide layer concentrations, below ~ 40%, the oxyhydroxides formed are stable relative to isolated regions of Mg(OH)₂ and MgO. Regions containing more than 50% hydroxide lamella are particularly unstable, facilitating dehydroxylation of Mg(OH)₂ layers near lamellar oxide nuclei and lamellar nucleation and growth behavior. On the other hand, oxyhydroxide regions with < 40% Mg(OH)₂ lamella are increasingly stable with respect to separate Mg(OH)₂ and MgO regions for lower hydroxide layer concentrations. This explains why low concentrations of hydroxide lamella can persist in oxyhydroxide regions during dehydroxylation, whereas high concentrations do not, as indicated by SAD. More generally, during dehydroxylation the intermediate oxyhydroxide energies combine with the elastic deformation (bending) energy of the layers to

guide the dehydroxylation process. These observations indicate dehydroxylation proceeds by a lamellar nucleation and growth mechanism. Initially, lamellar oxide nuclei form by dehydration of a double hydroxide $\text{Mg}(\text{OH})_2$ layer/layer-region, as in reaction (3). Growth occurs via the formation of additional

partial/full oxide layers nearby, creating lamellar oxyhydroxide regions, which can grow parallel and perpendicular to the lamella in the $\text{Mg}(\text{OH})_2$ matrix.

Such a lamellar nucleation and growth process can exhibit lamellar oxyhydroxide intergrowth or two-phase (oxide + hydroxide) behavior via relatively slow nucleation/fast growth or fast nucleation/slow growth, respectively. Previous electron diffraction studies of dehydroxylation^{4,5} are consistent with competition between these processes. These mechanisms may have important implications for optimizing $\text{Mg}(\text{OH})_2$ carbonation, as controlled dehydroxylation during carbonation may have the potential to create reactive intermediate interfaces with large areas to enhance carbonation reactivity. A range of dehydroxylation control may be possible during carbonation, as initial studies indicate dehydroxylation can occur in advance of carbonation.

$\text{Mg}(\text{OH})_2$ DEHYDROXYLATION/CARBONATION

Our dehydroxylation studies have identified a range of materials that are of interest as potential carbonation reaction intermediate materials during the carbonation process. Of particular interest to optimizing $\text{Mg}(\text{OH})_2$ carbonation reactivity, is the relative carbonation reactivity of these materials during the dehydroxylation/carbonation process. The range of potential reaction pathways possible for carbonation are outlined in Figure 8, which shows how the hydroxide, intermediate oxyhydroxides, and oxide could all theoretically participate in carbonate formation.

Table 1 shows the compositional analysis of a series of dehydroxylation/carbonation reactions for $\text{Mg}(\text{OH})_2$ single crystal fragments. The observed values for the carbonate and hydroxide compositions are derived from analysis of the total H and C present in each sample. Based on agreement with known standards run immediately before and after the sample runs, the error in MgCO_3 and $\text{Mg}(\text{OH})_2/\text{MgO}/\text{total}$ dehydroxylation compositions are estimated to be $\pm 2\%$ and $\pm 6\%$, respectively. The H series reactions were carried out in a sealed autoclave under dry CO_2 , without added water. The M series was reacted in a Setaram TGS2 thermogravimetric analysis system under either an atmosphere of dry CO_2 (M1) or dry CO_2 bubbled through water at 20°C (i.e., ~ 18 torr water vapor pressure: M2).

Analysis of single-crystal $\text{Mg}(\text{OH})_2$ fragments partially-carbonated over a wide range of reaction conditions (varying CO_2 pressure, temperature, and time) shows a strong relationship between the extent of carbonation and the extent of dehydroxylation, independent of the reaction conditions used. Chemical analysis found all partially carbonated samples contain hydroxide, oxide (and/or oxyhydroxide) together with carbonate. Over the broad range of reaction conditions explored, the extent of total dehydroxylation was always substantially greater than the extent of carbonation. Figure 9 shows the linear or near-linear relationship between the extent of

carbonation and total dehydroxylation. This relationship, together with the extent of dehydroxylation being substantially greater than the extent of carbonation, suggests carbonation primarily occurs via intermediate oxyhydroxide or oxide formation. Thus, dehydroxylation (i) occurs significantly in advance of carbonation and (ii) carbonation and dehydroxylation do not occur as a simple exchange reaction (i.e., carbon dioxide directly displacing two hydroxyl groups, with water evolution). Initial studies (M1 and M2) indicate increasing the partial pressure of water vapor during the carbonation process slows both the rate of dehydroxylation and the rate of carbonation, providing further support for dehydroxylation occurring in advance of carbonation locally. Importantly, the range and type of intermediate oxyhydroxides/oxides that can form in advance of carbonation should provide a degree of control over both their formation and potential carbonation reactivity.

Secondary ion mass spectrometry (SIMS) observations of single crystal $\text{Mg}(\text{OH})_2$ fragments before and after partial carbonation suggest carbonation primarily occurs at the crystal-gas interface, likely passivating the carbonation process. Figure 10 shows a plot of the C, H and O/Mg ratios as a function of their depth into a partially carbonated $\text{Mg}(\text{OH})_2$ basal plane, suggesting possible passivating MgCO_3 layer formation during dehydroxylation/carbonation. Optical microscopy observations of similar fragments (Figure 11) indicate substantial cracking and delamination of the crystals can occur during carbonation, providing an avenue to enhance their reactive surface area and overall carbonation reactivity. Maximizing the occurrence of such processes may be particularly important to optimizing carbonation reactivity, as they can provide a path around passivating layer formation.

DHRTEM Observations Parallel to the $\text{Mg}(\text{OH})_2$ Lamella Prior to Dehydroxylation

Figure 1) $\text{Mg}(\text{OH})_2$ lamella prior to dehydroxylation (~ 1 torr H_2O)

Figure 2) Line profile showing the $\text{Mg}(\text{OH})_2$ interlamellar spacings in the region shown in Figure 1. All the peak-to-peak spacings measure $4.8 \pm 0.5 \text{ \AA}$ in good agreement with the interlamellar spacing of $\text{Mg}(\text{OH})_2$ determined by XPD ($4.769 \text{ \AA}$).

DHRTEM Observations Parallel to the $\text{Mg}(\text{OH})_2$ Lamella During Dehydroxylation

Figure 3) Behavior of the lamella during dehydroxylation (~ 1 torr H_2O)

Figure 4) Line profile showing oxide, hydroxide, and oxyhydroxide interlamellar spacings in the region shown in Figure 3. These spacings are in three groups: (i) 2.5 ± 0.4 Å (7 spacings ▼, MgO spacing 2.43 Å via XPD), (ii) 4.8 ± 0.6 Å (14 spacings ▼, $\text{Mg}(\text{OH})_2$ spacing 4.77 Å via XPD), (iii) 7.0 ± 0.6 Å (5 spacings ▼, MgO + $\text{Mg}(\text{OH})_2$ spacing 7.20 Å). Two additional spacings (▼) of 8.9 Å are also observed, which may correspond to $\text{Mg}_3\text{O}_2(\text{OH})_2$ oxyhydroxide lamella (9.6 Å) or dehydroxylating lamella in transition locally.

SAD of the Dehydroxylation Process

Figure 5) Selected area diffraction (SAD) perpendicular to the layers: a) $\text{Mg}(\text{OH})_2$ aligned along $[0001]$ prior to dehydroxylation, b) the $\text{Mg}(\text{OH})_2$ matrix containing lamellar oxyhydroxide regions during dehydroxylation, c) the product MgO aligned along $[111]$. The oxyhydroxide pattern initially formed corresponds to an in plane hexagonal Mg-Mg distance of $3.04 \text{ \AA}$, which slowly decreases to that for MgO $2.98 \text{ \AA}$. The Mg-Mg distance observed for the $\text{Mg}(\text{OH})_2$ matrix is constant at $3.15 \text{ \AA}$.

Figure 6) Intralamellar Mg-Mg distances observed by SAD during dehydroxylation.

$Mg_{x+y}O_x(OH)_{2y}$	x	y	% Hydroxide	ΔE (kcal/ mol Mg)
MgO	1	0	0%	0
$Mg_5O_4(OH)_2$	4	1	20%	-8.2
$Mg_3O_2(OH)_2$	2	1	33%	-5.1
$Mg_2O(OH)_2$	1	1	50%	+5.7
$Mg_3O(OH)_4$	1	2	67%	+8.2
$Mg_4O(OH)_6$	1	3	75%	+9.5
$Mg_5O(OH)_8$	1	4	80%	+9.5
$Mg(OH)_2$	0	1	100%	0

Figure 7) Lamellar oxyhydroxide $Mg_{x+y}O_x(OH)_{2y}$ reaction intermediate energies vs. $y\{Mg(OH)_2\} + x MgO$.

Figure 8) Gas-phase carbonization of $\text{Mg}(\text{OH})_2$: potential reaction pathways. Atom color codes: Mg=green, O=red, H=white, C=grey.

Table 1) Carbonation of Brucite Single Crystal Fragments.

A Comparison of Mole Percent MgCO_3 , MgO , Mg(OH)_2 as a Function of Reaction Conditions.

Run	% MgCO_3	% $\text{MgO}^{(1)}$	% $\text{Mg(OH)}_2^{(1)}$	% Total Dehydroxylation ⁽²⁾	Time (h)	P_{CO_2} (psi)	Temperature (°C)
M1	4.84	24.73	70.43	29.57	19	15	385
M2 ⁽³⁾	1.22	10.85	87.93	12.07	19	15	385
H1.1	0.47	8.39	91.14	8.86	1	2900	455
H2.1	0.46	13.88	85.66	14.34	5.5	2220	403
H3.1	0.66	7.19	92.14	7.86	13	920	476
H4.1	0.28	9.16	90.56	9.44	5.5	1660	508
H5.1	0.52	8.68	90.80	9.20	5.5	1640	532
H6.2	0.19	8.55	91.26	8.74	58	1830	409
H7.2	3.99	11.38	84.63	15.37	60	1650	551
H9.1	6.22	17.20	76.59	23.41	120	950	551
H10.2	13.94	27.38	58.68	41.32	60	920	587
H11.1	19.31	73.21	7.48	92.52	64	460	589
H12.1	18.99	70.20	10.81	89.19	12	490	600

(1) % MgO and Mg(OH)_2 describe the relative amount of MgO and Mg(OH)_2 in the sample.

These can coexist in lamellar oxyhydroxide regions.

(2) % Total Dehydroxylation = % MgCO_3 + % MgO .

(3) 15 psi CO_2 + 0.3 psi H_2O .

Figure 9) Total $\text{Mg}(\text{OH})_2$ dehydroxylation vs. carbonation.

Figure 10) SIMS depth profile of a partially carbonated $\text{Mg}(\text{OH})_2$ crystal fragment.

Strain fields and cracking viewed perpendicular to the layers.

Delamination and cracking viewed parallel to the layers

Figure 11) Disruption of $\text{Mg}(\text{OH})_2$ crystal fragments during dehydroxylation/carbonation observed by optical microscopy.

CONCLUSIONS

Mg(OH)₂ dehydroxylation proceeds by a lamellar nucleation and growth mechanism. Lamellar oxyhydroxide nuclei form and grow in the Mg(OH)₂ matrix, resulting in MgO regions that can eventually surface reconstruct to form well-known, (100)-faceted MgO nanocrystals.⁵ These transient oxyhydroxide regions exhibit novel two-dimensional Vegard's law-like behavior, accounting for the intermediate Mg-Mg in-plane distances observed. More generally, competition between dehydroxylation nucleation and growth starting at the crystal edges can lead to a process with relatively strong two-phase character or lamellar oxyhydroxide intergrowth behavior, respectively. Thus, a range of dehydroxylation reaction intermediate materials may be made available for carbonation during dehydroxylation/carbonation processes. As such, controlled dehydroxylation prior to and/or during carbonation may have the potential to substantially enhance Mg(OH)₂ carbonation reactivity, which, in turn, should significantly enhance the economic viability of this CO₂ mineral sequestration process.

Carbonation appears to primarily occur via intermediate oxyhydroxides or oxides, with the extent of overall dehydroxylation being substantially greater than the level of carbonation. For the carbonation reaction conditions studied to date, the extent of carbonation observed has been found to be a linear or near-linear function of the extent of dehydroxylation for dehydroxylation/carbonation of Mg(OH)₂ crystal fragments. Preliminary studies indicate the presence of water vapor may inhibit carbonation by inhibiting the concurrent dehydroxylation process.

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ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles (peer reviewed)

- McKelvy, M.J., Sharma, R., Chizmeshya, A.V.G., Streib, K., Carpenter, R.W. “Mg(OH)₂ Dehydroxylation: A Lamellar Nucleation and Growth Process,” to be submitted shortly.
- Chizmeshya, A.V.G., McKelvy, M.J., Sharma, R., Carpenter, R.W. “Mg(OH)₂ Dehydroxylation: A Non-Empirical Density Function Approach,” to be submitted shortly.

Conference Presentations

- McKelvy, Michael J., Sharma, Renu, Chizmeshya, Andrew V.G., Bearat, Hamdallah, Carpenter, Ray W. and Streib, Ken “Mg(OH)₂ Dehydroxylation: The Path to Brucite CO₂ Mineral Sequestration,” the *Third Carbon Dioxide Mineral Sequestration Forum* at the Federal Energy Technology Center, Pittsburgh, Pennsylvania, June 29, 1999.
- McKelvy, Michael J., Sharma, Renu, Chizmeshya, Andrew V.G., Carpenter, Ray W., Streib, Ken “Mg(OH)₂ Dehydroxylation: A Lamellar Nucleation and Growth Process,” *University Coal Research Contractors Review Meeting*, Pittsburgh, Pennsylvania, June 1-2, 1999.
- McKelvy, M.J., Carpenter, R.W., Sharma, R., Streib, K. “Atomic-Level Imaging of CO₂ Disposal as a Carbonate Mineral: Optimizing Mg(OH)₂ Carbonation,” the *Second Carbon Dioxide Mineral Sequestration Forum*, Albany, Oregon, November 3, 1998.
- McKelvy, M.J., Carpenter, R.W., Sharma, R. “Atomic-Level Imaging of CO₂ Disposal as a Carbonate Mineral: Optimizing Reaction Process Design,” the *Carbon Dioxide Mineral Sequestration Forum*, Los Alamos, New Mexico, June 30, 1998.

