THE KINETICS OF BINDING CARBON DIOXIDE IN MAGNESIUM CARBONATE

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The Kinetics of Binding Carbon Dioxide in Magnesium Carbonate

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INTRODUCTION

Humans currently consume about 6 Gigatons of carbon annually as fossil fuel. Estimates are that the approximately 10,000 Gtons of earth’s coal reserves could provide the planet with energy for 1600 years. As we discussed in more detail elsewhere in these proceedings, energy consumption is directly correlated with the standard of living of a country and inversely related to population growth. Thus, prosperity requires abundant, low cost energy. The developing countries, as well as the U.S. and other developed nations, can not afford to stop using coal. However, political and other pressures may demand that coal’s long-term use be severely curtailed if we continue to dispose of CO₂ into the atmosphere. The availability of a CO₂ fixation technology would maintain coal’s viability and possibly could make coal even more competitive. In some sense, the coal industry has a unique advantage over many other anthropogenic and natural emitters of CO₂ in that it owns large point sources of CO₂ from which this gas could be isolated and disposed of. If the increased energy demands of a growing world population are to be satisfied from coal, the implementation of sequestration technologies will likely be unavoidable.

Our method of sequestration involves binding carbon dioxide as magnesium carbonate, a thermodynamically stable solid, for safe and permanent disposal, with minimal environmental impact. The technology is based on extracting magnesium hydroxide from common ultramafic rock for thermal carbonation and subsequent disposition. The economics of the method appear to be promising, however, many details of the proposed process have yet to be optimized. Realization of a cost effective method requires development of optimal technologies for efficient extraction and thermal carbonation. There are a number of proposed schemes other than our own for collecting and/or disposing of CO₂, including ocean disposal as liquid CO₂ or clathrates, the use of bacteria in the ocean to collect CO₂, planting of trees and plants, and underground disposal. The advantage of our method over others is that it is a complete solution that is both permanent and safe, and, therefore, does not leave behind a legacy for future generations. Although development work remains to be done, we are optimistic that the cost of our proposed sequestration process can be kept sufficiently low to maintain coal’s competitiveness in the energy market.

OUTLINE OF THE PROPOSED SEQUESTRATION PROCESS

A significant fraction of the world is covered with carbonated minerals, mostly rich in calcium and to a lesser extent magnesium, giving obvious proof that mineral carbonates are stable. Essentially, what we are proposing is to make use of the huge quantity of mineral in the world that has not been carbonated by natural events, but that could be carbonated. Magnesium bearing minerals constitute the most abundant and technologically available source of such material. Uncarbonated, calcium bearing materials are comparatively less common and we believe would be more costly to process.
Figure 1. Artist's rendition showing the flow of material in a CO$_2$ sequestration scheme for a process using serpentine as the source of magnesium. The processing rates are geared to accommodate the emissions from a coal fired power plant producing 1 GW of electric power at 33 % conversion efficiency.
In particular, peridotites and serpentinites, which are approximately 30-50% MgO by weight, are available in quantities far exceeding what is required to consume the world’s anthropogenic CO₂. Most of our research to date has focused on developing processes relying on serpentinite, which in its purest form has the composition 3MgO-2SiO₂-2H₂O, and, therefore, contains 43.6 wt% MgO.

The direct carbonation of serpentinite, as well as other common minerals, is relatively slow. In order to economically bind the CO₂ in the host substrate, it appears that the magnesium must be extracted from the mineral. Fortunately, methods for extracting magnesium from minerals were worked out in some detail around the time of World War II prior to the advent of sea water extraction processes.² The economics of the processes were never optimized but appeared to be quite viable. Making use of this early research, we have set out to develop an economical process whereby the magnesium is extracted by first dissolving the mineral in hydrochloric acid. Through a multi-step extraction process, Mg(OH)₂ is precipitated out of solution and then thermally carbonated. Most of the HCl is recovered and reused in the extraction process. A simple schematic of the basic material flow is shown in Fig. 1 for a system using a peridotite with 45.8 wt% MgO. Although improvements are necessary, technologies for collecting and transporting CO₂ are relatively well understood. Thus, the focus of our work has been on the bottom half of Fig. 1 including the direct carbonation step. Many of the details of each step and the economics have been discussed preliminarily elsewhere.²⁻¹²⁻¹³

