**ATOMIC-LEVEL MODELING OF CO₂ DISPOSAL AS A CARBONATE MINERAL:
A SYNERGETIC APPROACH TO 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 mineral 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. In this investigation Mg(OH)₂ was selected as a model Mg-rich lamellar hydroxide carbonation feedstock material due to its chemical and structural simplicity. 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.

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 optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and C and H 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 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.

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INTRODUCTION

Mg(OH)₂ Carbonation: A Model Mg-Rich Lamellar Hydroxide 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 model Mg-rich lamellar hydroxide process candidate, which generates the stable naturally occurring mineral magnesite (MgCO₃) and water according to reaction:

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. Mg-rich lamellar hydroxide (e.g. Mg(OH)₂ and serpentine based minerals) carbonation processes, which involve simultaneous dehydroxylation and carbonation, show them 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 at the onset of dehydroxylation. These early stages of decomposition are of particular interest, since carbon dioxide may react to form magnesite (MgCO₃) locally as soon as dehydroxylation begins in that region. In a companion study (DE-FG2698-FT40112) we reported 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 were combined with *in-situ* selected area diffraction (SAD) of the dehydroxylation process. Here, we combine these observations with advanced computational modeling studies using a non-empirical density functional theory (DFT) approach, and state-of-the-art *ab initio* band structure techniques 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.

EXECUTIVE SUMMARY

OBJECTIVES

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 optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and C and H 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 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

As mentioned above, 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 oxyhydroxide compounds ($\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$) are expected to form along the $\text{Mg(OH)}_2 \rightarrow \text{MgO}$ reaction path. These new phases differ in free energy by only ~1-2 kcal/mol from equivalent stoichiometric mixtures of MgO and Mg(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 x-ray determinations of the structural behavior of the hydroxide upon 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 and periclase) and have predicted the detailed form of the oxyhydroxide spectrum.

CO₂ surface reactivity has also be analyzed using judiciously chosen cluster models of MgO, $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$ and Mg(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 CO₂ on MgO has a complex structure involving a physisorption precursor region, and a dissociation channel involving a distortion of the CO₂ 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.

RESEARCH CONDUCTED DURING THE NO-COST EXTENSION PERIOD

The present Innovative Concepts award was granted a no-cost extension of one additional year (beginning August 1, 2000 and ending July 31, 2001). At the time of writing the first year report (Report # 40580R01) the research focus for the extension period was proposed to include: (i) the molecular dynamics simulations of dehydroxylation/ carbonation, as well as the study of cracking and surface defect formation using classical techniques, (ii) a more detailed study of the co-adsorption of CO₂ and H₂O on MgO nano-crystallites. Shortly after the submission of the first-year report, the National Working Group on Mineral Sequestration (managed by DOE/NETL) switched its focus from brucite, to the more cost-effective serpentinite (Mg₃Si₂O₅(OH)₄) hydroxyl magnesium-bearing mineral feedstocks, as well as olivine (MgSiO₃) and forsterite (Mg₂SiO₄). The pertinent carbonation reactions for brucite, serpentine and olivine (i.e., forsterite), respectively, are as follows:

Due to this development the extension period research emphasis of the present project was re-focused in order to make most effective use of the remaining funds and project resources. The working group identified a number of important issues concerning the suitability of various serpentinite feedstock minerals for carbonation by fall of 2000. It was determined that carbonation reactions proceeded more readily in a liquid-solid (aqueous) setting than in the gas-solid form, and that pre-heating of ground serpentinite significantly promotes the carbonation. In order to be able to explore some of these issues we embarked on the development of: (i) a special purpose, highly efficient quantum molecular dynamics code (named MDG) for the treatment of hydroxyl mineral dehydroxylation/carbonation investigations, (ii) a simulation procedure aimed at elucidating the connection between vibrational spectra and the dehydroxylation, and subsequent carbonation behavior and (iii) further refinement and development of synthetic (predictive) spectroscopic characterization that directly complements, and aids in the interpretation of, experimental XRD, EELS, IR, Raman and Photoelectron spectroscopy. All of these plans were undertaken with the full consultation and approval of NETL contract officers.

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.

The final phase of the project performance period (extension) focused on expanding the simulation treatment to more complex, but also more abundant and cost-effective, candidate mineral feedstock. The initial emphasis was on understanding the mechanisms associated with the dehydroxylation process. Preliminary experimental results by members of the Mineral Sequestration Working Group indicate that increased carbonation reactivity is achieved for partially dehydroxylated feedstock (meta-serpentine). The initial modeling efforts focusing on the mobility of hydroxyl groups at high temperature, and their diffusion mechanisms and characteristics will have direct significance to the experimental research. Relating the mechanisms to spectroscopic signatures (FTIR, Raman), whenever possible, will also significantly advance the reaction design of highly carbonation reactive materials.