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APPENDIX II: Year 2 Technical Progress Report

ATOMIC-LEVEL IMAGING OF CO₂ DISPOSAL AS A CARBONATE MINERAL: OPTIMIZING REACTION PROCESS DESIGN

Type of Report: Annual

Reporting Period Start Date: August 1, 1999

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Principal Authors: M.J. McKelvy,* R. Sharma, A.V.G. Chizmeshya, H. Bearat, and R.W. Carpenter.

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ABSTRACT

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Permanent and safe methods for CO₂ capture and disposal/storage need to be developed. Mineralization of stationary-source CO₂ emissions as carbonates can provide such safe capture and long-term sequestration. Mg-rich lamellar-hydroxide based minerals (e.g., brucite and serpentine) offer a class of widely available, low-cost materials, with intriguing mineral carbonation potential. Carbonation of such materials inherently involves dehydroxylation, which can disrupt the material down to the atomic level. As such, controlled dehydroxylation before and/or during carbonation may provide an important parameter for enhancing carbonation reaction processes. Mg(OH)₂ was chosen as the model material for investigating lamellar hydroxide mineral dehydroxylation/carbonation mechanisms due to (i) its structural and chemical simplicity, (ii) interest in Mg(OH)₂ gas-solid carbonation as a potentially cost-effective CO₂ mineral sequestration process component, and (iii) its structural and chemical similarity to other lamellar-hydroxide-based minerals (e.g., serpentine-based minerals) whose carbonation reaction processes are being explored due to their low-cost CO₂ sequestration potential. Fundamental understanding of the mechanisms that govern dehydroxylation/carbonation processes is essential for cost optimization of any lamellar-hydroxide-based mineral carbonation sequestration process.

In the first project year, we used environmental-cell (E-cell), dynamic high-resolution transmission electron microscopy (DHRTEM) to directly observe the Mg(OH)₂ dehydroxylation process at the atomic-level for the first time. We also carried out exploratory semi-empirical modeling studies of the intermediate materials formed. Dehydroxylation was discovered to be a lamellar nucleation and growth process, which includes intermediate lamellar oxyhydroxide formation. These intermediates offer a series of new carbonation reaction pathways, with the potential to enhance carbonation reactivity. We also initiated studies to probe dehydroxylation/carbonation reaction mechanisms, using elemental analysis, SIMS and optical microscopy.

In the second year, a wide range of studies has substantially enhanced our understanding of the reaction mechanisms associated with Mg(OH)₂ carbonation reactivity. These include E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, TGA, XRD, and elemental analysis. Detailed advanced modeling studies were carried out in collaboration with DOE/NETL grant DE-FG26-99FT40580. *We have discovered intermediate (e.g., oxyhydroxide) formation is a key component of both rehydroxylation/carbonation and dehydroxylation/carbonation processes, which can be controlled to dramatically enhance carbonation reactivity at ambient temperature and CO₂ pressure.* The ability of Mg(OH)₂ to form nanostructured materials during controlled dehydroxylation is another key component governing carbonation reactivity. Together with delamination and cracking, these factors enhance carbonation by increasing the reactive carbonation surface area. On the other hand, carbonation can slow high-surface-area reactive intermediate formation via the formation of passivating carbonate layers. MgO crystal growth during dehydroxylation can also inhibit carbonation. Initial studies indicate that Fe impurities can phase separate during dehydroxylation, but, at low concentrations, do not initially appear to substantially inhibit carbonation, at least locally. All of the above factors must be adroitly balanced to enhance carbonation reactivity.

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EXECUTIVE SUMMARY

OBJECTIVE

The goal of this project is to develop an atomic-level understanding of the mechanisms that govern the kinetics of the complex $\text{Mg}(\text{OH})_2$ carbonation process to facilitate engineering of improved carbonation materials and processes for CO_2 disposal. $\text{Mg}(\text{OH})_2$ carbonation serves as a model system for developing a better fundamental understanding of Mg-rich lamellar-hydroxide-based mineral carbonation processes. These processes are of current interest due to their cost-effective CO_2 mineral sequestration potential. Environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM), including parallel electron energy loss spectroscopy (PEELS) is used to probe dehydroxylation/rehydroxylation-carbonation reaction processes down to and at the atomic level. A battery of complementary techniques is incorporated to further elucidate these processes at the macroscopic and microscopic level (i.e., *in-situ* and *ex-situ* studies). As the dehydroxylation-carbonation process involves dehydroxylation, carbonation and potential competition between them, developing an atomic-level understanding of the dehydroxylation process is first targeted to provide a foundation from which to explore the overall carbonation process. Initially, the primary focus has been on high purity $\text{Mg}(\text{OH})_2$ single crystal fragments to elucidate basic reaction processes for highly crystalline material. Investigations of the effects of material reconstruction, crystalline defects, and impurities (e.g., Fe, Ca) on dehydroxylation/carbonation processes are targeted to better understand their impact on carbonation reactivity.

ACCOMPLISHMENTS TO DATE

We have broadened our studies beyond our core atomic-level E-cell DHRTEM studies to better understand $\text{Mg}(\text{OH})_2$ dehydroxylation/carbonation mechanisms at the macroscopic, microscopic, and atomic level. Our studies have also been expanded to include rehydroxylation/carbonation processes to better understand the role of oxyhydroxide intermediate formation in carbonation reactivity. We have carried out integrated studies of partially dehydroxylated/carbonated powders and single crystal fragments using optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and elemental analysis. These studies are being integrated with advanced computational modeling studies in collaboration with the DOE UCR Innovative Concepts project “Atomic-Level Modeling of CO_2 Disposal as a Carbonate Mineral: a Synergetic Approach to Optimizing Reaction Process Design,” (grant # DE-FG26-99FT40580).

$\text{Mg}(\text{OH})_2$ dehydroxylation proceeds as a lamellar nucleation and growth process. Initially, lamellar oxide nuclei form (e.g., $\cdots\text{OH}/\text{Mg}/\text{OH}/\text{OH}/\text{Mg}/\text{OH}\cdots \rightarrow \cdots\text{OH}/\text{Mg}/\text{O}/\text{Mg}/\text{OH}\cdots + \text{H}_2\text{O}$) within the hydroxide matrix. Growth occurs with the formation of additional nearby oxide lamella, creating lamellar oxyhydroxide regions, which can grow both parallel and perpendicular to the $\text{Mg}(\text{OH})_2$ lamella. This process can take on lamellar solid solution (oxyhydroxide) or two-phase [$\text{Mg}(\text{OH})_2 + \text{MgO}$] character via slow nucleation/rapid growth and rapid nucleation/slow growth, respectively. The free energies (400 °C) of the entire solid solution series of oxyhydroxide intermediates is within 2 kcal/mol of stoichiometrically equivalent $\text{Mg}(\text{OH})_2 +$

MgO mixtures, indicating the entire series can be accessible during carbonation. Importantly, dehydroxylation is reversible, via oxide/oxyhydroxide nanostructure formation. This creates a broad range of new intermediate oxyhydroxide carbonation pathways via dehydroxylation or rehydroxylation.

Macroscopic and microscopic studies of gas-phase dehydroxylation-carbonation processes indicate dehydroxylation generally precedes carbonation locally, consistent with the creation of dehydroxylation intermediates with higher carbonation reactivity. Simultaneous rehydroxylation of partially dehydroxylated material was found to greatly enhance its gas-phase carbonation reactivity *at ambient temperature*, further underscoring the importance of transitory intermediate formation. In addition to forming lamellar oxyhydroxide intermediates, dehydroxylation can also result in substantial delamination, intralamellar cracking, and surface reconstruction to form nanostructured materials, due to the strain associated with $\text{Mg}(\text{OH})_2/\text{MgO}$ layer bending. These phenomena provide important pathways, which can be used to combat the formation of near surface carbonate passivation, as observed by SIMS. These highly porous structures can also lead to novel phenomena, such as $\text{Mg}(\text{OH})_2$ carbonation reactivity decreasing during dehydroxylation-carbonation with increasing CO_2 gas pressure (water vapor evolution during dehydroxylation inhibits CO_2 diffusion to available carbonation sites more effectively at higher gas pressures). Overall, these intermediate materials offer broad potential for enhancing carbonation reactivity. Their formation and the interplay of the cumulative factors that govern carbonation reactivity is only just now beginning to be understood, underscoring the potential for substantial improvements in carbonation reactivity via materials and process engineering. Furthermore, the close structural and chemical similarity between $\text{Mg}(\text{OH})_2$ and the Mg-rich, lamellar-hydroxide-based serpentine minerals, suggest these materials also possess large untapped potential for (i) enhanced carbonation reactivity and (ii) substantially lower mineral sequestration process costs.

INTRODUCTION

Mineral Carbonation: An Attractive Candidate Process for CO₂ Sequestration

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Mineralization of stationary-source CO₂ emissions as carbonates can provide safe capture and long-term sequestration. The resulting carbonates (e.g., magnesium and calcium carbonate, MgCO₃ and CaCO₃) occur in nature in quantities that far exceed those that could result from carbonating the world's known fossil fuel reserves. Furthermore, they have already proven stable over geological time, eliminating the safety and cost concerns associated with long-term storage of CO₂ in compressed form. Conversion of CO₂ into Mg/CaCO₃ effectively disposes of CO₂ by accelerating the natural processes that already occur in nature.

Mg-rich minerals and mineral derivatives are being investigated as low-cost mineral carbonation feedstock materials by the CO₂ Mineral Sequestration Working Group (comprised of members from the Albany Research Center, our CO₂ Mineral Sequestration Research Group at Arizona State University, Los Alamos National Laboratory, the National Energy Technology Laboratory and Science Applications International Corporation).¹ The primary focus of the Working Group, which is managed by the Department of Energy, is to evaluate the economic viability of mineral carbonation processes as long-term options for reducing atmospheric CO₂ emissions. A major challenge in cost-competitive process development is to accelerate these carbonation reaction(s) to a high degree of completion on an industrial time scale. The associated reaction rates depend on many materials and process parameters, providing substantial potential for rate enhancement. However, the effects of many of these parameters are poorly understood, especially at the atomic level, severely limiting their effective use. A fundamental understanding of the mechanisms that govern key carbonation processes is needed to create the foundation for reaction process optimization via materials and process engineering.

Mg-Rich Lamellar-Hydroxide-Based Minerals: Candidate Feedstock Materials for Cost Competitive CO₂ Mineral Sequestration

Carbonation of Mg-rich lamellar-hydroxide-based minerals (e.g., the serpentine-based minerals and brucite: Mg(OH)₂) is a leading CO₂-mineral-sequestration, process candidate. Optimizing the carbonation reaction rate and its degree of completion is key to lowering process cost. Mg(OH)₂ was chosen as the model material for investigating lamellar hydroxide mineral dehydroxylation/carbonation mechanisms due to (i) its structural and chemical simplicity,² (ii) the interest in Mg(OH)₂ gas-solid carbonation as a potentially cost-effective CO₂ mineral sequestration process component,³⁻⁵ and (iii) its structural and chemical similarity to other lamellar-hydroxide-based minerals (e.g., serpentine, see Figure 1), whose carbonation reaction processes are being explored due to their CO₂ sequestration potential.¹ This project focuses on developing an atomic-level understanding of the reaction mechanisms that govern dehydroxylation/rehydroxylation-carbonation processes for this model lamellar hydroxide feedstock material. The long-term goal is to develop the necessary atomic-level mechanistic

understanding to engineer improved carbonation materials and processes for Mg-rich lamellar-hydroxide-based minerals.

Mg(OH)₂ Dehydroxylation: The First Step in Carbonation

As Mg(OH)₂ dehydroxylation, depicted in reaction (2), is intimately associated with the carbonation process, its mechanisms are of direct interest in understanding and optimizing the carbonation process. Although Mg(OH)₂ dehydroxylation has been extensively studied, relatively little is known about the atomic-level nature of the process, especially in the early stages of dehydroxylation. The early stages of the process are of particular interest, since carbon dioxide may react to form magnesite (MgCO₃) locally as soon as dehydroxylation begins in that region. In our first year progress report, we reported our discovery that Mg(OH)₂ dehydroxylation is governed by a lamellar nucleation and growth process. Environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM) was used to directly observe the *in-situ* process at the atomic-level for the first time. These observations were combined with preliminary advanced computational modeling studies using a non-empirical density functional theory (DFT) approach to better elucidate the atomic-level dehydroxylation process. In this second year report, we describe our studies that have lead to a deeper understanding of the lamellar nucleation and growth process, including (i) analysis of the interrelationship between oxyhydroxide intermediate and nanostructure formation and (ii) advanced modeling studies of the oxyhydroxide intermediate materials formed in collaboration with DOE/NETL grant DE-FG26-99FT40580.

Mg(OH)₂ Dehydroxylation/Rehydroxylation-Carbonation Processes

In last year's report, we described combining the first-year dehydroxylation studies with preliminary dehydroxylation/carbonation studies of single crystal Mg(OH)₂ fragments to better elucidate dehydroxylation/carbonation reaction mechanisms. We found dehydroxylation generally occurred in advance of carbonation during Mg(OH)₂ carbonation, suggesting intermediate formation may be important to carbonation reactivity during simultaneous dehydroxylation-carbonation. We also discovered initial evidence for passivating carbonate layer formation and substantial delamination and cracking of the Mg(OH)₂ feedstock material during dehydroxylation-carbonation.

