TITLE: ATOMIC-LEVEL IMAGING OF CO_2 DISPOSAL AS A CARBONATE MINERAL: OPTIMIZING REACTION PROCESS DESIGN

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ABSTRACT

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 $Mg(OH)_2$, to facilitate engineering of improved carbonation materials and processes for CO_2 disposal. The chemical and structural simplicity of $Mg(OH)_2$ 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 (i.e., *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

We have continued to extend our studies beyond E-cell DHRTEM to develop a better understanding of the $Mg(OH)_2$ 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.

$Mg(OH)_2$ dehydroxylation is governed 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 MgO + $Mg(OH)_2$ 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. Internal blister formation occurs early during dehydroxylation, with matrix cracking proceeding inward from the lamellar crystal edge and basal plane surfaces to connect with the internal blisters that have formed. 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 was found to 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 shows an amorphous magnesium carbonate containing material is formed in the process. The above dehydroxylation mechanisms and their ability to create nanoporous reaction matrices also impacts direct gas-phase $Mg(OH)_2$ 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 $Mg(OH)_2$ carbonation reaction rates *increase* with *decreasing* CO_2(g) pressure above the critical pressure needed for carbonate formation. Hence, direct gas-phase $Mg(OH)_2$ carbonation reactivity can be optimized at the lowest CO_2 pressure at which $MgCO_3$ is stable. Higher CO_2 pressures inhibit H_2O(g) diffusion out of and CO_2(g) diffusion into the nanoporous reaction matrix that forms, slowing both dehydroxylation and carbonation. Initial studies 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.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

Fossil fuels, especially coal, can support global energy demands for centuries to come, if the environmental problems associated with CO_2 emissions can be overcome. Mineralization of stationary-source CO_2 emissions as carbonates can provide permanent and environmentally benign CO_2 sequestration. The primary challenge remaining for CO_2 mineral sequestration is economically viable process development. 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 ($MgCO_3$). Enhancing the carbonation reaction rate and its degree of completion are key to developing an economically viable process. This project focuses on developing an atomic-level understanding of the reaction mechanisms that govern carbonation reactivity for the model $Mg(OH)_2$ system. The goal is to provide the mechanistic understanding to facilitate engineering of improved carbonation materials and processes for permanent CO_2 disposal.

PLANS FOR THE COMING YEAR

The primary focus will be to (i) continue to investigate the ability of dehydroxylation/rehydroxylation to enhance carbonation reactivity, (ii) probe the effect of select defects/impurities on the above mechanisms and carbonation reactivity, and (iii) begin to extend our understanding of the above $Mg(OH)_2$ model-system reaction mechanisms to more cost effective, but more complex, Mg-rich lamellar hydroxide feedstock materials (e.g., serpentine-based materials).

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 CO_2 Mineral Sequestration Reaction Processes," *Proc. 25th International Technical Conference on Coal Utilization & Fuel Systems*, (2000) 897-908.
- Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, "Developing an Atomic-Level Understanding to Enhance CO_2 Mineral Sequestration Reaction Processes via Materials and Reaction Engineering," *Proc. 17th International Pittsburgh Coal Conference*, 18A, 2, 8-20 (2000).
- Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, "Developing a Mechanistic Understanding of CO_2 Mineral Sequestration Reaction Processes," *Proc. 26th International Technical Conference on Coal Utilization & Fuel Systems*, (2001) 777-788 .
- Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, R.W. Carpenter, and Ken Streib, "Magnesium Hydroxide Dehydroxylation: *In Situ* Nanoscale Observations of Lamellar Nucleation and Growth," *Chem. Mater*., in press; web release February 8, 2001 (http://pubs.acs.org/subscribe/journals /cmatex/browse_asap .html).
- Hamdallah Bearat, Michael J. McKelvy, Andrew V. G. Chizmeshya, Renu Sharma, and Ray W. Carpenter, "Magnesium Hydroxide Dehydroxylation/Carbonation Reaction Processes: Implications for Carbon Dioxide Mineral Sequestration," *J. Am. Ceram. Soc.* (submitted).
- A.V.G. Chizmeshya, M.J. McKelvy, R. Sharma, R.W. Carpenter and H. Bearat, "Density Functional Theory Study of the Decomposition of $Mg(OH)_2$: A Lamellar Dehydroxylation Model," *Mater. Chem. and Phys.*, (submitted).
- Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, "Developing a Mechanistic Understanding of Lamellar Hydroxide Mineral Carbonation Reaction Processes to Reduce CO_2 Mineral Sequestration Process Cost," *Proc. First National Conference on Carbon Sequestration,* Washington D.C., May 2001 (submitted).