KEY RESULTS and DISCUSSION

The modeling results obtained so far can be broadly classified into four areas: (i) studies of the initial stages of dehydroxylation of brucite, (ii) detailed “fingerprinting” of salient physico-chemical characteristics (synthetic XRD spectra based on predicted structures, vibrational spectra including IR frequencies of key bands, electron energy loss spectra (EELS)) (iii) initial studies of the adsorption and bonding properties of carbon dioxide to the prototypical substrates along the reaction path (hydroxide → intermediate phase → oxide), and (iv) the initial study of hydroxyl diffusion and mobility in heat-modified serpentine-type minerals, and its spectroscopic characterization. The results and progress we have made in each of these areas is discussed in turn.

(i) Modeling the Lamellar Dehydroxylation of Brucite

A non-empirical density functional theory based on a modified ionic description (SEVIB) was used to explore the energetics, elastic and structural behavior of bulk periodic lamellar systems of composition Mg_{x+y}O_x(OH)_{2y} (see Figure 1, below) representing a solid solution series between brucite (Mg(OH)₂) and periclase (MgO). Our results suggest that lamellar dehydroxylation can represent a viable thermodynamic path for brucite decomposition. In particular, we find that an entire range of oxyhydroxide intermediate phases become energetically accessible at temperatures near 500°C (see Figure 1). A series of solid solution phases representing various degrees of hydroxide content have been proposed on the basis of free energy minimization. Future work should focus on exploring the possibility of symmetry lowering distortions to these prototypical structures, leading to even lower formation energies. The optimized crystalline oxyhydroxide basal plane Mg-Mg bond lengths exhibit an interesting Vegard-like behavior in which the variation of the packing distance from the MgO to the Mg(OH)₂ value is directly proportional to the hydroxide content. This behavior is consistent with the observations obtained in the companion grant DE-FG26-98FT40112, based on time-averaged video

tape imaging and direct selected area diffraction observations of the actual *in-situ* dehydroxylation process observed using DHRTEM.

Figure 1: Structural progression of intermediate oxyhydroxide phases along the decomposition path between brucite (left most structure) and periclase (right most structure). Green, red and white spheres represent Mg, O and H respectively. The parameter u ranges from 0 to 1 and represents the degree of “hydration”, e.g., in relation to the formula $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$ the parameter $u=y/(x+y)$.

In addition to the energy and structure of oxyhydroxide phases, it is of great interest to examine the trends in elastic behavior. The cracking and fissuring observed in brucite, once dehydroxylation has set in, suggests that the bending modulus of individual layers, and in particular its dependence on local hydroxide content, plays a key role in the actual decomposition process. In order to gain some preliminary insight into this effect we have computed the bulk elastic characteristics of the relevant phases. Our results indicate that oxide like compressibility is attained at the early onset of dehydroxylation, as can be seen from Figure 2, below.

Figure 2: Free energies at 500°C (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 Mg(OH)_2 . The bulk moduli of the intermediates are shown in blue.

It is likely that intralamellar and interlamellar strain associated with this highly non-linear behavior is strongly connected with the cracking and delamination found experimentally. Molecular dynamics studies based on the SEVIB description, aimed at exploring the role of lattice strain and kinetic effects on oxyhydroxide formation, are currently underway. A detailed summary of the computational approach employed, as well as a more complete description of the modeling results, is contained in the draft publication preprint included with this report, entitled “Density Functional Theory Study of the Decomposition of $\text{Mg}(\text{OH})_2$: A Lamellar Dehydroxylation Model”.

In order to appraise the quantitative significance of the SEVIB modeling studies we have also carried out a number of state-of-the-art band structure calculations based on the Generalized Gradient Approximation (GGA) of Density Functional Theory (DFT). Using the CRYSTAL98 periodic all-electron code² we computed from first principles the structure and energy of the molecules (H_2O , CO_2) and solid phases (MgO , $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$, $\text{Mg}(\text{OH})_2$). This program uses a linear combination of gaussian type orbitals (LCGTO) approximation to expand the true crystalline wave functions. We also make extensive use of the WIEN97 periodic all-electron code³, which is based on a full potential linearized plane wave approximation (FPLAPW). Together, these two codes represent the state-of-the-art in all-electron *ab initio* modeling. The computational resources at our disposal (dual 750MHz Pentium III platform with 1Gigabyte or RAM) limit our application with these codes to about 60 atoms. This is usually sufficient for modeling high symmetry systems and adsorption of small molecules on slab-represented solid involving several layers. Figure 3 contains a plot of the band-structure and charge density of $\text{Mg}(\text{OH})_2$ in its equilibrium configuration. The shaded region to the right of the band-structure plot (left panel) is the density of states (DOS) which exhibits a band gap of about 4 eV in the local density approximation (LDA), confirming that insulator character of brucite.