During the second project year we have extended these studies. First, they were expanded to include rehydroxylation-carbonation, as well as dehydroxylation-carbonation. A wide range of investigations were undertaken and have substantially enhanced our understanding of the reaction mechanisms associated with Mg(OH)₂ carbonation reactivity. These include E-cell DHRTEM (including parallel electron energy loss spectroscopy – PEELS), optical microscopy, FESEM, ion beam analysis, SIMS, TGA, XRD, and elemental analysis. Detailed advanced modeling studies of carbonation processes were also carried out in collaboration with DOE/NETL grant DE-FG26-99FT40580. We have discovered dehydroxylation/rehydroxylation intermediate (e.g., oxyhydroxide) formation is a key component of both

dehydroxylation/carbonation and rehydroxylation/carbonation processes, with essentially the entire lamellar oxyhydroxide solid solution series ($\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$) accessible during $\text{Mg}(\text{OH})_2$ dehydroxylation/rehydroxylation. The ability of $\text{Mg}(\text{OH})_2$ to form nanostructured materials during controlled dehydroxylation is another key component affecting carbonation reactivity. Together with delamination and cracking, these factors enhance carbonation by increasing the reactive carbonation surface area. On the other hand, carbonation can slow high-surface-area reactive intermediate formation via the formation of passivating carbonate layers. MgO crystal growth during dehydroxylation can also inhibit carbonation. In addition, $\text{Mg}(\text{OH})_2$ feedstock impurities may also play important roles in carbonation reactivity. Although initial studies indicate Fe impurities can phase separate during $\text{Mg}(\text{OH})_2$ dehydroxylation at low concentrations, they do not appear to substantially inhibit carbonation, at least locally. All of the above factors must be adroitly balanced to enhance carbonation reactivity. Our initial efforts to combine oxyhydroxide intermediate formation with controlled nanostructure formation to probe their ability to enhance carbonation reactivity have proven quite promising, as we have already *achieved carbonation reaction rates at ambient temperature and CO_2 pressure that are similar to those previously reported for optimum ambient CO_2 pressure $\text{Mg}(\text{OH})_2$ carbonation (at 375 °C).*

EXPERIMENTAL

MATERIALS: Natural single crystal brucite from Delora, Canada was used as the starting material. Elemental analysis by proton-induced X-ray emission and total carbon analysis showed the material to contain 0.16% Mn, 0.06% C, 0.01% Cl and 0.01% Si by weight. X-ray powder diffraction was used to structurally characterize the starting material [$a=3.147(1)$ Å and $c=4.765(1)$ Å], in good agreement with the known parameters for brucite [$a=3.147$ Å and $c=4.769$ Å].² E-cell DHRTEM samples were prepared in a He glovebox by either cold crushing at -196°C or scraping the crystal with a razor blade. Crystals were then dry loaded on to holey-carbon-coated copper grids for DHRTEM analysis. Single crystal fragments for carbonation studies were cleaved from the crystal matrix. High pressure carbonation/dehydroxylation reactions were carried out in a sealed autoclave. The samples were introduced to the autoclave in vitreous silica boats. The autoclave was sealed, dry CO_2 introduced, and the autoclave brought quickly to reaction temperature. *In situ* $\text{Mg}(\text{OH})_2$ dehydroxylation/rehydroxylation-carbonation reaction processes were investigated using a Setaram TGS2 thermogravimetric analysis system, with 1 µ sensitivity.

E-Cell DHRTEM: The *in-situ* studies of $\text{Mg}(\text{OH})_2$ dehydroxylation/rehydroxylation/carbonation were performed using a Philips 430 HRTEM (300 kV; 2.3 Å pt. to pt. resolution) equipped with a Gatan Imaging energy Filter (GIF) and a 0-5 torr E-cell. Dehydroxylation was induced by electron beam heating and resistive heating using the sample holder, both with and without the presence of water vapor. Direct imaging of the reaction was recorded on videotape in real time (30 frame/sec). Water vapor (e.g., ~ 1 torr) was required to slow the dehydroxylation process sufficiently for direct imaging. Digital Micrograph was used to analyze the interlamellar spacings in four-frame time-averaged images of the dehydroxylation process parallel to the

brucite layers. Selected area diffraction of the reaction process was recorded as a function of time using internal gold island diffraction standards and photographic plates. *In situ* rehydroxylation-carbonation processes were followed by direct imaging, SAD and PEELS. $\text{Mg}(\text{OH})_2$ was first dehydroxylated *in situ* via resistive heating, followed by reaction at ambient temperature with ~ 800 mtorr of humid CO_2 .

GENERAL FACILITIES: The SIMS system used was a Cameca IMS 3f ion microscope. Base pressure in the sample chamber is 10^{-7} torr. Depth resolution can be better than 10 nm. Lateral resolution is $\sim 5\text{-}20\ \mu\text{m}$ in point analysis mode and lateral image resolution is $\sim 1\ \mu\text{m}$. The digital optical microscope system used was a Mititoyo Ultraplan FS-110, with bright and dark field, polarized light, Nomarski, and reflected and transmitted illumination capabilities together with extra-long working distance objectives and fraction of a micron resolution. X-ray powder diffraction (XPD) studies were carried out using a RigakuD/MAX-IIB X-ray diffractometer with $\text{CuK}\alpha$ radiation, line focus, and graphite monochromator. Ion beam analyses of partially carbonated $\text{Mg}(\text{OH})_2$ single crystal samples were performed using a 1.7 MV General Ionex Tandetron system. Mg was analyzed via Rutherford backscattering spectroscopy (RBS) analysis using 2 MeV He^{++} ions. Carbon analysis used a $\text{C}(\alpha, \alpha)\text{C}$ reaction occurring at 4.63 MeV. Oxygen analysis used a similar reaction at 3.05 MeV. H analysis was performed by forward scattering using 2.8 MeV He^{++} ions. Total hydroxide, oxide and carbonate contents for the partially dehydroxylated/carbonated single crystal fragments were determined using a Perkin Elmer PE 2400 Series CHNS analysis system. Careful use of standards before and after sample analysis showed an absolute error of ± 0.2 wt%. The field emission scanning electron microscope (FESEM) system used was a Hitachi S-4100 equipped with an Oxford Instruments ISIS energy dispersive spectrometer.

MODELING: *Ab initio* density functional theory calculations and non-empirical electron-gas modeling based on the VIB method⁶ were used to investigate the relative stability, elastic behavior and structural trends of the intermediate oxyhydroxides as a function of composition. The methods used are described in detail in the attached manuscript submitted for publication in *Chemistry of Materials*. Similar methods were used for the carbonation modeling studies. These are described in detail in the annual report for the DOE UCR Innovative Concepts project “Atomic-Level Modeling of CO_2 Disposal as a Carbonate Mineral: a Synergetic Approach to Optimizing Reaction Process Design,” (grant #DE-FG26-99FT40580), which is fully collaborating with the project described herein.

RESULTS AND DISCUSSION

Mg(OH)₂ DEHYDROXYLATION

During the first year of this project, DHRTEM observations parallel to the $\text{Mg}(\text{OH})_2$ lamella during dehydroxylation were found to show the general lamellar nature of the process. *In situ* selected area diffraction (SAD) studies confirmed a lamellar nucleation and growth process governed $\text{Mg}(\text{OH})_2$ dehydroxylation. After initial oxide layer nucleation, as described in

equation 1, growth occurs via the formation of additional partial/full oxide layers nearby, creating lamellar oxyhydroxide regions, which can grow parallel and perpendicular to the lamella

in the $\text{Mg}(\text{OH})_2$ matrix. Preliminary advanced modeling of the lamellar oxyhydroxide $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$ reaction intermediates was reported last year. During the second year of this project, detailed advanced modeling studies have provided a much better understanding of the nature of the intermediate oxyhydroxides, as highlighted in Figures 2 and 3. Both thermodynamic stability and elastic behavior appear key to the intermediate oxyhydroxide formation, as shown in Figure 2. Oxyhydroxides containing low or high concentrations of oxide lamella are more stable, but not dramatically so, as all compositions are thermodynamically accessible by 500 °C. The oxyhydroxide bulk moduli reveal a dramatic increase in material stiffness early during dehydroxylation, substantially increasing the host-layer bending (deformation) energy needed for dehydroxylation. This significantly slows dehydroxylation for all but low oxide layer concentrations. The greater lamellar flexibility present during initial dehydroxylation combines with the lower stability of intermediate composition oxyhydroxides to promote relatively rapid dehydroxylation to higher oxide layer concentrations. This explains the high concentration of oxide lamella initially found in the oxyhydroxide regions observed by electron diffraction and the enhanced resistance of these regions to further dehydroxylation.

The presence of lamellar oxyhydroxide solid solution behavior during dehydroxylation is confirmed by the in-plane structural behavior of the $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$ oxyhydroxide solid solution series determined by VIB-based non-empirical electron gas modeling. Figure 3 shows that two-dimensional Vegard' s-law-like behavior is predicted for the oxyhydroxides,⁷ as proposed based on the above SAD studies (see attached copy of manuscript submitted to *Chemistry of Materials*). As a result, determination of the in-plane packing distance during dehydroxylation allows direct evaluation of the composition of the lamellar oxyhydroxide regions *in situ*. Table 1 shows the range of oxyhydroxide compositions observed based the present investigation and re-evaluation of previous *in situ* SAD observations of the dehydroxylation process.^{8,9} In each study, the in-plane packing distance (e.g., Mg-Mg distance) and composition of the host $\text{Mg}(\text{OH})_2$ matrix remains unchanged during dehydroxylation and is largely unaffected by oxyhydroxide nucleation and growth. However, essentially the full range of packing distances and compositions has been observed during nucleation and growth of the lamellar oxyhydroxide solid solution series, indicating these new lamellar materials are broadly accessible, at least locally. Thus, essentially the entire oxyhydroxide solid solution series is accessible during dehydroxylation-carbonation, opening the door to a broad new range of intermediate carbonation reaction pathways, with potentially enhanced carbonation reactivity.

Slow nucleation/rapid growth and rapid nucleation/slow growth processes generally favor lamellar oxyhydroxide ($\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$) intermediate formation and two-phase (e.g., $\text{MgO} + \text{Mg}(\text{OH})_2$) intermediate behavior, respectively (Figure 4). Host-layer bending during lamellar nucleation and growth also induces substantial local elastic strain. Such strain likely induces cracking, delamination and reconstruction to form nanostructured materials, during

dehydroxylation. This offers the exciting possibility of controlling nanostructure formation by controlling the relative rates of lamellar nucleation and growth during dehydroxylation.

Optical microscopy observation of the dehydroxylation process has provided substantial insight into the microscopic effects of the lamellar nucleation and growth process. Figures 5 and 6 show the progression of dehydroxylation for a single crystal brucite fragment observed perpendicular to its upper basal plane at different times during the dehydroxylation process. Figure 5 shows typical observations of blisters, likely associated with delamination, that occur early in the dehydroxylation process. Figure 6 shows images taken as a function of time for dehydroxylation of a single crystal fragment at 380 °C, a temperature at which nano-reconstruction routinely occurs. Initial dehydroxylation is associated with blister formation, quickly followed by crack formation onset. Major crack nucleation centers soon develop, with extensive cracking extending to the submicron level after two hours. Thermogravimetric analysis of similar low-temperature dehydroxylation processes indicate that dehydroxylation is only ~93% complete under these conditions, indicating the resulting material contains ~7% residual oxyhydroxide/hydroxide. Such low-temperature dehydroxylated materials have also undergone nano-reconstruction.¹⁰ Thus, low-temperature dehydroxylation forms high-surface-area materials via delamination and cracking of $\text{Mg}(\text{OH})_2$ crystallites to micron/sub-micron dimensions, which simultaneously surface reconstruct to form nano-structured materials. Combining the formation of these high-surface-area materials with dehydroxylation/rehydroxylation intermediate (e.g., lamellar oxyhydroxide) formation has been found to greatly enhance their carbonation reactivity, as discussed in the subsequent section “Enhancing the Carbonation Reaction Process.”

$\text{Mg}(\text{OH})_2$ DEHYDROXYLATION/CARBONATION

As discussed above, our $\text{Mg}(\text{OH})_2$ dehydroxylation studies have identified the formation of a solid solution series of lamellar oxyhydroxide intermediate materials, which form at least locally, en route to MgO formation. These materials are of particular interest as they offer a range of potential new carbonation reaction pathways. A major focus of our dehydroxylation/rehydroxylation-carbonation studies described below, is to better understand the role of such intermediate materials in carbonation and their potential to enhance carbonation reactivity.

During the second project year, we have substantially expanded our preliminary studies of dehydroxylation/carbonation reactions for $\text{Mg}(\text{OH})_2$ single crystal fragments. Table 2 shows the compositional analysis of a series of partially dehydroxylated and carbonated $\text{Mg}(\text{OH})_2$ single crystal fragments as a function of CO_2 pressure at 585 ± 5 °C. The observed values for the carbonate and hydroxide compositions are derived from analysis of the total H and C present in each sample. Based on agreement with known standards run immediately before and after the sample runs, the error in MgCO_3 and $\text{Mg}(\text{OH})_2/\text{MgO}$ compositions are estimated to be $\pm 2\%$ and $\pm 6\%$, respectively. The reactions were carried out in a sealed autoclave under dry CO_2 , without added water. Hence, the only water vapor present evolved from $\text{Mg}(\text{OH})_2$ dehydroxylation. The extent of dehydroxylation was always observed to be substantially greater than the extent of

carbonation, suggesting carbonation primarily occurs via intermediate (e.g., oxyhydroxide/oxide) formation. Thus, dehydroxylation and carbonation do not occur as a simple exchange reaction (i.e., carbon dioxide directly displacing two hydroxyl groups, with water evolution). Instead, dehydroxylation and carbonation appear to be concurrent individual processes, with dehydroxylation intermediate formation providing a key step in the carbonation process. The range and type of intermediate oxyhydroxides/oxides that can form in advance of carbonation should provide a degree of control over both the intermediate materials formed and their potential carbonation reactivity.

