

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

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ABSTRACT

OBJECTIVE

The aim of the current innovative concepts project is to develop a specialized advanced computational methodology to complement the ongoing experimental inquiry of the atomic level processes involved in CO₂ mineral sequestration. The ultimate goal is to integrate the insights provided by detailed predictive simulations with the data obtained from environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM), optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and elemental analysis. The modeling studies are specifically designed to enhance the synergism with, and complement the analysis of, existing mineral-CO₂ reaction process studies being carried out under DOE UCR Grant DE-FG2698-FT40112. Direct contact between the simulations and the experimental measurements is provided by computing, from first principles, the equilibrium structures, elastic, optical, and vibrational properties of Mg(OH)₂ (brucite), MgO (periclase), MgCO₃ (magnesite), as well as the energetics of the dehydroxylation reaction ($\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$), and the reactivity of CO₂ with MgO and Mg(OH)₂. From these calculations, thermodynamic and kinetic characteristics of the reaction conditions can be inferred. This kind of information, when integrated with the atomic level data obtained from experimental gas-solid dehydroxylation/carbonation studies, will be used to design optimized reaction processes leading to the practical and cost-effective sequestration of CO₂ in mineral form.

ACCOMPLISHMENTS TO DATE

Atomic level imaging has shown that Mg(OH)₂ dehydroxylation proceeds as a lamellar nucleation and growth process. Lamellar oxide nuclei initially form within a pure hydroxide matrix followed by the subsequent growth of adjacent oxide lamella. These transitory, morphologically distinct lamellar regions then grow both parallel and perpendicular to the Mg(OH)₂ lamella. By combining first principles, semi-empirical and classical simulation techniques, we have examined the dehydroxylation reaction of Mg(OH)₂ and demonstrated that metastable

lamellar oxyhydroxide compounds ($\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$) are expected to form along the $\text{Mg}(\text{OH})_2 \rightarrow \text{MgO}$ reaction path, providing a broad range of new carbonation reaction intermediate pathways. These new phases differ in free energy by only $\sim 1\text{-}2$ kcal/mol from equivalent stoichiometric mixtures of MgO and $\text{Mg}(\text{OH})_2$ – energies small in comparison with typical elastic strain energies associated with local bending of lamella during dehydroxylation. Computed bulk moduli indicate that a rapid increase in layer stiffness occurs during dehydroxylation further increasing the elastic strain energies associated with decreasing hydroxide layer concentrations. In addition, calculated structural trends along the solid solution series yield a Vegard-like behavior in the dependence of the basal plane Mg-Mg separation on degree of dehydration. This is consistent with electron diffraction determinations of the structural behavior of the hydroxide during dehydration. *Ab initio* methods also provide a useful and unique point of contact with spectroscopic measurements such as EELS and x-ray, as synthetic spectra can be compared directly with those observed in order to elucidate salient bonding and structural trends. Using the full potential linearized augmented plane wave (FPLAPW) method we have accurately simulated the energy loss near edge spectrum (ELNES) of known compounds (brucite, periclase and magnesite) and have predicted the detailed form of the oxyhydroxide spectrum. These studies are being fully integrated with our collaborative E-cell DHRTEM studies of the *in situ* $\text{Mg}(\text{OH})_2$ dehydroxylation/carbonation process at the atomic level.

CO_2 surface reactivity has also been analyzed using judiciously chosen cluster models of MgO, $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$ and $\text{Mg}(\text{OH})_2$ surfaces. A limited number of periodic slab calculations have also been performed to validate the simpler cluster treatments. In our preliminary studies we have found that the energy surface for the dissociative reaction of CO_2 on MgO has a complex structure involving a physisorption precursor region, and a dissociation channel involving a distortion of the CO_2 from its gas phase conformation. Such results provide a preliminary fundamental understanding of the early chemical events involved in the carbon dioxide mineralization process. By integrating these results with our atomic-level/microscopic imaging studies, a more comprehensive understanding of carbonation in this model Mg-rich lamellar-hydroxide mineral system is beginning to emerge.

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 CO_2 emissions can be overcome. Mineralization of stationary-source CO_2 emissions as carbonates can provide safe capture and long-term sequestration. Carbonation of Mg-rich lamellar-hydroxide-based minerals (e.g., the model $\text{Mg}(\text{OH})_2$ system and serpentine based minerals) is a leading process candidate, which generates the stable, naturally-occurring mineral magnesite (MgCO_3). 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 $\text{Mg}(\text{OH})_2$ 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 balance of the contract time will be spent on the molecular dynamics simulations of dehydroxylation/carbonation, as well as the study of cracking and surface defect formation using classical techniques. We also plan to undertake a brief study of the co-adsorption of CO_2 and H_2O on MgO nano-crystallites. The latter investigation would be directly relevant to the experimental work on carbonation, providing insight into role played by the water vapor in the carbonation reaction.

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

- 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.
- 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.
- 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.

Students Supported under this Grant

- Renee Olsen, undergraduate (Ph.D.) student in the Department of Physics and Astronomy, Arizona State University