Figure 3: The band structure (left panel) and charge density (right panel) of brucite in the equilibrium structure (static lattice approximation). The calculations were carried out using the FPLAPW method within the generalized gradient approximation of density functional theory.

The right panel of the figure shows a crude plot of the charge density difference between the true ground state electronic density of brucite and that of a superposition of atoms corresponding to Mg, O and H (the accuracy of the plot decreases towards the edges of the area shown, and this is an artifact of the plotting scheme used and **does not** reflect inaccuracy in the computational method). The plotted

density is coplanar with hydroxyls from adjacent brucite layers and a detailed analysis indicates the absence of “hydrogen bonding”. These figures are meant to convey in some sense the degree of detail contained in *ab initio* calculations.

In Table 1 we provide a synopsis of some preliminary results obtained at the beginning of the performance period for the *ab initio* treatment of brucite. The parameters RK_{max} , l_{max} , G_{max} and N_k pertain to the FPLAPW treatment and govern the convergence in the numerical procedure. Rows marked “CRYSTAL98” refer to well-converged LCGTO calculations. Experimental results quoted are those of Catti *et al*⁴. It is important to emphasize that no experimental input, except for fundamental constants, were used in any of these calculations. In this sense, the outcome of the simulation represents a prediction. These results were used as a benchmark before proceeding to more elaborate numerical investigation and clearly demonstrate that the GGA provides a superior description to the LDA for hydroxide compounds. Also shown in the table are the PIB and SEVIB electron-gas model results (see attached manuscript for additional details). These latter methods avoid the band-structure step in the calculation, and therefore proceed much more quickly (typically orders of magnitude faster) than the *ab initio* calculations.

Table 1: Representative *ab initio* results for Brucite. First five columns denote computational parameters obtained using WIEN97. The CRYSTAL98 results were obtained using an un-optimized Gaussian basis-set. Cell parameters a and c are given in Angstroms, internal positions of the oxygen (z_O) and hydrogen (z_H) are given in fractional units.

RK_{max}	l_{max}	G_{max}	N_k	DFT	$V(\text{\AA}^3)$	$a(\text{\AA})$	$c(\text{\AA})$	z_O	z_H	$d_{OH}(\text{\AA})$	$-\Phi(\text{Ry})$
2	10	11	1	LDA	52.74	3.714	4.415	0.212	0.440	1.016	699.6785
2	10	11	1	GGA	59.88	3.671	5.131	0.184	0.382	1.005	703.6368
3	12	12	50	LDA	36.66	3.075	4.476	0.223	0.448	1.005	700.1096
			CRYSTAL98	LDA	38.09	3.130	4.488	0.226	0.447	0.993	699.9386
				EXP	40.7	3.14	4.77	0.222	0.429	0.990	
3	12	12	50	GGA	45.43	3.163	5.244	0.196	0.388	1.007	703.9781
			CRYSTAL98	GGA	41.89	3.187	4.772	0.220	0.427	0.984	703.8221
				EXP	40.7	3.14	4.77	0.222	0.429	0.990	
				SEVIB	40.82	3.15	4.75	0.228	0.434	0.979	
				PIB	36.48	3.12	4.33	0.285	0.505	0.953	

State properties can also be accurately computed using the all-electron codes, as demonstrated in Table 2, where we present some preliminary results for the compression equation of state. The degree of discrepancy between GGA and experiment is typical for this approach. The results obtained using the electron-gas modeling methods are comparable in quality to those shown here, but only when treating systems with an inherently ionic character (see attached manuscript for a more elaborate discussion on this point and its resolution for electron gas models). The great advantage of *ab initio* methods is that no assumptions are made concerning the bonding character in the system of interest. The great advantage in using *ab initio* quantum mechanical methods is that metals, insulators and even superconductors can be treated with the same approach, and with uniformly consistent outcome in terms of predictive capability.

Table 2: Equation of state results for brucite using the CRYSTAL98 all-electron treatment within the generalized gradient approximation. Atomic units are used (Energy: 1 a.u. = 27.212.eV, Distance: 1 a.u. = 0.529177 Å). H is the static lattice enthalpy, and Φ is the internal crystalline energy per unit cell. Values beneath the primary table are the volume, bulk modulus and bulk modulus derivative.