The extent of dehydroxylation and carbonation shows intriguing behavior as a function of pressure, as seen in Figures 7 and 8. Whereas, the extent of dehydroxylation generally decreases with increasing CO₂ pressure, the extent of carbonation increases, then decreases as the pressure is increased. These observations are consistent with highly-porous oxyhydroxide/oxide matrix formation and its partial carbonation during the dehydroxylation-carbonation process. The decrease in dehydroxylation observed with increasing pressure follows from the decreasing rate of water diffusion out of the porous hydroxide/oxyhydroxide/oxide/carbonate matrix expected with increasing CO₂ pressure. Locally higher partial pressures of H₂O(g) develop at higher CO₂ pressures, inhibiting the dehydroxylation process. The extent of carbonation shows even more intriguing behavior as a function of CO₂ pressure. A peak in % carbonation is observed near the decomposition pressure expected for MgCO₃ at 585 °C.

Above the MgCO₃ decomposition pressure, *increasing the reactant CO₂ pressure resulted in a dramatic decrease in carbonation reactivity*. This observation is critical for mineral carbonation process engineering, as it is generally assumed increasing the reactant CO₂ activity should increase the extent of carbonation. The overall dehydroxylation-carbonation process is best understood at the nanoscale. As discussed above, dehydroxylation is inhibited by increasing CO₂ pressures. This results in higher local H₂O(g) pressures, inhibition of carbonation reactive intermediate formation via dehydroxylation and slower CO₂(g) diffusion to the dehydroxylating matrix. All of these factors serve to inhibit carbonation, as observed by the decrease in extent of carbonation with increasing CO₂ reaction pressure in the high-pressure region of Figure 7.

Equally intriguing behavior was observed below the pressure at which MgCO₃ becomes unstable with respect to MgO and CO₂. Since, at these low pressures MgCO₃ cannot form at 585 °C, substantial carbonation must be occurring during the sample heat up or cool down cycles. These cycles were carried out under carbon dioxide pressure and lasted ~ 30-40 minutes. To determine the effect of the cool down process on the extent of dehydroxylation and carbonation, samples were quenched from 585 °C to ambient temperature, with simultaneous evacuation of the carbon dioxide present. Figures 7 and 8 include the data from two quenched runs, one above and one below the MgCO₃ decomposition pressure. Whereas, the run above the decomposition pressure agrees well with the unquenched runs, the run below the decomposition pressure shows essentially no carbonation within experimental error ($\pm 2\%$), while exhibiting extensive dehydroxylation consistent with the unquenched samples. This indicates that substantial carbonation can occur relatively quickly during cool down for extensively dehydroxylated Mg(OH)₂.

Dehydroxylation-carbonation studies as a function of temperature at 370 psi of CO₂ further underscore the relationship between simultaneous dehydroxylation and carbonation processes, as shown in Figure 9. Both the extent of dehydroxylation and carbonation increases with increasing temperature until the critical temperature for MgCO₃ formation is reached (the temperature above which MgCO₃ becomes unstable with respect to MgO and CO₂). The relatively small amount of carbonate formation observed for the sample above this temperature is likely associated with carbonation of extensively dehydroxylated material during the cool down process, as observed for the above pressure dependent dehydroxylation-carbonation studies at 585 °C. *In situ* thermogravimetric analysis studies were combined with elemental analysis to further explore the carbonation reactivity of such highly dehydroxylated intermediate materials as a function of temperature and the presence of H₂O(g), as discussed below.

ENHANCING THE CARBONATION REACTION PROCESS

Combined thermogravimetric and elemental analysis studies of *in situ* Mg(OH)₂ carbonation processes involving dehydroxylation and rehydroxylation suggest intermediate oxyhydroxide formation can play a major role in enhancing carbonation reaction rates (Figure 10 and Table 3). 5 mg single crystal Mg(OH)₂ fragments were used as the starting material to reduce the effect of structural defects (surface and internal), particle size, and surface impurities (e.g., MgO or MgCO₃). Samples were initially dehydroxylated by heating under dry He at 2 °C/min to 375 °C and holding them isothermal for two hours, resulting in high-surface-area materials that are ~93% dehydroxylated. The reaction gas was then changed to dry or humid (bubbled through a degassed, distilled water bubbler at 20 °C) CO₂. Both processes resulted in relatively rapid carbonation of 1% of the sample, after which no further carbonation occurred (similar runs changing from dry to humid He at 375 °C exhibited no change in weight, indicating the weight gain for humid CO₂ results from carbonation. Slight weight losses between positions 2 and 3 are similarly assigned to dehydroxylation). Cooling to ambient temperature (23 °C) under dry CO₂ results in little reaction, whereas the same process using humid CO₂ results in relatively rapid rehydroxylation and carbonation, indicating that simultaneous rehydroxylation substantially enhances the carbonation reaction rate.

The above reaction processes are consistent with the formation of high-surface-area material, which is 93% dehydroxylated. Initial exposure to CO₂, under dry or humid conditions, results in only 1% carbonation, after which the reactive carbonation sites have been consumed. On cooling to room temperature under humid CO₂, substantial carbonation and rehydroxylation occur. This indicates the rehydroxylation process greatly enhances carbonation reactivity. This observation is similar to the above studies of the simultaneous dehydroxylation-carbonation process, which indicate enhancing dehydroxylation under controlled conditions directly enhances carbonation. Thus, it appears the carbonation process is dramatically enhanced by the formation of transitory intermediate materials, such as the Mg_{x+y}O_x(OH)_{2y} lamellar oxyhydroxides, during dehydroxylation/rehydroxylation processes.

ATOMIC-LEVEL OBSERVATIONS OF REHYDROXYLATION-CARBONATION PROCESSES

For the model Mg-rich lamellar hydroxide, Mg(OH)₂, heat activation (dehydroxylation) can

disrupt macroscopic single crystals into micron-size fragments comprised of intergrown oxide/oxyhydroxide nanocrystals. As discussed above, these materials have high gas-phase carbonation reactivity during rehydroxylation. XPD analysis of the resulting carbonated material shows no peaks characteristic of magnesite or any other carbonate, indicating the carbonated material is highly disordered (e.g., amorphous), which is not unexpected for an ambient temperature gas phase carbonation process. Direct high temperature carbonation of $\text{Mg}(\text{OH})_2$ routinely produced crystalline magnesite, as evidenced by XPD. We have successfully used parallel electron energy loss spectroscopy (PEELS) to directly observe the rehydroxylation carbonation process in our E-cell DHRTEM reaction system. Direct imaging of the process supports the formation of highly disordered material, as suggested by the above XPD studies. The carbon and oxygen K-edges observed during *in situ* carbonation of two separate samples are shown in Figure 11.

The C K-edge spectra clearly show carbonate formation has occurred. The absence/weak presence of the third peak in the magnesite spectra (~ 319 eV) in the *in situ* carbonated spectra is consistent with the formation of an amorphous carbonate during *in situ* carbonation. The O K-edge spectra of the *in situ* carbonated samples indicate substantial oxide-rich material is present together with the carbonate (e.g., the pre-edge feature at ~ 522 eV for the carbonate is only weakly apparent for the *in situ* carbonated sample). This indicates that only a small fraction of the sample has carbonated so far. This level of reaction control should facilitate future *in situ* PEELS observation of the complete carbonation process. These studies will include detailed advanced modeling analysis of the spectra, via collaboration with DOE/NETL grant DE-FG26-99FT40580, to better characterize the amorphous carbonate materials that form.

ON THE COMPETITION BETWEEN $\text{Mg}(\text{OH})_2$ DELAMINATION, CRACKING AND NANOSTRUCTURE FORMATION AND PASSIVATING CARBONATE LAYER FORMATION

Dehydroxylation-carbonation reaction rates for $\text{Mg}(\text{OH})_2$ single crystal fragments were generally observed to decrease over time consistent with passivating carbonate layer formation. This is consistent with the observation of carbonate surface layer formation, as observed by near-surface SIMS studies and reported in our first year technical progress report. In terms of its effect on carbonation reactivity, such carbonate passivating layer formation is countered by the $\text{Mg}(\text{OH})_2$ cracking, delamination and nano-reconstruction processes associated with dehydroxylation (see attached manuscripts submitted to *Chemistry of Materials* and the 17th International Pittsburgh Coal Conference and our 25th International Technical Conference on Coal Utilization & Fuel Systems Proceedings article, (2000) pp. 897-908). We have made and are in the process of making extensive optical microscopy and FESEM observations of these processes to better understand their role in carbonation reactivity. The aggregate insight these observations provide into carbonation reactivity will be described in next year's report. Overall, these factors have the potential to counter the carbonation inhibiting effects of passivating layer formation by disrupting the solid state structure down to the atomic level and creating high surface area reaction intermediates.

Ion beam analysis of partially dehydroxylated and carbonated single crystal samples has provided new insight into the dehydroxylation-carbonation reaction interface as a function of

depth from the crystal surface, as shown in Table 4. As expected, the extent of carbonate formation and dehydroxylation decreases with increasing sample depth. Of particular interest, is the increase in carbonate to oxide ratio with increasing reaction depth, which increased from 2:1 at the crystal surface to 4:1 approximately 0.2 mm below the surface. This is likely associated with slower dehydroxylation rates and higher $\text{H}_2\text{O}(\text{g})$ partial pressures deeper in the crystal during the dehydroxylation-carbonation reaction. This suggests one can substantially improve the MgCO_3/MgO product ratio by controlling the rate of dehydroxylation during dehydroxylation-carbonation processes.

INITIAL OBSERVATIONS OF IMPURITY EFFECTS

FESEM studies of partially dehydroxylated/carbonated samples perpendicular to the host $\text{Mg}(\text{OH})_2$ single crystal lamella revealed occasional formation of triangular/hexagonal features. These features were often associated with trace Fe impurity segregation/concentration, with local concentrations as high as 5% being observed, as seen in Figure 12. Preliminary studies indicate these features do not appear to significantly affect the extent of carbonation present locally, as the extent of carbonation across them and into the neighboring Fe-deficient matrix material was essentially unchanged.

TABLES

Table 1. In-Plane Packing Distances Observed by SAD for the Oxyhydroxide, $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$, Regions and the $\text{Mg}(\text{OH})_2$ Matrix during *In Situ* Dehydroxylation. The Composition Range is Determined by Comparison with Figure 3.

Study	$\text{Mg}(\text{OH})_2$ Matrix (packing distance)	$\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$ (packing distance)	$\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$ composition (% $\text{Mg}(\text{OH})_2$)
Gordon & Kingery ⁸	3.15 Å	3.14 → 2.98 Å	94% → 0%
Kim, et al. ⁹	3.15 Å	3.00 → 2.98 Å	12% → 0%
Present Study	3.15 Å	3.04 → 2.98 Å	35% → 0%

Table 2. Phase Analysis of Samples Dehydroxylated/Carbonated for 16 hours at 585 °C as a Function of CO_2 Pressure.*

Sample	Time (hr)	P_{CO_2} (psi)	Temp. (°C)	MgCO_3 wt. %	MgO wt. %	$\text{Mg}(\text{OH})_2$ wt. %
HB23.1	16	20	588	5.10	88.39	6.51
HB22.1	16	80	586	7.32	82.55	10.14
HB20.1	16	150	588	7.03	81.69	11.28
HB24.1	16	200	587	5.61	87.39	7.00
HB25.1	16	240	588	6.76	81.76	11.49
HB26.1	16	300	586	10.71	77.09	12.20
HB15.1	16	300	588	20.51	63.94	15.55
HB14.1	16	310	588	21.55	62.48	15.97
HB27.1	16	400	589	26.09	55.26	18.64
HB28.1	16	640	588	26.04	57.93	16.03
HB32.1	16	800	583	16.47	20.19	63.34
HB16.1	16	940	589	11.20	24.72	64.09
HB29.1	16	1560	580	4.08	15.44	80.48
HB31.1	16	2070	581	1.76	7.01	91.23
HB17.1	16	2700	588	1.44	14.69	83.88
HB55.1	16	150	588	1.37	95.75	2.88
HB56.1	16	1080	580	8.25	44.58	47.17

* The MgCO_3 and $\text{Mg}(\text{OH})_2$ compositions are determined by carbon and hydrogen elemental analysis, respectively. The MgO composition is determined by difference, assuming the remainder of the sample is MgO . These analyses offer bulk phase composition and do not discriminate between the presence of mixed $\text{MgO} + \text{Mg}(\text{OH})_2$ materials and lamellar oxyhydroxide materials. Runs HB55.1 and HB56.1 were simultaneously quenched to 20 °C and evacuated at the end of 16 hrs. All other runs were cooled under CO_2 in 30-40 minutes.

Table 3: Sample Compositions for Reaction Positions in Figure 10*

Reaction	Humid CO ₂			Dry CO ₂		
Position	%MgCO ₃	%MgO	%Mg(OH) ₂	%MgCO ₃	%MgO	%Mg(OH) ₂
1	0.0	93.0	7.0	0.0	93.6	6.4
2	1.1	91.9	7.0	0.9	92.7	6.4
3	1.1	92.5	6.4	0.9	92.9	6.2
4**	8.1	76.6	15.3	1.4	92.4	6.2

* Compositions are given in mol% and determined by weight change for positions 1-3, as described in the text.

** The final compositions for humid and dry CO₂ are determined by total C & H analysis and TGA assuming only carbonation occurs, respectively. The humid compositions agree well with the final weight gain observed on cooling (between position 3 and 4; 7.8% TGA vs. 8.0% estimated from C & H elemental analysis). The dry compositions agree well with those from C & H analysis (1.2 % MgCO₃, 95.3% MgO, 3.5% Mg(OH)₂). The slight increase in %MgCO₃/%Mg(OH)₂ may be associated with traces of H₂O left in the TGA system from dehydroxylation.

Table 4: Ion Beam Mg(OH)₂, MgCO₃, and MgO Composition Analysis as a Function of Depth from the Basal Plane (0001) of a Brucite Single Crystal Reacted for 16 hours at 589 °C under 940 psi of CO₂.

