

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

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ABSTRACT

OBJECTIVE

The goal of this project is to develop an atomic-level understanding of the mechanisms that govern the kinetics of the complex Mg(OH)₂ carbonation process to facilitate engineering of improved carbonation materials and processes for CO₂ disposal. Mg(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 CO₂ mineral sequestration potential. Environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM) is used to probe the 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 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 Mg(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., 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 Mg(OH)₂ dehydroxylation/carbonation mechanisms at the macroscopic, microscopic, and atomic level. 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 CO₂ Disposal as a Carbonate Mineral: a Synergetic Approach to Optimizing Reaction Process Design,” (grant # DE-FG26-99FT40580).

Mg(OH)₂ dehydroxylation proceeds as a lamellar nucleation and growth process. Initially, lamellar oxide nuclei form (e.g., ...OH/Mg/OH/OH/Mg/OH... → ...OH/Mg/O/Mg/OH... + H₂O) 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 Mg(OH)₂ lamella. 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. 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 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 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. 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 Mg(OH)₂/MgO layer bending. These phenomena provide important pathways, which can be used to combat the formation of near surface carbonate passivation. These highly porous structures can also lead to novel phenomena, such as Mg(OH)₂ carbonation reactivity decreasing with increasing CO₂ gas pressure (water vapor evolution during dehydroxylation inhibits CO₂ diffusion to available carbonation sites more effectively at higher gas pressures). Overall, these intermediate materials offer broad potential for enhancing carbonation reactivity

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

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. Carbonation of Mg-rich lamellar-hydroxide-based minerals (e.g., the model Mg(OH)₂ system and serpentine based minerals) is a leading process candidate, which generates the stable, naturally-occurring mineral magnesite (MgCO₃). Optimizing the carbonation reaction rate and its degree of completion are key to process cost and viability. This project focuses on investigating the process reaction mechanisms for the model Mg(OH)₂ carbonation system at the atomic level to provide the mechanistic understanding to facilitate the engineering of improved carbonation materials and processes for carbon dioxide disposal.

PLANS FOR THE COMING YEAR

The primary focus will be to explore (i) the ability of controlled dehydroxylation/rehydroxylation to enhance carbonation reactivity via intermediate (e.g., oxyhydroxide) nano-structure formation and (ii) the effects of impurities (e.g., Ca) on dehydration/carbonation mechanisms and reactivity.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Publications

- 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 "Mg(OH)₂ Dehydroxylation: *In Situ* Atomic-Level Observations of Lamellar Nucleation and Growth," *Science* (submitted).
- A.V.G. Chizmeshya and M.J. McKelvy, "Structure and Properties of Lamellar Oxyhydroxide Intermediate Phases formed during Mg(OH)₂ Dehydroxylation: A Non-Empirical Density Function Approach," *J. Phys. Cond. Matt.* (submitted).

Conference Presentations

- 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.
- M.J. McKelvy, H. Bearat, A.V.G. Chizmeshya, R. Sharma, R.W. Carpenter, and K. Streib, "The Role of Dehydroxylation in Mg(OH)₂ Carbonation: Implications for Lamellar Hydroxide Mineral Carbonation," *Fourth CO₂ Mineral Sequestration Forum*, Tempe, Arizona, 1999.
- A.V.G. Chizmeshya and M.J. McKelvy, "Advanced Simulation and Modeling of Lamellar Hydroxide Minerals: Dehydroxylation and Carbonation," *Fourth CO₂ Mineral Sequestration Forum*, Tempe, Arizona, 1999.
- 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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- H. J. Ziock, E. M. Broscha, A.V.G. Chizmeshya, D. J. Fauth, F. Goff, P. M. Goldberg, G. Guthrie, K. S. Lackner, M. J. McKelvy, D. N. Nilsen, W. K. O'Connor, P. C. Turner, Y. Soong, R. Vaidya, and R. Walters, "Carbon Dioxide Disposal by Mineral Sequestration in an Industrial Setting," *Second Dixy Lee Ray Memorial Symposium on Utilization of Fossil Fuel Generated Carbon Dioxide in Agriculture and Industry*, Washington, D.C., 1999.
- 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.
- 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.

Conference Presentations (continued)

- 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.

Students Supported under this Grant

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