V (a.u.)	P (GPa)	a (a.u.)	c (a.u.)	z _O	z _H	Φ (Ry) (a.u.)	H(P) (a.u.)
299.70439	-5.0	6.1839	9.0566	0.2168	0.4215	-351.90986	-351.96079
283.23079	0.0	6.0220	9.0181	0.2204	0.4265	-351.91106	-351.91106
266.20198	2.5	5.9576	8.6604	0.2289	0.4432	-351.91029	-351.88767
262.48166	5.0	5.9413	8.5864	0.2296	0.4452	-351.90984	-351.86523
245.12439	10.0	5.8454	8.2783	0.2389	0.4631	-351.90626	-351.82294
239.16350	15.0	5.7957	8.1948	0.2341	0.4611	-351.90317	-351.78163

CRYSTAL 98: $V_0 = 41.2 \text{ Å}^3$ $K_0 = 49 \text{ GPa}$ $K_0' = 7.2$
EXPERIMENT: [Ref. 5] $V_0 = 40.7 \text{ Å}^3$ $K_0 = 46 \text{ GPa}$ $K_0' = 5.3$

Preliminary work of this kind is essential whenever a new system is being explored using first principles modeling techniques. It is crucial to determine the range of applicability and accuracy of each method in the beginning in order to optimize the research effort over the long term. We are in an excellent position to extend our treatment to other, possibly more complex, hydroxyl bearing mineral systems.

(ii) Fingerprinting via synthetic (predicted) spectra: Electron Energy Loss Spectrum (EELS)

Electron energy loss spectra (EELS) in general, and the energy loss near edge spectrum (ELNES) in particular, provide very detailed information about the local bonding environment around each atom. This technique is very commonly used in materials science and the geological arena to investigate subtle structural changes associated with phase transitions as well as chemical changes observed in solid state reactions. It is in this sense that the method is applied to the dehydroxylation/carbonation problem.

What is measured experimentally is the double differential scattering cross-section of energetic electrons. This can be compactly expressed in terms of the dynamic form factor, $S(\mathbf{Q}, E)$, as:

$$\frac{d^2\sigma}{dE d\Omega} = 4 \frac{q_f}{q_i} \frac{1}{Q^4} S(\mathbf{Q}, E) \quad (6)$$

where q_i and q_f are the initial and final wavevectors involved in the scattering and $\mathbf{Q} = \mathbf{q}_f - \mathbf{q}_i$ is the difference momentum difference. The dynamic form factor itself depends explicitly on this latter quantity through the interaction operator, which is evaluated in matrix elements between initial and final scattering states, restricted by conservation of energy $E_f - E_i = E$, where E is the energy transferred from the fast electron to the atom, namely:

$$S(\mathbf{Q}, E) = \sum_{i,f} \left| \langle \Psi_i | e^{i\mathbf{Q} \cdot \mathbf{R}} | \Psi_f \rangle \right| \delta(E + E_i - E_f). \quad (7)$$

We employ the method recently suggested by Nelheibel⁶ to evaluate the dynamic form factors, and the EELS intensity, using the full Bloch states of the crystalline systems. These are obtained by solving the

all-electron band structure self-consistently for the crystalline system of interest. This approach represents a significant improvement over previous theoretical schemes in which badly converging sums over atom shells had to be invoked, and approximate orbitals had to be employed in the evaluation of the matrix elements⁷. In addition, since averaging over direction is not required the full $\mathbf{Q}$ -dependence of the EELS spectrum can be investigated, providing a rich source of information about the directional bonding in the material being probed. Our approach also uses the WIEN97 full-potential linearized augmented plane wave description, which includes a fully relativistic treatment of core electrons and their energy shifts. Thus, very few fundamental assumptions are invoked in the simulation of the spectra and this leads to a reasonable degree of predictive capability.

Using this approach we have calculated the for K-edge carbon and oxygen ELNES in the case of oxide (MgO), hydroxide (Mg(OH)₂), carbonate (MgCO₃), as well as the carbon K-edge spectrum of other carbon bearing molecules such as CO₂ and CO₃²⁻. The purpose of these calculations is to elucidate the character of a carbonated sample prepared, and characterized, *in-situ* within the DHRTEM as a part of study being performed in the companion UCR grant DE-FG26-98FT40112. This material is particularly intriguing, since it results from our discovery of a new oxyhydroxide carbonation reaction pathway with substantial gas-phase carbonation reactivity at ambient temperature and CO₂ pressure.

Figure 4: All-electron ab initio calculations of ELNES for carbon and oxygen K-edges in reference carbonate spectrum (top traces in left and middle plots), and Mg(OH)₂ samples dehydrated *in situ*, followed by *in situ* DHRTEM rehydroxylation/carbonation (bottom traces in left and middle figures). In both cases the orange curves represent the simulated/predicted spectra. The right panel contains a comparison of simulated carbon K-edge spectra for a number of carbon bearing molecules. A broadening function of width 0.75 eV was convoluted with all raw theoretical spectra in order to account for instrumental broadening. The angular integration range was restricted to simulate an instrumental collection aperture of approximately 10 mrad (half-angle).