Depth	%Mg(OH) ₂	%MgCO ₃	%MgO	MgCO ₃ /MgO
Surface	27.1	50	22.9	2.2
0.1 mm	50	40	10	4.0
0.2 mm	70	24	6	4.0

FIGURES

Figure 1. A lamellar view of the Mg-rich lamellar hydroxide minerals (a) brucite, $\text{Mg}(\text{OH})_2$, and (b) serpentine (lizardite). Note the close structural similarities, with both structures containing Mg lamella and hydroxide lamella. The green, red and white spheres correspond to the Mg, O, and H atom positions, respectively. The grey tetrahedra with small red spheres at the corners correspond to the silica (SiO_4) groups connected in lamellar sheets, which also contain hydroxyl groups.

Figure 2 Free energies (red) and enthalpies (green) for representative lamellar oxyhydroxide intermediate materials (x oxide layers for every y hydroxide layers) relative to stoichiometrically equivalent amounts of MgO and $\text{Mg}(\text{OH})_2$. The bulk moduli of the intermediates are shown in blue. The inset shows the structure of the $\text{Mg}_5\text{O}(\text{OH})_2$ oxyhydroxide intermediate, which contains equal numbers of oxide and double hydroxide layers, viewed parallel to the layers. The green, red, and white spheres represent the Mg, O and H atom positions, respectively.

Figure 3 In-plane (e.g., Mg-Mg) packing distances for the intermediate lamellar oxyhydroxides, $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$, as a function of hydroxide layer composition. A small systematic overestimate of 0.02 Å in all the computed distances, determined by VIB-based non-empirical electron gas modeling, is inferred by comparison with the known values for MgO and $\text{Mg}(\text{OH})_2$. The computed values shown are shifted to allow for the overestimate. The line extrapolates between the experimentally observed (XPD) in-plane packing distances for MgO and $\text{Mg}(\text{OH})_2$.

Figure 4. Models of relatively rapid nucleation/slow growth and slow nucleation/rapid growth lamellar nucleation and growth processes. The two-phase ($\text{Mg}(\text{OH})_2 + \text{MgO}$) and homogeneous lamellar oxyhydroxide character of these processes is consistent with previous low-magnification TEM SAD observations of $\text{Mg}(\text{OH})_2$ dehydroxylation (see Table 1).^{8,9}

Figure 5. The onset of low-temperature dehydroxylation is frequently associated with delamination “blister” formation. The above bright field optical microscopy images are taken perpendicular to the $\text{Mg}(\text{OH})_2$ single crystal basal planes just after the onset of low-temperature dehydroxylation.

Figure 6. The microscopic progression of low-temperature dehydroxylation (380 °C): (a) blister formation after one minute; (b) the onset of cracking perpendicular to the host lamella after two minutes; (c) formation and growth of cracking nucleation centers after 30 minutes; (d) extensive cracking down to the micron/sub-micron level after two hours. The images are shown in grey scale to emphasize crack growth and propagation.

Figure 7. Percent carbonate formed vs. CO₂ pressure for brucite single crystals reacted at 585°C ($\pm 5^\circ\text{C}$) for 16 hours ($\pm 15\text{min}$). The triangles represent samples cooled down under CO₂ in 30-40 minutes. The squares represent samples that were quenched to ambient temperature from 585 °C and simultaneously evacuated.

Figure 8. Percent dehydroxylation vs. CO₂ pressure for brucite single crystals reacted at 585°C ($\pm 5^\circ\text{C}$) for 16 hours ($\pm 15\text{min}$). The triangles represent samples cooled down in CO₂ in 30-40 minutes. The squares represent samples that were quenched to ambient temperature from 585 °C and simultaneously evacuated.

Figure 9. MgO, MgCO₃, and Mg(OH)₂ compositional analysis for partially dehydroxylated/carbonated brucite single crystal fragments as a function of reaction temperature for 4 hours at 370 psi CO₂.

Figure 10. *In situ* thermogravimetric analysis studies of carbonation of low-temperature (375 °C) calcined Mg(OH)₂. After stabilizing at ~ 93% dehydroxylation (position 1), the atmosphere was changed from dry He to humid (~ 70% humidity) and dry CO₂ for the separate runs at 375 °C, as shown. Slight carbonation (~ 1%) occurs initially (by position 2), but does not continue (position 3). Cooling to ambient temperature (position 4) results in little reaction under dry CO₂, whereas humid CO₂ shows strong carbonation and rehydroxylation behavior, as confirmed by carbon and hydrogen elemental analysis. The slight dip between position 3 and 4 is associated with instrumental/buoyancy effects.

Figure 11. Electron loss near edge structure spectra observed during *in situ* carbonation of partially dehydroxylated Mg(OH)₂. The spectra are expected to change slightly via further background subtraction refinement. The orange curves are theoretical *ab initio* C K-edge spectra for magnesite (left) and O K-edge spectra for magnesite (upper right) and MgO (lower right).

Figure 12. Field emission scanning electron microscopy (FESEM) analysis of triangular surface features that form during dehydroxylation-carbonation processes. Fe impurities segregate into the above triangular regions during dehydroxylation/carbonation, but seem to have little effect on carbonation reactivity at these low concentrations, as discussed in the text.

Figure 13. Possible $\text{Mg}(\text{OH})_2$ carbonation reaction pathways during dehydroxylation and/or rehydroxylation. The intermediate lamellar oxyhydroxide solid solution series, $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$, is represented by nominal compositions of $\text{Mg}_3\text{O}(\text{OH})_4$ and $\text{Mg}_3\text{O}_2(\text{OH})_2$. The green, red, white, and black spheres correspond to the Mg, O, H, and C atom positions, respectively. Whereas MgO and $\text{Mg}(\text{OH})_2$ can form by dehydroxylation and rehydroxylation, respectively (potentially cycling back and forth at low temperatures), carbonate formation is thermodynamically dictated as a one way reaction (below the MgCO_3 decomposition temperature).

CONCLUSIONS

Mg(OH)₂ dehydroxylation proceeds as a lamellar nucleation and growth process. Lamellar oxide nuclei nucleate within the brucite matrix, followed the formation of additional nearby oxide lamella, creating lamellar oxyhydroxide regions. These regions can grow both parallel and perpendicular to the Mg(OH)₂ lamella within the brucite matrix, leaving the matrix structure largely undisturbed until it is consumed. This process can take on lamellar solid solution (oxyhydroxide) or two-phase [Mg(OH)₂ + MgO] character via slow nucleation/rapid growth and rapid nucleation/slow growth, respectively. Lamellar nucleation and growth also induces substantial local elastic strain that likely leads to the widely observed cracking, delamination and nano-reconstruction of the host matrix. Locally this strain will depend on the slow nucleation/rapid growth vs. rapid nucleation/slow growth character of the dehydroxylation process. As a result, it may be possible to control the nano-reconstruction process by controlling the lamellar nucleation and growth process.

The free energies (400 °C) of the entire solid solution series of oxyhydroxide intermediates is within 2 kcal/mol of stoichiometrically equivalent Mg(OH)₂ + MgO mixtures, indicating the entire series is theoretically accessible during dehydroxylation/carbonation. Compositional analysis based on *in situ* SAD measurements indicates that essentially the entire solid solution series has been observed as intermediates during the dehydroxylation process. Importantly, low-temperature Mg(OH)₂ dehydroxylation is reversible, via oxide/oxyhydroxide nanostructure formation. This opens the door to a wide range of potential new intermediate oxyhydroxide carbonation pathways via dehydroxylation or rehydroxylation, as shown in Figure 13.

Macroscopic and microscopic studies of gas-phase carbonation indicate dehydroxylation generally precedes carbonation locally, consistent with the creation of dehydroxylation intermediates with higher carbonation reactivity. Simultaneous rehydroxylation of partially dehydroxylated material was found to greatly enhance its gas-phase carbonation reactivity *at ambient temperature*, further underscoring the importance of transitory intermediate formation. This observation, which includes substantial carbonation reaction rates at ambient temperature and CO₂ pressure, may open the door to new CO₂ mineral sequestration processes under ambient conditions, with broader applications and the potential for substantially reducing process cost. In addition to forming lamellar oxyhydroxide intermediates, dehydroxylation can also result in substantial delamination, intralamellar cracking, and surface reconstruction to form nanostructured materials, as discussed above. These phenomena can be used to combat the formation of near surface carbonate passivating layers, which likely inhibit carbonation. The highly porous structures that result from dehydroxylation and form during dehydroxylation/carbonation can also lead to novel phenomena, such as Mg(OH)₂ carbonation reactivity increasing with decreasing CO₂ gas pressure.

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ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Articles

- Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, Hamdallah Bearat, and R.W. Carpenter, “Mg(OH)₂ Dehydroxylation: Implications for Enhancing CO₂ Mineral Sequestration Reaction Processes,” *Proc. 25th International Technical Conference on Coal Utilization & Fuel Systems*, (2000) pp. 897-908.
- Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, R.W. Carpenter, and Ken Streib “Magnesium Hydroxide Dehydroxylation: *In Situ* Atomic-Level Observations of Lamellar Nucleation and Growth,” *Chemistry of Materials* (submitted).
- A.V.G. Chizmeshya and M.J. McKelvy, “Density Functional Theory Study of the Decomposition of Mg(OH)₂: A Lamellar Dehydroxylation Model,” *J. Phys. Cond. Matt.* (submitted).
- Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, “Developing an Atomic-Level Understanding to Enhance CO₂ Mineral Sequestration Reaction Processes via Materials and Reaction Engineering,” *Proc. 17th International Pittsburgh Coal Conference*, September 11-15, 2000 (submitted).

Conference Presentations

- Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, Hamdallah Bearat, and R.W. Carpenter, “Atomic-Level Imaging of CO₂ Mineral Sequestration: Optimizing Reaction Process Design,” *University Coal Research Contractors Review Conference*, Pittsburgh, Pennsylvania, June 6-7, 2000.
- Andrew V.G. Chizmeshya, Renee Olsen, and Michael J. McKelvy, “Atomic-Level Modeling of Mineral Carbonation Reaction Processes: Integrating Experiment with Theory,” *University Coal Research Contractors Review Conference*, Pittsburgh, Pennsylvania, June 6-7, 2000.
- Andrew V.G. Chizmeshya, Renee Olsen, and Michael J. McKelvy, “Atomic-Level Modeling of CO₂ Disposal as a Carbonate Mineral: A Synergetic Approach to Optimizing Reaction Process Design,” *DOE Basic Energy Sciences Combustion Research Meeting*, Chantilly, Virginia, May 30 - June 2, 2000.

Conference Presentations (Continued)

- Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, Hamdallah Bearat, and R.W. Carpenter, “Atomic-Level Imaging Of CO₂ Disposal as a Carbonate Mineral: Optimizing Reaction Process Design,” *DOE Basic Energy Sciences Combustion Research Meeting*, Chantilly, Virginia, May 30 - June 2, 2000.
- Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, Hamdallah Bearat, and R.W. Carpenter, “Mg(OH)₂ Dehydroxylation: Implications for Enhancing CO₂ Mineral Sequestration Reaction Processes,” *25th International Technical Conference on Coal Utilization & Fuel Systems*, Clearwater, Florida, 2000.
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- H. Bearat, M. Schade, A.V.G. Chizmeshya, C. Redmacher, and M.J. McKelvy, “Mg(OH)₂ Dehydroxylation/Carbonation: A Microscopic View,” *Fourth CO₂ Mineral Sequestration Forum*, Tempe, Arizona, 1999.
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- M.J. McKelvy, R. Sharma, A.V.G. Chizmeshya, H. Bearat, R.W. Carpenter, and K. Streib, “Mg(OH)₂ Dehydroxylation: The Path to Brucite CO₂ Mineral Sequestration,” *Third CO₂ Mineral Sequestration Forum*, Pittsburgh, Pennsylvania, 1999.
- M.J. McKelvy, R. Sharma, A.V.G. Chizmeshya, R.W. Carpenter and K. Streib, “Mg(OH)₂ Dehydroxylation: A Lamellar Nucleation and Growth Process,” *University Coal Research Contractors Review Conference*, Pittsburgh, Pennsylvania, 1999.

Conference Presentations (Continued)

- M.J. McKelvy, R.W. Carpenter, R. Sharma, and Ken Streib, “Atomic-Level Imaging of CO₂ Disposal as a Carbonate Mineral: Optimizing Mg(OH)₂ Carbonation,” *Second CO₂ Mineral Sequestration Forum*, Albany, Oregon, 1998.
- M.J. McKelvy, R.W. Carpenter, and R. Sharma, “Atomic-Level Imaging Of CO₂ Disposal as a Carbonate Mineral: Optimizing Reaction Process Design,” M.J. McKelvy, R.W. Carpenter, and R. Sharma, *First CO₂ Mineral Sequestration Forum*, Los Alamos, New Mexico, 1998.

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APPENDIX III: Year 3 Technical Progress Report

ATOMIC-LEVEL IMAGING OF CO₂ DISPOSAL AS A CARBONATE MINERAL: OPTIMIZING REACTION PROCESS DESIGN

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ABSTRACT

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Permanent and safe methods for CO₂ capture and disposal/storage need to be developed. Mineralization of stationary-source CO₂ emissions as carbonates can provide such safe capture and long-term sequestration. Mg-rich lamellar-hydroxide based minerals (e.g., brucite and serpentine) offer a class of widely available, low-cost materials, with intriguing mineral carbonation potential. Carbonation of such materials inherently involves dehydroxylation, which can disrupt the material down to the atomic level. As such, controlled dehydroxylation, before and/or during carbonation, may provide an important parameter for enhancing carbonation reaction processes. Mg(OH)₂ was chosen as the model material for investigating lamellar hydroxide mineral dehydroxylation/carbonation mechanisms due to (i) its structural and chemical simplicity, (ii) interest in Mg(OH)₂ gas-solid carbonation as a potentially cost-effective CO₂ mineral sequestration process component, and (iii) its structural and chemical similarity to other lamellar-hydroxide-based minerals (e.g., serpentine-based minerals) whose carbonation reaction processes are being explored due to their low-cost CO₂ sequestration potential. Fundamental understanding of the mechanisms that govern dehydroxylation/carbonation processes is essential for minimizing the cost of any lamellar-hydroxide-based mineral carbonation sequestration process. This report covers the third year progress of this grant, as well as providing an integrated overview of the progress in years 1-3, as we have been granted a one-year no-cost extension to wrap up a few studies and publications to optimize project impact.