Conference Presentations

- M.J. McKelvy, R.W. Carpenter, and R. Sharma, "Atomic-Level Imaging Of CO_2 Disposal as a Carbonate Mineral: Optimizing Reaction Process Design," M.J. McKelvy, R.W. Carpenter, and R. Sharma, *First CO_2 Mineral Sequestration Forum*, Los Alamos, New Mexico, 1998.
- M.J. McKelvy, R.W. Carpenter, R. Sharma, and Ken Streib, "Atomic-Level Imaging of CO_2 Disposal as a Carbonate Mineral: Optimizing $Mg(OH)_2$ Carbonation," *Second CO_2 Mineral Sequestration Forum*, Albany, Oregon, 1998.
- 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 CO_2 Mineral Sequestration," *Third CO_2 Mineral Sequestration Forum*, Pittsburgh, Pennsylvania, 1999.

Conference Presentations (continued)

- 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.

- 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, R.W. Carpenter and K. Streib, "$Mg(OH)_2$ Dehydroxylation: A Lamellar Nucleation and Growth Process," Symposium Q, *Materials Research Society Meeting*, Boston, Massachusetts, 1999.

- 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 CO_2 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 CO_2 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 CO_2 Mineral Sequestration Forum*, Tempe, Arizona, 1999.

- Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, Hamdallah Bearat, and R.W. Carpenter, "$Mg(OH)_2$ Dehydroxylation: Implications for Enhancing CO_2 Mineral Sequestration Reaction Processes," *25^{th} International Technical Conference on Coal Utilization & Fuel Systems*, Clearwater, Florida, 2000.

- Andrew V.G. Chizmeshya, Renee Olsen, and Michael J. McKelvy, "Atomic-Level Modeling of CO_2 Disposal as a Carbonate Mineral: A Synergetic Approach to Optimizing Reaction Process Design," *DOE Basic Energy Sciences Combustion Research Meeting*, Chantilly, Virginia, 2000.

- Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, Hamdallah Bearat, and R.W. Carpenter, "Atomic-Level Imaging of CO_2 Disposal as a Carbonate Mineral: Optimizing Reaction Process Design," *DOE Basic Energy Sciences Combustion Research Meeting*, Chantilly, Virginia, 2000.

- Michael J. McKelvy, Renu Sharma, Andrew V.G. Chizmeshya, Hamdallah Bearat, and R.W. Carpenter, "Atomic-Level Imaging of CO_2 Mineral Sequestration: Optimizing Reaction Process Design," *University Coal Research Contractors Review Conference*, Pittsburgh, Pennsylvania, 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, 2000.

- Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, "Developing an Atomic-Level Understanding to Enhance CO_2 Mineral Sequestration Reaction Processes via Materials and Reaction Engineering," *17^{th} Annual International Pittsburgh Coal Conference*, Pittsburgh, Pennsylvania, 2000.

Conference Presentations (continued)

- Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, "Developing an Atomic-Level Understanding to Enhance CO_2 Mineral Sequestration Reaction Processes via Materials and Reaction Engineering," *Summit 2000, the Annual Meeting of the Geological Society of America*, Reno, Nevada, 2000.
- Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, "Methods for Developing an Atomic-Level Understanding of Carbon Dioxide Mineral Sequestration Reaction Processes," *2001 SME Meeting*, Denver, Colorado, 2001.
- Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, "Developing a Mechanistic Understanding of CO_2 Mineral Sequestration Reaction Processes," *26th International Technical Conference on Coal Utilization & Fuel Systems*, Clearwater, Florida, 2001.

Students Supported under this Grant

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