Figure 4 contains some representative results for *in situ* DHRTEM PEELS observations of Mg(OH)₂ dehydroxylation followed by *in situ* rehydroxylation/carbonation at ambient temperature using 800 mTorr of humid CO₂. the case of a carbonation study in which a brucite sample which was first dehydroxylated and then exposed to a humid CO₂ environment. A comparison of the calculated and measured spectra clearly shows that some type of carbonate material was formed. It is gratifying that the double-peaked features at the onset of the carbon K-edge is very well reproduced by the *ab initio* simulation. The measured spectra corresponding to the carbonated samples shown in the bottom traces of the left and middle panels exhibit a similar, but somewhat blunted, series of features similar to those in the reference carbonate. This may be associated with the formation of a disordered carbonate, as suggested by DHRTEM and XRD measurements. Comparing the top two reference traces in the

right-most panel (MgCO_3 and CO_3^{2-}) is evident that for a carbonate “propeller” the magnitude of the first near-edge feature is affected by ionic bonding to Magnesium ions. Alternatively, this change can be interpreted as a depletion of intensity between the low energy near edge features, which is consistent with the change observed in the carbon K-edge signature of the *in situ* carbonated sample. In any event, more analysis is needed to understand the origin and character of the carbonate formed during the *in situ* carbonation. Our results so far suggest that the combining measurement with modeling will be very fruitful in the future.

(iii) Adsorption and Bonding of H_2O and CO_2 on oxide/hydroxide surfaces

It is a widely known fact that the calcined low-density MgO product material obtained after dehydroxylation of brucite is highly reactive. Our own recent experimental studies point to the likely existence of metastable oxyhydroxide intermediates along the $\text{Mg}(\text{OH})_2 \rightarrow \text{MgO}$ decomposition reaction path. Comparatively little literature exists on the modeling of CO_2 adsorption on alkaline earth oxide based materials, although there is some experimental work and no clear consensus on the strength of the bonding of CO_2 on MgO. While low temperature experiments have confirmed the formation of ordered physisorbed CO_2 layers⁸, little has been done to characterize the chemisorption properties over the kind of temperatures and pressures relevant to our experiments. With these observations in mind we have undertaken a detailed modeling investigation aimed at elucidating the details of the reaction mechanism of CO_2 on oxide and oxyhydroxide material surfaces. The reactivity of water with MgO, and in particular the question of molecular versus dissociative adsorption is still being debated in the literature, and experimental results disagree in their predictions (FTIR on single crystal $\text{MgO}(100)$ show no evidence of dissociation while HREELS studies on highly ordered films and IR on powders postulate hydroxylation of the surface). It is therefore of great interest to examine the reactivity of H_2O with MgO using modeling techniques as well.

Ultimately, a full understanding of the co-adsorption of CO_2 and H_2O on brucite and MgO surfaces would be highly desirable, but modeling of this complex system is a very ambitious long term project. The simplest context in which to address the microscopic aspects of the carbonation problem is the situation in which brucite has been heavily dehydroxylated. In this case the morphology observed experimentally consists of networked MgO crystallites a few nanometers to a few tens of nanometers in size. From our preliminary adsorption studies we have identified that the oxygen site on MgO is preferred for carbon bonding (*via* charge transfer from the π -manifold of states on the distorted CO_2 molecule, to the oxygen-like p-band of the MgO), but, because of the packing of the crystallites, low-coordination corner sites are unavailable leaving 4-coordinate edge sites and 5-coordinate face sites. For this reason we have recently initiated a detailed modeling study of CO_2 reactivity on $\text{MgO}(100)$, both within the context of clusters and using more accurate slab representations for control purposes.

Figure 5: Left panel: schematic describing the parameter definitions for the mapping of the potential energy surface of CO₂ on MgO(100). Right panel: calculated potential energy surface for low energy physisorption of CO₂ on MgO(100).

Instead of approaching this using a molecular dynamics strategy we have adopted a cluster-based method in which detailed reaction energy hypersurfaces are constructed on the basis of available reaction coordinates (degrees of freedom). Semi-empirical quantum chemical methods (such as PM3) are currently being tested, but a limited set of all-electron *ab initio* density functional theory based on the GGA are also being carried out as a benchmark.

The energetic topology of the computed hypersurfaces provides valuable information about the reaction, including the most plausible dissociation/adsorption path, the magnitude of the energetic barriers encountered on its approach to the preferred adsorption site(s), and finally, binding and dissociation energies. Figure 5 illustrates a finite cluster representation of the CO₂ interaction with MgO(100) [Mg₁₃O₁₄²⁻]. The CO₂ conformation is initially fixed at its free gas phase value ($b_{CO}=1.18$ Å, $\theta_{OCO}=180^\circ$), and the parallel orientation and mean distance to the surface are varied.