In the first project year, we used environmental-cell (E-cell), dynamic high-resolution transmission electron microscopy (DHRTEM) to directly observe the Mg(OH)₂ dehydroxylation process at the atomic-level for the first time. We also carried out exploratory semi-empirical modeling studies of the intermediate materials formed. *Dehydroxylation was discovered to be a lamellar nucleation and growth process, which includes intermediate lamellar oxyhydroxide formation. These intermediates offer a series of new carbonation reaction pathways, which may be able to enhance carbonation reactivity.* We also initiated studies to probe dehydroxylation/carbonation reaction mechanisms via C and H elemental analysis, optical microscopy and SIMS.

In the second year, we expanded our studies to better understand the mechanisms that govern Mg(OH)₂ carbonation reactivity. These investigations incorporated a range of techniques, including E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, TGA, XRD, and elemental analysis. In collaboration with DOE/NETL grant DE-FG26-99FT40580, we integrated advanced computational modeling studies with our experimental observations. *We found intermediate (e.g., oxyhydroxide) formation is a key component of both rehydroxylation-carbonation and dehydroxylation-carbonation processes, which, if controlled, can dramatically enhance carbonation reactivity, even at ambient temperature and CO₂ pressure.* Critical to optimizing this enhanced reactivity is the ability of Mg(OH)₂ to form nanostructured materials during controlled dehydroxylation, providing access to high surface area, carbonation reactive intermediate materials. Mechanisms that can inhibit carbonation include passivating carbonate layer formation and MgO crystal growth during dehydroxylation. These mechanisms combine

with delamination, cracking and nanostructured materials formation to control carbonation reactivity.

In the third year of the project, we primarily focused on developing a deeper understanding of nanostructure and oxyhydroxide formation and their impact on carbonation reactivity, due to their dramatic ability to enhance carbonation reaction rates and potential application to other Mg-rich lamellar hydroxide minerals of interest (e.g., serpentine-based minerals). These investigations include E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and elemental analysis. Highlights include: 1) *in situ* atomic-level observations of the dramatically enhanced ambient-temperature carbonation reactivity of dehydroxylated $\text{Mg}(\text{OH})_2$ under humid conditions, which produces an amorphous hydroxycarbonate; 2) the discovery of rapid Mg diffusion during dehydroxylated- $\text{Mg}(\text{OH})_2$ rehydroxylation, via *in situ* atomic-level E-cell DHRTEM, which appears to be key to the above enhanced carbonation reactivity; and (iii) developing an integrated overview of the impact of $\text{Mg}(\text{OH})_2$ cracking, delamination, nanoreconstruction, oxide crystal growth, and passivating carbonate layer formation on carbonation intermediate formation and carbonation reactivity based on macroscopic, microscopic, and nanoscopic dehydroxylation/rehydroxylation/carbonation mechanistic observations.

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EXECUTIVE SUMMARY

OBJECTIVE

The objective of this project is to develop an atomic-level understanding of the mechanisms that govern the carbonation kinetics of the prototypical Mg-rich lamellar-hydroxide-based mineral $\text{Mg}(\text{OH})_2$, to facilitate engineering of improved carbonation materials and processes for CO_2 disposal. The chemical and structural simplicity of $\text{Mg}(\text{OH})_2$ provides a model system to develop a deeper fundamental understanding of Mg-rich lamellar-hydroxide-based mineral carbonation reaction mechanisms. The potential for these mineral carbonation processes to be economically viable has helped generate substantial interest in CO_2 mineral sequestration as a possible carbon management option (e.g., carbonation of the chemically and structurally more complex Mg-rich lamellar hydroxide serpentine-based minerals). Environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM) is used to probe the associated reaction processes down to the atomic level. A battery of complementary techniques is used to further elucidate key reaction mechanisms at the macroscopic and microscopic levels (via *in-situ* and *ex-situ* studies). As carbonation involves dehydroxylation, carbonation and potential competition between them, this project focuses on developing an atomic-level understanding of dehydroxylation and carbonation reaction mechanisms and their impact on carbonation reactivity. Particular emphasis is placed on the mechanisms that have the greatest impact on carbonation reactivity.

ACCOMPLISHMENTS TO DATE

In year 3 we have continued to extend our studies beyond E-cell DHRTEM to develop a better understanding of the $\text{Mg}(\text{OH})_2$ reaction mechanisms associated with carbonation processes. We have again expanded our *in situ/ex situ* mechanistic studies of dehydroxylation/rehydroxylation-carbonation reaction processes to include optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and elemental analysis. Integrating these investigations with advanced computational modeling {together with the DOE UCR Innovative Concepts project “Atomic-Level Modeling of CO_2 Disposal as a Carbonate Mineral: a Synergetic Approach to Optimizing Reaction Process Design,” (grant # DE-FG26-99FT40580)} has produced an enhanced atomic-level understanding of key reaction mechanisms.

We have discovered $\text{Mg}(\text{OH})_2$ dehydroxylation is governed by a lamellar nucleation and growth process, which can result in intermediate lamellar oxyhydroxide formation. Slow nucleation/rapid growth and rapid nucleation/slow growth favor oxyhydroxide and $\text{MgO} + \text{Mg}(\text{OH})_2$ intermediate formation, respectively. This process can also result in extensive nanoscale crystal fracture, resulting in a morphological evolution of the reaction matrix involving internal blister formation, lattice cracking and morphological reconstruction, which has the ability to form nanoporous materials. Blister formation occurs internally, before lattice cracking can connect these regions with the exterior reaction atmosphere. Matrix cracking proceeds inward from the lamellar crystal edge and basal plane surfaces, connecting with the internal blisters that have formed to create high-surface-area intermediate materials with enhanced carbonation reactivity. Together with the potential to form carbonation reactive oxyhydroxide

intermediate materials, these mechanisms provide exciting potential for engineering feedstock materials and processes with enhanced carbonation reactivity.

Although, the high-surface-area materials that result from low-temperature dehydroxylation were found to have a limited number of carbonation reactive sites, their controlled rehydroxylation can create/expose many more reactive sites resulting in *a dramatic increase in carbonation reactivity at ambient temperature*. *In situ* E-cell DHRTEM combined with parallel electron energy loss spectroscopy has shown an amorphous magnesium carbonate containing material is formed in the process. Analogous atomic-level observations of the rehydroxylation process have discovered dramatic Mg mobility leads to the reformation of $\text{Mg}(\text{OH})_2$. Such high Mg mobility is apparently key to the greatly enhanced carbonation reactivity of dehydroxylated $\text{Mg}(\text{OH})_2$ observed under humid conditions.

The $\text{Mg}(\text{OH})_2$ dehydroxylation mechanisms discussed above and their ability to create nanoporous reaction matrices also impacts direct gas-phase $\text{Mg}(\text{OH})_2$ carbonation, including providing mechanistic avenues that can bypass passivating carbonate layer formation and enhance carbonation reactivity. They are also associated with the novel observation that $\text{Mg}(\text{OH})_2$ carbonation reaction rates *increase* with *decreasing* $\text{CO}_2(\text{g})$ pressure above the critical pressure needed for carbonate formation. Hence, direct gas-phase $\text{Mg}(\text{OH})_2$ carbonation reactivity can be optimized at the lowest CO_2 pressure at which MgCO_3 is stable. Higher CO_2 pressures further inhibit $\text{H}_2\text{O}(\text{g})$ diffusion out of and $\text{CO}_2(\text{g})$ diffusion into the nanoporous reaction matrix that forms, slowing both dehydroxylation and carbonation. Investigations of the role of Fe impurities during dehydroxylation/carbonation suggest they can segregate into Fe-rich regions during dehydroxylation, possibly reducing their impact on carbonation reactivity in the process. Similar mechanisms may be more broadly applicable to Mg/Ca-rich lamellar-hydroxide-based mineral (e.g., serpentine) carbonation processes, offering substantial potential for reducing CO_2 mineral sequestration process costs.

The detailed discussion of our accomplishments that follows integrates an overview of our aggregate progress in developing an atomic-level understanding of the mechanisms that govern $\text{Mg}(\text{OH})_2$ carbonation reactivity, with a more detailed summary of our third year progress.

INTRODUCTION

Mineral Carbonation: An Attractive Candidate Process for CO₂ Sequestration

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Mineralization of stationary-source CO₂ emissions as carbonates can provide safe capture and long-term sequestration. The resulting carbonates (e.g., magnesium and calcium carbonate, MgCO₃ and CaCO₃) occur in nature in quantities that far exceed those that could result from carbonating the world's known coal reserves. Furthermore, they have already proven stable over geological time, eliminating the safety and cost concerns associated with long-term storage of CO₂ in compressed form. Conversion of CO₂ into Mg/CaCO₃ effectively disposes of CO₂ by accelerating the natural processes that already occur in nature.

Mg-rich minerals and mineral derivatives are being investigated as low-cost mineral carbonation feedstock materials by the CO₂ Mineral Sequestration Working Group (comprised of members from the Albany Research Center, our CO₂ Mineral Sequestration Research Group at Arizona State University, Los Alamos National Laboratory, the National Energy Technology Laboratory and Science Applications International Corporation).¹ The primary focus of the Working Group, which is managed by the Department of Energy's Office of Fossil Energy, is to evaluate the economic viability of mineral carbonation processes as long-term options for reducing atmospheric CO₂ emissions. A major challenge in cost-competitive process development is to accelerate these carbonation reaction(s) to a high degree of completion on an industrial time scale. The associated reaction rates depend on many materials and process parameters, providing substantial potential for rate enhancement. However, the effects of many of these parameters are poorly understood, especially at the atomic level, severely limiting their effective use. A fundamental understanding of the mechanisms that govern key carbonation processes is needed to create the foundation for reaction process improvement via materials and process engineering.

Mg-Rich Lamellar-Hydroxide-Based Minerals: Candidate Feedstock Materials for Cost Competitive CO₂ Mineral Sequestration

Carbonation of Mg-rich lamellar-hydroxide-based minerals (e.g., the serpentine-based minerals and brucite: Mg(OH)₂) is a leading CO₂-mineral-sequestration, process candidate. Increasing the carbonation reaction rate and its degree of completion is key to lowering process cost. Mg(OH)₂ was chosen as the model material for investigating lamellar hydroxide mineral dehydroxylation/carbonation mechanisms due to (i) its structural and chemical simplicity,² (ii) the interest in Mg(OH)₂ gas-solid carbonation as a potentially cost-effective CO₂ mineral sequestration process component,³⁻⁵ and (iii) its structural and chemical similarity to other lamellar-hydroxide-based minerals (e.g., serpentine, see Figure 1), whose carbonation reaction processes are being explored due to their low-cost CO₂ sequestration potential.¹ This project focuses on developing an atomic-level understanding of the reaction mechanisms that govern dehydroxylation/rehydroxylation-carbonation processes for this model lamellar hydroxide feedstock material. The long-term goal is to develop the necessary atomic-level mechanistic

understanding to engineer improved carbonation materials and processes for Mg-rich lamellar-hydroxide-based minerals.

Mg(OH)₂ Dehydroxylation: The First Step in Carbonation

As Mg(OH)₂ dehydroxylation (reaction 1), is intimately associated with carbonation (reaction 2),

its mechanisms are of direct interest in understanding and optimizing the carbonation process. Although Mg(OH)₂ dehydroxylation has been extensively studied, relatively little was known about the atomic-level nature of the process, especially in the early stages of dehydroxylation, prior to this investigation. The early stages of the process are of particular interest, since carbon dioxide may react to form magnesite (MgCO₃) locally as soon as dehydroxylation begins in that region. In our first year progress report, we reported our discovery that Mg(OH)₂ dehydroxylation is governed by a lamellar nucleation and growth process. Environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTM) was used to directly observe the *in-situ* process at the atomic-level for the first time. These observations were combined with preliminary advanced computational modeling studies using a non-empirical density functional theory (DFT) approach to better elucidate the atomic-level dehydroxylation process. In our second year report, we described our studies that lead to a deeper understanding of the lamellar nucleation and growth process, including (i) analysis of the interrelationship between oxyhydroxide intermediate and nanostructure formation and (ii) advanced modeling studies of the oxyhydroxide intermediate materials formed in collaboration with DOE/NETL grant DE-FG26-99FT40580. In this, our third year report, we extend this understanding to direct atomic level observations of dehydroxylated Mg(OH)₂ rehydroxylation. These studies have discovered very high Mg mobility during gas-phase rehydroxylation, which leads to rapid Mg(OH)₂ crystal growth. Such Mg mobility is very likely key to the dramatically enhanced carbonation reactivity observed for dehydroxylated Mg(OH)₂ at ambient temperature under the humid conditions discussed below.

Mg(OH)₂ Dehydroxylation/Rehydroxylation-Carbonation Processes

In the first year report, we described combining the first-year dehydroxylation studies with preliminary dehydroxylation-carbonation studies of single crystal Mg(OH)₂ fragments to better elucidate dehydroxylation-carbonation reaction mechanisms. We found dehydroxylation generally occurred in advance of carbonation during Mg(OH)₂ carbonation, suggesting intermediate formation may be important to carbonation reactivity during simultaneous dehydroxylation-carbonation. We also discovered initial evidence for passivating carbonate layer formation and substantial delamination and cracking of the Mg(OH)₂ feedstock material during dehydroxylation-carbonation.