The relative orientation and position of the molecule is represented schematically and these conventions are used for all the cluster work, and periodic slab work to be described. In the periodic context the angle θ is measured between the projection of the internuclear line between the CO₂ oxygens and a row of surface magnesium atoms passing through the oxygen adsorption site. In summary, we find the following: CO₂ exhibits associative chemisorption on MgO(100) with a binding energy of 43 kcal/mol (1.8 eV) while on MgO(110) the binding increases to 69 kcal/mol (2.9 eV). In both cases the final geometries were obtained from a well-converged GGA calculation using surface unit cells corresponding to a 0.25 monolayer CO₂ coverage.

The final adsorption geometries are shown in Figure 6, which also illustrates the areal size of the surface unit cells involved. In the case of the MgO(110) adsorption case, we have calculated the band structure of the CO₂ sublattice in the absence of the substrate to investigate the degree of adsorbate-adsorbate interaction. We find that there is a weak residual interaction, which can account for a net attraction between molecules of magnitude 0.2 eV per cell. The value quoted above for the heat of adsorption includes this contribution. When viewed on the whole, these results confirm the expected behavior, which is that the CO₂ molecule should tend to prefer bonding at lower coordination sites on the oxide.

Figure 6: View of the adsorption geometry for CO₂ on the MgO(100) face (left panel) and the MgO(110) face (right panel). Green, red and grey spheres represent magnesium, oxygen and carbon, respectively. Graph at right: Plot of the adsorption energy of a CO₂ molecule approaching the an oxygen site on the MgO(100) surface, along the reaction path.

In the present case the increase in bonding is about 1 eV in going from the (100) face to the (110) face. The corresponding opening O-C-O angles within the adsorbed CO₂ molecules are $\sim 140^\circ$ and $\sim 155^\circ$, respectively, while equilibrium distances between the carbon and oxygen adsorption site are 1.54 Å and 1.42 Å, respectively. It is also evident from Figure 6 that the adsorbed CO₂ molecule is not aligned with the Mg-O-Mg rows of the (110) surface, but that the lowest energy configuration exhibits an angle of $\sim 30^\circ$ between the CO₂ molecular plane and the sagital row of Mg-O-Mg surface atoms.

Another important quantity in the practical interpretation of bond formation is the magnitude and shape of the activation barrier to chemisorption. We have performed semi-quantitative calculations using a limited basis set (N21** -3G) using DFT and a ten atoms cluster. The results indicate the presence of a weak, ~ 0.2 eV (4.5 kcal/mol) activation barrier, as shown in plot in the right-most frame of Figure 6. Note that the slightly reduced binding energy with respect to our earlier quote is due to the difference in the basis set used, and the fact that a cluster, rather than a periodic slab, is being used. The physisorption precursor, represented by a dip in the energy surface near 2.6 Å, is also clearly visible.

Figure 7: View of the adsorption geometry for H₂O on the MgO(100) in a $\sqrt{2} \times \sqrt{2}$ surface unit cell corresponding to a 0.25 monolayer coverage. Green, red and white spheres represent magnesium, oxygen and hydrogen, respectively.

Finally, we explored the adsorption of water on MgO(100) using a GGA-based slab DFT calculation and found no evidence for chemisorption. Instead, a weakly physisorbed state was consistently recovered in the computer experiments exhibiting a binding energy of about 15 kcal/mol (~ 620 meV) at a $\text{O}_{\text{H}_2\text{O}}$ -surface separation of about 2.1 Å. To confirm this finding we also repeated the calculation, but starting from a dissociated state in which the a proton and hydroxyl ion are places an Angstrom above a surface oxygen and magnesium site, respectively. Evolution of the system under the action of quantum mechanical forces leads to a barrierless recombination to H_2O , and subsequent re-arrangement to a physisorbed configuration in which the protons on the water molecule form weak hydrogen bonds with nearest neighbor surface oxygen sites (see Figure 7). These findings suggest that water exists in a non-reactive state on oxide surfaces. The co-adsorption of water and carbon dioxide is therefore the next system to consider. As mentioned earlier, this is beyond the scope of the present study, but seems to be the next logical step. This is especially true in view of the important role that water vapor appears to play in mediating the carbonation reaction in brucite. Any conclusions reached in this regard for the brucite will have immediate significance for other Mg-rich lamellar feedstock material candidates including serpentinite minerals. Results of this kind provide us with important guidance with respect to the initial formation of carbonate on oxides and hydroxides by providing benchmarks for the energetic tendencies of bond formation under a variety of situations. A report focusing on the calculation of adsorption properties described here, is currently in progress and will soon be submitted for publication.

(iv) Intra-layer strain and polymorphism in Serpentine: Vibrational Effects

The variation in the crystallographic morphology of lizardite (ideal topological layered form), antigorite (modulated) and chrysotile (coiled) can be generally understood in terms of a double-layer model consisting of a hydroxy-silicate sheet (top layer) and a brucite-like hydroxyl sheet (bottom layer). Impurity and/or defect induced stress initiates different strains in the top and bottom layers, resulting in a long-ranged structural relaxation. In chrysotile, the result is a “jelly-roll” like coiling of the hydroxy-silicate sheets, which can be observed on a macroscopic scale. In antigorite, the strain differential produces a wave-like modulated structure with characteristic periodicity ranging from dozens to hundreds of Angstroms.

Figure 8: Model of axially strained single sheets of lizardite. The bending strain corresponds to a radius of curvature (at the Mg plane) of about 50 Å parallel to $[11\bar{2}0]$. Left frame: the initial lizardite sheet; right frame: strained sheet which preserves the Mg-Mg distances within the Mg-plane.

An exhaustive literature search has revealed that a microscopic structural model for the strain relationship in the serpentine layers currently does not exist. A reliable model for the strain effects due to various impurities (Fe, Al, Cr, etc.) should significantly contribute to the interpretation of structural (e.g., X-ray and HRTEM) and vibrational spectroscopic investigations.

In order to obtain some initial insight into these effects, we have performed a quantum molecular dynamics simulation of small serpentine fragments consisting of one sheet containing several units of $\text{Mg}_3\text{Si}_5\text{O}_2(\text{OH})_4$. A series of small programs were written to generate the initial structures for the axially sheet optimization simulations. A suitable representative cluster is first defined and then structurally optimized (e.g., brought close to its structural ground state configuration). Starting with a stoichiometric planar sheet of lizardite a reference point within the sheet is then chosen and the sheet is radially strained (or “bent”) relative to a rotation center a distance R away. This strained angular positions of the atoms for this radial strain are then relaxed. A typical example is shown in Figure 8, which illustrates the concept for a single sheet of lizardite. Finite temperature quantum molecular dynamics simulations were then performed on a series of representative lizardite fragments with varying degrees of curvature. In a typical simulation at 300K, the four Mg ions at the corners of the sheet were constrained at their minimum force positions consistent with a specified bending stress. With no additional external stresses the system was then allowed to evolve for 5,000-10,000 time steps (e.g., several pico-seconds). Some preliminary results are shown in Figure 9 below. The figure on the left compares the spectral density of vibrational modes for a flat sheet of lizardite as shown in the left panel of Figure 8, for two temperatures. The results indicate that the hydroxyl band frequencies (features near $\sim 3600 \text{ cm}^{-1}$) exhibit no discernible shift as a result of moderate temperature change. By way of contrast, the effect of bending strain within the sheets (see caption for specifics) is rather pronounced as can be seen in the right panel of Figure 10, which indicates that a $\sim 70 \text{ cm}^{-1}$ upward shift in hydroxyl frequencies is expected.

Figure 9: Spectral density plots (vibrational spectra) obtained from simulations of a ~ 380 atom cluster of nominal composition $\text{Mg}_3\text{Si}_5\text{O}_2(\text{OH})_4$: (a) Isothermal simulation (total time = 1 ps) at room temperature (300K, blue curve) and at 527°C (800K, red curve), illustrating the effect of thermal broadening on the spectral features for a lamellar 1T lizardite cluster. The features near $3600\text{-}3700 \text{ cm}^{-1}$ are associated with hydroxyl vibrations, while the peaks $< 1000 \text{ cm}^{-1}$ are due to Si-O and Mg-O vibrations. Note the negligible shift in frequency due to heating. (b) the change in the vibrational spectrum induced by a bending strain associated with a radius of curvature (at the Mg plane) of about $50 \text{ \AA}$ parallel to $[11\bar{2}0]$. Note the pronounced ($\sim 70 \text{ cm}^{-1}$) shift induced in the hydroxyl band near 3600 cm^{-1} . A visible feature is also induced at the first hydroxyl harmonic frequency $\sim 7200 \text{ cm}^{-1}$.

These results have significant implications for the interpretation of the vibrational spectra of various serpentinites since these polymorphs exhibit a broad range of sheet-strain topology and character, as indicated earlier. It is a long-range goal of theoretical studies of the kind initiated under this project, to elucidate the connection between vibrational spectra and complex structural morphology in this important CO₂ sequestration mineral feedstock class.

(v) Heat-activation: The role of thermally induced hydroxyl diffusion

We also recently performed benchmark simulations on stoichiometric and defective serpentine clusters, which have been partially dehydroxylated (a vacancy in a brucite-like-layer hydroxide site is created) in order to elucidate the role of hydroxyl site stability and diffusion. In the case of well-equilibrated non-defective clusters at T=350K we find average bond lengths within several percent of published values for Mellini lizardite.