In our second year, we discovered dehydroxylation/rehydroxylation intermediate (e.g., oxyhydroxide) formation is a key component of both dehydroxylation-carbonation and rehydroxylation-carbonation processes, with essentially the entire lamellar oxyhydroxide solid solution series ($\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$) accessible during $\text{Mg}(\text{OH})_2$ dehydroxylation/rehydroxylation. The ability of $\text{Mg}(\text{OH})_2$ to form nanostructured materials during controlled dehydroxylation is another key component affecting carbonation reactivity. Together with delamination and cracking, these factors enhance carbonation by increasing the reactive carbonation surface area. On the other hand, carbonation can slow high-surface-area reactive intermediate formation via the formation of passivating carbonate layers. MgO crystal growth during dehydroxylation can also inhibit carbonation. In addition, $\text{Mg}(\text{OH})_2$ feedstock impurities may also play important roles in carbonation reactivity. Although initial studies indicate Fe impurities can phase separate during $\text{Mg}(\text{OH})_2$ dehydroxylation at low concentrations, they do not appear to substantially inhibit carbonation, at least locally. All of the above factors must be adroitly balanced to enhance carbonation reactivity. Our efforts to combine oxyhydroxide intermediate formation with controlled nanostructure formation to probe their ability to enhance carbonation reactivity proved quite promising, as we *achieved carbonation reaction rates at ambient temperature and CO_2 pressure similar to those previously reported for optimum ambient CO_2 pressure $\text{Mg}(\text{OH})_2$ carbonation (at 375 °C).*

In the third year of the project, we primarily focused on developing a deeper understanding of the reaction matrix morphology, nanostructure and oxyhydroxide formation and their impact on carbonation reactivity, due to their dramatic ability to enhance carbonation reaction rates and potential application to other Mg-rich lamellar hydroxide minerals of interest (e.g., serpentine-based minerals). These investigations include E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and elemental analysis. Highlights include: 1) *in situ* atomic-level observations of the dramatically enhanced ambient-temperature carbonation reactivity of dehydroxylated $\text{Mg}(\text{OH})_2$ under humid conditions, which produces an amorphous hydroxycarbonate; 2) the discovery (via *in situ* atomic-level E-cell DHRTEM) of dramatically enhanced Mg diffusion during dehydroxylated- $\text{Mg}(\text{OH})_2$ rehydroxylation, which appears to be a key mechanistic tool for enhancing carbonation reactivity; and (iii) developing an integrated overview of the impact of $\text{Mg}(\text{OH})_2$ cracking, delamination, nanoreconstruction, oxide crystal growth, and passivating carbonate layer formation on carbonation intermediate formation and carbonation reactivity based on macroscopic, microscopic, and nanoscopic dehydroxylation/rehydroxylation/carbonation mechanistic observations.

EXPERIMENTAL

MATERIALS: Natural single crystal brucite from Delora, Canada was used as the starting material. Elemental analysis by proton-induced X-ray emission and total carbon analysis showed the material to contain 0.16% Mn, 0.06% C, 0.01% Cl and 0.01% Si by weight. X-ray powder diffraction was used to structurally characterize the starting material [$a=3.147(1)$ Å and $c=4.765(1)$ Å], in good agreement with the known parameters for brucite [$a=3.147$ Å and $c=4.769$ Å].⁶ E-cell DHRTEM samples were prepared in a He glovebox by either cold crushing at -196°C or scraping the crystal with a razor blade. Crystals were then dry loaded on to holey-carbon-coated copper grids for DHRTEM analysis. Single crystal fragments for carbonation

studies were cleaved from the crystal matrix. High pressure carbonation/dehydroxylation reactions were carried out in a sealed autoclave. The samples were introduced to the autoclave in vitreous silica boats. The autoclave was sealed, dry CO₂ introduced, and the autoclave brought quickly to reaction temperature. *In situ* Mg(OH)₂ dehydroxylation/rehydroxylation-carbonation reaction processes were investigated using a Setaram TGS2 thermogravimetric analysis system, with 1 μ sensitivity.

E-Cell DHRTEM: The *in-situ* studies of Mg(OH)₂ dehydroxylation/rehydroxylation/carbonation were performed using a Philips 430 HRTEM (300 kV; 2.3 Å pt. to pt. resolution) equipped with a Gatan Imaging energy Filter (GIF) and a 0-5 torr E-cell. Dehydroxylation was induced by electron beam heating and resistive heating using the sample holder, both with and without the presence of water vapor. Direct imaging of the reaction was recorded on videotape in real time (30 frame/sec). Water vapor (e.g., ~ 1 torr) was required to slow the dehydroxylation process sufficiently for direct imaging. Digital Micrograph was used to analyze the interlamellar spacings in four-frame time-averaged images of the dehydroxylation process parallel to the brucite layers. Selected area diffraction of the reaction process was recorded as a function of time using internal gold island diffraction standards and photographic plates. *In situ* rehydroxylation-carbonation processes were followed by direct imaging, SAD and PEELS. Mg(OH)₂ was first dehydroxylated *in situ* via resistive heating, followed by reaction at ambient temperature with ~800 mtorr of humid CO₂.

GENERAL FACILITIES: The SIMS system used was a Cameca IMS 3f ion microscope. Base pressure in the sample chamber is 10⁻⁷ torr. Depth resolution can be better than 10 nm. Lateral resolution is ~5-20 μm in point analysis mode and lateral image resolution is ~1 μm. The digital optical microscope system used was a Mititoyo Ultraplan FS-110, with bright and dark field, polarized light, Nomarski, and reflected and transmitted illumination capabilities together with extra-long working distance objectives and fraction of a micron resolution. X-ray powder diffraction (XPD) studies were carried out using a RigakuD/MAX-IIB X-ray diffractometer with CuKα radiation, line focus, and graphite monochromator. Ion beam analyses of partially carbonated Mg(OH)₂ single crystal samples were performed using a 1.7 MV General Ionex Tandetron system. Mg was analyzed via Rutherford backscattering spectroscopy (RBS) analysis using 2 MeV He⁺⁺ ions. Carbon analysis used a C(alpha, alpha)C reaction occurring at 4.63 MeV. Oxygen analysis used a similar reaction at 3.05 MeV. H analysis was performed by forward scattering using 2.8 MeV He⁺⁺ ions. Total hydroxide, oxide and carbonate contents for the partially dehydroxylated/carbonated single crystal fragments were determined using a Perkin Elmer PE 2400 Series CHNS analysis system. Careful use of standards before and after sample analysis showed an absolute error of ± 0.2 wt%. The field emission scanning electron microscope (FESEM) system used was a Hitachi S-4100 equipped with an Oxford Instruments ISIS energy dispersive spectrometer.

MODELING: *Ab initio* density functional theory calculations and non-empirical electron-gas modeling based on the VIB method⁶ were used to investigate the relative stability, elastic behavior and structural trends of the intermediate oxyhydroxides as a function of composition. The methods used are described in detail in the attached reprint published in *Chemistry of Materials*.⁶ Similar methods were used for the carbonation modeling studies. These are

described in detail in the 2000 annual report for the DOE UCR Innovative Concepts project “Atomic-Level Modeling of CO₂ Disposal as a Carbonate Mineral: a Synergetic Approach to Optimizing Reaction Process Design,” (grant #DE-FG26-99FT40580), which fully collaborated with the project described herein.

RESULTS AND DISCUSSION

Mg(OH)₂ DEHYDROXYLATION

Our DHRTEM observations parallel to the Mg(OH)₂ lamella during dehydroxylation discovered the general lamellar nature of the process (see appended copy of *Chem. Mater.* **13** (3), 921-6 (2001)).⁶ *In situ* selected area diffraction (SAD) studies confirmed Mg(OH)₂ dehydroxylation is best described as a lamellar nucleation and growth process. After initial oxide layer nucleation, as described in equation 3, growth occurs via the formation of additional partial/full oxide layers nearby, creating lamellar oxyhydroxide regions, which can grow parallel and perpendicular to the

lamella in the Mg(OH)₂ matrix. Advanced computational modeling, in collaboration with the above UCR Innovative Concepts project (grant #DE-FG26-99FT40580), has provided a deeper understanding of the nature of the intermediate oxyhydroxides (see appended copy of *Mater. Chem. and Phys.*, (2001), in press).⁷ We have found that essentially the entire oxyhydroxide solid solution series is accessible during dehydroxylation/rehydroxylation-carbonation, opening the door to a broad new range of intermediate carbonation reaction pathways, with potentially enhanced carbonation reactivity (Figure 2).⁶⁻⁸

Slow nucleation/rapid growth and rapid nucleation/slow growth processes generally favor lamellar oxyhydroxide (Mg_{x+y}O_x(OH)_{2y}) intermediate formation and two-phase (e.g., MgO + Mg(OH)₂) intermediate behavior, respectively (Figure 3). Host-layer bending during lamellar nucleation and growth also induces substantial local elastic strain. Such strain likely induces cracking, delamination and reconstruction, which can lead to the formation of nanostructured materials during dehydroxylation. This offers the exciting possibility of providing some control over nanostructure intermediate formation by controlling the relative rates of lamellar nucleation and growth during dehydroxylation.

Optical microscopy observation of the dehydroxylation process has provided substantial insight into the microscopic effects of the lamellar nucleation and growth process as a function of reaction progression.⁹ Dehydroxylation of Mg(OH)₂ to form MgO is accompanied by a large volume decrease, which results from an ~50% collapse of the interlayer distance (Figure 2). It is also accompanied by an ~5% decrease in the in-plane packing distance, as confirmed by macroscopic observations of single crystal fragments during dehydroxylation (Figure 4). This induces substantial interlamellar and intralamellar strain at the nanoscale during dehydroxylation, as discussed above.⁶ Early in the dehydroxylation process, blisters are observed to form in the Mg(OH)₂ crystal interior, as shown in Figure 5. These regions can be associated with the onset of dehydroxylation internally, with blisters forming in the lamellar interior of the crystal via

equation (1). The external onset of dehydroxylation is characterized by translamellar and lamellar cracking, which are commonly observed as water escapes from the $\text{Mg}(\text{OH})_2$ crystallite matrix during dehydroxylation.¹⁰ As seen in Figure 6, external dehydroxylation is often initiated at the edges of freshly-cleaved, $\text{Mg}(\text{OH})_2$ single-crystal fragments. As dehydroxylation continues, new cracks branch away from the primary cracks, with overall crack propagation continuing inward from the crystal edge. Crack nucleation centers can also form independently in the central region of the basal surface (Figure 6e), indicating crack formation can nucleate at basal surface sites (e.g., defect sites), as well as at edge sites. Basal plane nucleation typically results in the formation of crack centers that nucleate and grow on the basal plane surface, as shown in Figure 7. At lower temperatures basal plane cracks initially nucleate as linear cracks on the basal plane surface (Figure 7a), followed by crack center formation (Figure 6e). At higher temperatures, basal-plane crack centers can form early in the dehydroxylation process. The upward bending of the basal planes in Figures 7b and 7c indicate that water evolution exerts strong local pressure perpendicular to the basal plane surface during crack center formation.

The onset of crack formation at the crystal edge or step surface is often associated with the formation of planar cracks that intersect at 120° angles, as seen in Figures 6b, 6c, 8a and 8b. Laue X-ray diffraction analysis of the crystal orientation prior to dehydroxylation shows the crack propagation occurs along the 11-20 direction, indicating these surfaces can be selectively exposed during dehydroxylation. Hence, their gas-phase carbonation reactivity is of particular interest and will be the subject of future advanced computational modeling studies. Although crystal cracking along crystallographic directions was observed routinely, primary and secondary cracking and the formation of crack centers were more commonly observed (Figures 8c-e). The formation of basal-plane crack centers can be correlated with basal-plane surface defects, as seen in Figure 8d and e. Thus, crack propagation and dehydroxylation is promoted by roughening the basal plane surfaces of the brucite crystal fragments.

As crack propagation continues beyond the nucleation and initial growth stage, externally nucleated cracks, including basal-plane nucleated crack centers and edge-nucleated cracks, intersect internal blisters leading to the formation of a highly porous reaction matrix. Extensive dehydroxylation ultimately disrupts the material down to the sub-micron/nanoscale. Such extensive low-temperature dehydroxylation can also lead to morphological reconstruction to form well-known nanostructured materials, which typically consist of intergrown cubic MgO nanocrystals, with edge dimensions as low as ~ 1 nanometer, depending on the dehydroxylation conditions.^{11,12} Figure 9 shows the larger intergrown MgO nanocrystals that can form via moderate temperature (580°C) dehydroxylation. The combination of the high-surface-area materials that can be generated via the above crack propagation processes and nanoreconstruction, with the ability to form highly carbonation reactive intermediate materials during dehydroxylation/rehydroxylation, can dramatically impact carbonation reactivity.

We previously observed in project years 1 and 2, that partially dehydroxylated $\text{Mg}(\text{OH})_2$ exhibits strongly enhanced carbonation reactivity under humid conditions.^{8,13} In order to better understand the mechanisms that lead to this enhanced carbonation reactivity, we have imaged the rehydroxylation of partially dehydroxylated $\text{Mg}(\text{OH})_2$ down to the atomic level to elucidate the mechanism(s) whereby rehydroxylation can dramatically enhance carbonation reactivity. Figure

10 shows E-cell DHRTEM observations of the nucleation and growth of $\text{Mg}(\text{OH})_2$ lamella during $\text{Mg}(\text{OH})_2$ rehydroxylation after *in situ* dehydroxylation at 465 °C. Recrystallization shows very rapid Mg diffusion, as evidenced by rapid layer-by-layer $\text{Mg}(\text{OH})_2$ crystal growth on the $\text{Mg}(\text{OH})_2$ crystal surface. Rapid growth and movement of edge dislocations parallel to the lamella were also observed. In addition, edge dislocation motion was observed perpendicular to the lamella, with individual lamella breaking and reforming resulting in c-axis motion of the edge dislocations. All of the processes observed were highly dynamic. Such processes are likely to strongly contribute to the dramatically enhanced carbonation reactivity observed for low-temperature dehydroxylated $\text{Mg}(\text{OH})_2$ under humid conditions, by providing access to fresh carbonation reactive reaction sites.

$\text{Mg}(\text{OH})_2$ DEHYDROXYLATION/REHYDROXYLATION-CARBONATION

As discussed above, our $\text{Mg}(\text{OH})_2$ dehydroxylation studies have identified the formation of a solid solution series of lamellar oxyhydroxide intermediate materials, which form at least locally, en route to MgO formation. Such intermediate formation can be combined with $\text{Mg}(\text{OH})_2$ reaction matrix cracking and reconstruction down to the nanoscale, to form very high surface area intermediate materials. These high surface area materials are of particular interest as they can offer a range of potential new carbonation reaction pathways, as shown in Figure 2. The mechanisms associated with these materials provide exciting potential for engineering feedstock materials and processes with enhanced carbonation reactivity, as reported in our second year technical progress report and the referenced publications.^{6-9,13-15} Although, the high-surface-area materials that result from low-temperature dehydroxylation were found to have a limited number of carbonation reactive sites, their controlled rehydroxylation was found to create/expose many more reactive sites resulting in *a dramatic increase in carbonation reactivity at ambient temperature*.