Figure 10: Hydroxyl defect migration mechanism (diffusing hydroxyl drawn using large spheres for emphasis) as seen from two views (top figures: side view, bottom figures: top view). The connected net is the silica framework. Magnesium is shown as small green spheres. Note the change in the orientation of the objective hydroxyl as it migrates from the brucite-like layer (bottom) to the silica layer (top).

Figure 10 shows several views of the initial and final equilibrated structures at 350K. The simulation reveals a low-temperature defect migration mechanism, in which a hydroxyl diffuses from the “brucite” layer to the hollow defect site within the silica layer. The reaction occurred spontaneously within about ~0.3-0.5 picoseconds, with a concomitant energy gain of about ~ 1 eV. This shows that defects involving “inner” hydroxyls (those within the silica cage), whatever their origin, are unstable and short-lived. Diffusion involving this fundamental mechanism is consistent with our recent IR observations of an apparent step-wise change in the serpentine hydroxyl frequencies observed during 1T lizardite heat treatment. This change suggests the possible formation of silanol groups (e.g., Si-OH) within the poorly ordered meta serpentine that forms (12 to 1% residual hydroxyl content) after complete lizardite decomposition and before forsterite crystallization. A thorough experimental and theoretical characterization of this heat-activated meta-serpentine should be a high priority in future work, as it may play an important role in a practical aqueous carbonation process.

CONCLUSIONS

Simulations are most useful when they are carefully designed to answer questions relevant to a specific experimental investigation or technical problem. The close integration of theoretical modeling/simulation with experiment leads to scientific insight that is difficult to achieve independently – a powerful synergy. These notions were applied as a conceptual premise in the present Innovative Concepts Grant in which we strived to integrate advanced quantum mechanical modeling with Dynamic High Resolution Transmission Electron Microscopy (DHRTEM), Electron Energy Loss Spectroscopy (EELS) and infrared (IR) and Raman spectroscopy. The objective is to develop a detailed understanding of carbonation for the model Mg-rich lamellar hydroxide based mineral: $\text{Mg}(\text{OH})_2$, which ultimately will lead to the optimization of the relevant CO_2 mineral sequestration reaction processes, and a reduction in process cost. Such advances are absolutely essential to the development of a viable CO_2 sequestration technology.

The collective results of present modeling and simulation have contributed to several areas of general understanding in the mineralization of CO_2 . We have: (i) elucidated the dehydroxylation process in hydroxides, (ii) integrated advanced modeling of fundamental spectroscopies with atomic level investigation of the initial stages of carbonate formation, (iii) identified reaction sites on different candidate reactant surfaces, (iv) validated key chemical and physical concepts via spectroscopic “fingerprinting”, (v) implemented a specialized constrained dynamics procedure for simulating defective/strained cluster representations of real feedstock mineral surfaces, and (vi) used the latter methods to explore dynamical processes associated with dehydroxylation and carbonation activity. We have demonstrated that the interplay between theory/simulation and experiment is particularly valuable for spectroscopic characterization in the case when a new phase, such as a metastable intermediate of unknown structure, is formed in a reaction. We have suggested a number of plausible structures and reactions, for the CO_2 -oxide reaction, and for the dehydroxylation process. All of these can (and should) be further explored *via* more sophisticated simulation techniques in order to determine, by comparison with observed spectra, the likely composition and properties of various reaction products.

Our modeling studies suggest that: (i) carbonation appears to primarily occur via intermediate oxyhydroxides or oxides, with the extent of overall dehydroxylation being substantially greater than the level of carbonation, (ii) distorted carbonate “propellers” seem to be implicated in the initial rehydroxylation/carbonation observed after dehydroxylation of brucite, based on both predicted and observed electron energy loss spectra, (iii) low-coordination oxygen appears to be the preferred adsorption site for the initial chemisorption of CO_2 on MgO . In the second stage of the project we extended our investigations to more complex lamellar hydroxide minerals within the serpentinite class. An initial examination of the dehydroxylation process associated with the formation of potentially reactive meta-serpentine revealed that vibrational spectroscopy of the bound hydroxyl bands can be used to characterize the degree of bending strain in the lamellar structures. Furthermore, quantum molecular dynamics simulations were used to elucidate the mobility of individual hydroxyl molecules in the presence of defects. We discovered and characterized a hitherto unknown diffusion process by which a “silica-layer” hydroxyl vacancy is healed by the diffusion and occupation of the vacancy by a “brucite-layer” hydroxyl. We plan on submitting a letter for publication on this topic in the near future.

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ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Publications

- “Magnesium Hydroxide Dehydroxylation/Carbonation Reaction Processes: Implications for Carbon Dioxide Mineral Sequestration,” Hamdallah Béarat, Michael J. McKelvy, Andrew V. G. Chizmeshya, Renu Sharma, and Ray W. Carpenter, *J. Am. Ceram. Soc.* (2001), [**in press**].
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Students Supported under this Grant

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