ATOMIC-LEVEL OBSERVATIONS OF REHYDROXYLATION-CARBONATION PROCESSES

We have utilized *in situ* E-cell DHRTEM to observe the exceptional carbonation reactivity of low-temperature dehydroxylated $\text{Mg}(\text{OH})_2$ during rehydroxylation-carbonation to better understand the mechanisms that govern this exciting rapid carbonation process. As described in last year's report, rehydroxylation-carbonation is quite rapid at ambient temperature and yields an amorphous carbonate that appears to contain some rehydroxylated material as well. E-cell DHRTEM imaging of the process revealed the onset of ambient temperature rehydroxylation-carbonation is instantaneous upon exposure of low-temperature dehydroxylated $\text{Mg}(\text{OH})_2$ to even low pressures of humid CO_2 (Figure 11). The porous reaction matrix provided by low-temperature dehydroxylated $\text{Mg}(\text{OH})_2$ appears to absorb CO_2 and H_2O into the reaction matrix as well as their reacting with the matrix surface causing the swelling and breathing motion observed during rehydroxylation-carbonation. The amorphous carbonate containing product is confirmed to contain carbonate via parallel electron energy loss spectroscopy and selected area electron diffraction.¹⁴ During rehydroxylation-carbonation we occasionally observe lamella in addition to the general amorphous carbonate and hydroxide containing material formed, as seen in Figure 12. These lamella often have the layer repeat expected for $\text{Mg}(\text{OH})_2$ and sometimes a greater interlayer repeat. This is consistent with at least transitory rehydroxylation accompanying

carbonation at ambient temperature (as also evidenced by C and H elemental analysis), which, in turn, is likely associated with the formation of new oxyhydroxide-like intermediates that can dramatically enhance carbonation reactivity.

MICROSCOPIC OBSERVATIONS OF $Mg(OH)_2$ DEHYDROXYLATION/REHYDROXYLATION CARBONATION

As discussed in last year's report, dehydroxylation-carbonation reaction rates for $Mg(OH)_2$ single crystal fragments were generally observed to decrease over time consistent with passivating carbonate layer formation. In terms of its effect on carbonation reactivity, such carbonate passivating layer formation is countered by the $Mg(OH)_2$ cracking, delamination and nano-reconstruction processes associated with dehydroxylation.^{6-9,13-15} We have made extensive microscopic observations of these processes to better understand their role in carbonation reactivity. The importance of lattice cracking during dehydroxylation/rehydroxylation-carbonation is indicated in Figures 13 and 14 and compared with the extent of carbonation observed (Figure 15). At pressures below the critical carbonation pressure at 585 °C (~ 53.7 atm CO_2),⁸ the reacting crystals extensively dehydroxylate at 585 °C, followed by rapid rehydroxylation-carbonation on cooling, as discussed in last year's report. Above the critical carbonation pressure, carbonation occurs directly at 585 °C.^{8,9,14} The extent of crack formation, as observed via optical microscopy, is directly related to the extent of dehydroxylation in either process, as seen in Figures 13 and 14. This underscores the importance of matrix crack formation in enhancing H_2O and CO_2 diffusion out of and into the $Mg(OH)_2$ reaction matrix, respectively, which, in turn, generally enhances carbonation reactivity.

FIGURES

Figure 1. A lamellar view of the Mg-rich lamellar hydroxide minerals (a) brucite, $\text{Mg}(\text{OH})_2$, and (b) serpentine (lizardite). Note the close structural similarities, with both structures containing Mg lamella and hydroxide lamella. The green, red and white spheres correspond to the Mg, O, and H atom positions, respectively. The grey tetrahedra with small red spheres at the corners correspond to the silica (SiO_4) groups connected in lamellar sheets, which also contain hydroxyl groups.

Figure 2. Possible $\text{Mg}(\text{OH})_2$ carbonation reaction pathways during dehydroxylation and/or rehydroxylation. The intermediate lamellar oxyhydroxide solid solution series, $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$, is represented by nominal compositions of $\text{Mg}_3\text{O}(\text{OH})_4$ and $\text{Mg}_3\text{O}_2(\text{OH})_2$.⁶⁻⁸ The green, red, white, and black spheres correspond to the Mg, O, H, and C atom positions, respectively. Whereas MgO and $\text{Mg}(\text{OH})_2$ can form by dehydroxylation and rehydroxylation, respectively (potentially cycling back and forth at low temperatures), carbonate formation is thermodynamically dictated as a one way reaction (below the MgCO_3 decomposition temperature).

Figure 3. Models of relatively rapid nucleation/slow growth and slow nucleation/rapid growth lamellar nucleation and growth processes. The two-phase ($\text{Mg}(\text{OH})_2 + \text{MgO}$) and homogeneous lamellar oxyhydroxide character of these processes is consistent with previous low-magnification TEM SAD observations of $\text{Mg}(\text{OH})_2$ dehydroxylation.^{10,11}

Figure 4. Macroscopic observations of in-plane, basal-plane shrinkage during the dehydroxylation of a brucite single crystal fragment. Dehydroxylation was carried out as a function of heating time (minutes) at 475°C in air. t is expressed in minutes.

Figure 5. Optical micrograph showing blister formation during dehydroxylation for 1 min in air at 580°C. Optical axis is perpendicular to the basal plane layers.

Figure 6. Lattice cracking observed perpendicular to the layers during $\text{Mg}(\text{OH})_2$ dehydroxylation in static air at 375 °C; a) freshly cleaved crystal fragment (strain fields indicate some delamination occurred due to cleaving); b-f) crack propagation observed after 1, 2, 6, 15, and 30 hours, respectively.

Figure 7. FESEM micrographs showing basal-plane crack nucleation/growth, including the formation of crack centers. The images were taken after heating in air for 5 min, as a function of temperature: (a) 380°C, (b) 480°C, and (c) 580°C.

Figure 8. Optical micrographs viewed perpendicular to the brucite basal planes during dehydroxylation. Different nucleation locations for cracks during dehydroxylation (a) and (b) the onset of basal-plane cracking at 375°C forming 120° crack angles at the crystal edge (a) and a basal plane step (b); (c) Primary and secondary cracking nucleated from the crystal edge together with crack center formation (after 2 minutes at 475°C); (d) surface defects on a freshly cleaved brucite basal plane prior to dehydroxylation onset; (e) onset of dehydroxylation with extensive crack center formation indicating basal plane crack centers often nucleate at defect sites (1 min at 475°C).

Figure 9. FESEM image of the intergrown MgO nanostructure formed via $\text{Mg}(\text{OH})_2$ dehydroxylation at 580°C for 2 hours. The sample is gold coated. The image was taken using a Hitachi S4700 FEG-SEM (at 25kV and a 12.5mm working distance).

Figure 10. *In situ* HREM observations of rehydroxylation of an extensively dehydroxylated $\text{Mg}(\text{OH})_2$ fragment under ~ 1 torr H_2O (g). The $\text{Mg}(\text{OH})_2$ recrystallization process exhibits (1) the formation and annealing of defective $\text{Mg}(\text{OH})_2$ structures to form single crystal regions of $\text{Mg}(\text{OH})_2$ (the $\text{Mg}(\text{OH})_2$ crystallites formed in a and b, eventually grow together to form the defective region c), (2) rapid edge dislocation motion, parallel and perpendicular to the lamella (see white arrows), and (3) rapid layer by layer $\text{Mg}(\text{OH})_2$ crystal growth (e.g., black arrows in j and k show surface layer growth in less than a second) in this sequence.

Figure 11. *In situ* E-cell DHRTEM observations of the ambient temperature rehydroxylation-carbonation of an extensively dehydroxylated $\text{Mg}(\text{OH})_2$ fragment under 400 mtorr $\text{CO}_2 + \text{H}_2\text{O}$; (a) the $\text{Mg}(\text{OH})_2$ feedstock viewed parallel to the layers prior to dehydroxylation under the microscope vacuum at 465 °C; (b) initial exposure of dehydroxylated $\text{Mg}(\text{OH})_2$ to $\text{CO}_2 + \text{H}_2\text{O}(\text{g})$ initiates rehydroxylation-carbonation instantly; (c and d) rehydroxylation-carbonation continues rapidly, with the host matrix generally swelling as the reaction continues superimposed with intermittent breathing-like expansion/contraction behavior.

Figure 12. *In situ* E-cell DHRTEM observation of the ambient temperature rehydroxylation-carbonation process, showing the intermittent appearance and disappearance of $\text{Mg}(\text{OH})_2$ -like lamella during rehydroxylation-carbonation of an extensively dehydroxylated $\text{Mg}(\text{OH})_2$ fragment.

Figure 13. A comparison of the extent of $\text{Mg}(\text{OH})_2$ reaction matrix cracking (expressed as the number of fragments formed per $400 \mu^2$ of the basal plane surface) with the extent of dehydroxylation during dehydroxylation-carbonation as a function of CO_2 pressure after 16hrs at 585°C . Below the critical pressure for MgCO_3 formation, $\sim 53.7 \text{ atm CO}_2$ at 585°C , carbonation occurs on cooling to ambient temperature, once the temperature drops below the critical temperature for MgCO_3 formation at 53.7 atm . The solid triangles represent the fragment density, while the diamonds represent the extent of dehydroxylation.

Figure 14. Cracking of the brucite single crystal surface for select samples in Figure 13. Samples a through d are for samples reacted at 1.4, 10.2, 43.6, and 183.7 atm . Note, the first three samples dehydroxylated at 585°C and carbonated on cooling to ambient temperature, while the fourth sample carbonated directly at 585°C .

Figure 15. Wt % MgCO_3 formed vs. CO_2 pressure for similarly-sized $\text{Mg}(\text{OH})_2$ single crystal fragments reacted at $585^\circ\text{C} (\pm 5^\circ\text{C})$ for 16 hours. Triangles represent reactions in which the autoclave was air-cooled (~ 30 min, while the sample was still under CO_2) to ambient temperature at the end of each run. Squares represent reactions in which the autoclave was water quenched, immediately followed by CO_2 evacuation at the end of each run. The critical carbon dioxide pressure for MgCO_3 formation at 585°C (~ 53.7 atm) is shown.^{8,9,14} The very low extent of carbonation observed for the sample quenched from below the critical carbon dioxide pressure confirms that carbonation occurs on cooling (or at ambient temperature) for samples reacted below the critical carbon dioxide pressure.

CONCLUSIONS

$\text{Mg}(\text{OH})_2$ gas-phase carbonation reactivity is intimately associated with dehydroxylation/rehydroxylation processes. The extent of dehydroxylation is consistently observed to exceed the extent of carbonation for direct $\text{Mg}(\text{OH})_2$ carbonation reactions, indicating that dehydroxylation and carbonation are separate but intimately interrelated reaction processes. $\text{Mg}(\text{OH})_2$ dehydroxylation is a more complicated process than the simple two-phase process previously assumed and is best described as a lamellar nucleation and growth process that can lead to a solid solution series of lamellar oxyhydroxide intermediate materials with potentially enhanced carbonation reactivity, as shown in Figure 2. These intermediates may also form during rehydroxylation, providing similar new reaction pathways for rehydroxylation-carbonation. Relatively low-temperature dehydroxylation also induces a range of morphological changes that can serve to enhance carbonation reactivity, including translamellar cracking, delamination, and morphological reconstruction into nanostructured materials. Importantly, these phenomena can mitigate the ability of passivating carbonate layer formation to slow carbonation reaction rates.

The above mechanistic understanding leads to general approaches to enhance carbonation reaction rates. Highlights include, first, reaction rates for direct $\text{Mg}(\text{OH})_2$ carbonation are optimized at CO_2 reaction pressures that just exceed the minimum pressure needed to stabilize MgCO_3 formation. Progressively higher reaction pressures increasingly inhibit dehydroxylation and carbonation by slowing H_2O diffusion away from and CO_2 diffusion to the reaction sites, respectively. Second, dramatically enhanced carbonation reactivity can be achieved via rehydroxylation-carbonation for low-temperature dehydroxylated $\text{Mg}(\text{OH})_2$, even at ambient temperature. We have observed this process at the atomic-level/nanoscale via DHRTEM and parallel energy loss spectroscopy for the first time. Advanced computational modeling corroborates that the ambient temperature carbonation process yields an amorphous carbonate containing material during rehydroxylation-carbonation. We have also observed the rehydroxylation of partially dehydroxylated $\text{Mg}(\text{OH})_2$ via E-cell DHRTEM and found $\text{Mg}(\text{OH})_2$ recrystallization exhibits rapid Mg diffusion, which likely contributes to the dramatic increase in carbonation reactivity observed during rehydroxylation-carbonation. As $\text{Mg}(\text{OH})_2$ is a prototypical Mg-rich lamellar hydroxide based mineral, some of the above reaction mechanisms may also apply more generally (in whole or in part) to Mg-rich lamellar hydroxide based mineral (e.g., serpentine) dehydroxylation/rehydroxylation-carbonation reaction processes.

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- “Atomic-Level Imaging of CO₂ Disposal as a Carbonate Mineral: Optimizing Mg(OH)₂ Carbonation,” M.J. McKelvy, R.W. Carpenter, R. Sharma, and Ken Streib, presented at the Second CO₂ Mineral Sequestration Forum, Albany, Oregon, 1998.
- “Atomic-Level Imaging Of CO₂ Disposal as a Carbonate Mineral: Optimizing Reaction Process Design,” M.J. McKelvy, R.W. Carpenter, and R. Sharma, presented at the First CO₂ Mineral Sequestration Forum, Los Alamos, New Mexico, 1998.

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