<table>
<thead>
<tr>
<th>Equation Number</th>
<th>Chemical Reaction</th>
<th>Heat/ Equation, kJ</th>
<th>Normalizing Factor</th>
<th>Heat/mol CO₂ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg₃Si₂O₅(OH)₄ + 3CO₂ → 3MgCO₃ + 2SiO₂ + 2H₂O(l)</td>
<td>-190.8</td>
<td>1/3</td>
<td>-63.6</td>
</tr>
<tr>
<td>2</td>
<td>Mg₃Si₂O₅(OH)₄ + H₂O(l) → 3Mg(OH)₂ + 2SiO₂</td>
<td>52.5</td>
<td>1/3</td>
<td>17.5</td>
</tr>
<tr>
<td>3</td>
<td>Mg₃Si₂O₅(OH)₄ + 6HCl(aq) + 13H₂O(l) → 3(MgCl₂·6H₂O) + 2SiO₂</td>
<td>-234.3</td>
<td>1/3</td>
<td>-78.1</td>
</tr>
<tr>
<td>4</td>
<td>MgCl₂·6H₂O → Mg(OH)₂ + 2HCl(aq) + 4H₂O(l)</td>
<td>96.7</td>
<td>1/1</td>
<td>96.7</td>
</tr>
<tr>
<td>5</td>
<td>MgCl₂·6H₂O → MgCl₂·H₂O + 5H₂O(l)</td>
<td>103.3</td>
<td>2/1</td>
<td>206.6</td>
</tr>
<tr>
<td>6</td>
<td>MgCl₂·6H₂O → MgCl₂·H₂O + 5H₂O(g)</td>
<td>323.3</td>
<td>2/1</td>
<td>646.6</td>
</tr>
<tr>
<td>7</td>
<td>H₂O(g) → H₂O(l)</td>
<td>-44.0</td>
<td>10/1</td>
<td>-440.1</td>
</tr>
<tr>
<td>8</td>
<td>MgCl₂·H₂O → Mg(OH)Cl + HCl(aq)</td>
<td>-0.15</td>
<td>2/1</td>
<td>-0.3</td>
</tr>
<tr>
<td>9</td>
<td>MgCl₂·H₂O → Mg(OH)Cl + HCl(g)</td>
<td>74.7</td>
<td>2/1</td>
<td>149.4</td>
</tr>
<tr>
<td>10</td>
<td>HCl(g) → HCl(aq)</td>
<td>-74.9</td>
<td>2/1</td>
<td>-149.7</td>
</tr>
<tr>
<td>11</td>
<td>2Mg(OH)Cl + 6H₂O → Mg(OH)₂ + MgCl₂·6H₂O</td>
<td>-109.5</td>
<td>1/1</td>
<td>-109.5</td>
</tr>
<tr>
<td>12</td>
<td>Mg(OH)₂ + CO₂ → MgCO₃ + H₂O(l)</td>
<td>-81.1</td>
<td>1/1</td>
<td>-81.1</td>
</tr>
</tbody>
</table>

Table 1 summarizes the thermodynamics and mass balance equations relevant to the process outlined in Fig. 1. The overall process is exothermic and is defined by the following net reaction:

$$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2(\text{g}) \rightarrow 3\text{MgCO}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O} \quad (1)$$

As written, equation 1 occurs very slowly except at very high pressures and temperatures. For example, in relatively unoptimized experiments, we have achieved near 25% completion in this reaction by exposing 100 μm serpentinite powder to 340 atm of CO₂ at 500°C for two hours. Thus, in order to make the reaction go to completion under less costly conditions, we extract a more reactive form of magnesium by first dissolving the serpentine in hydrochloric acid as follows:

$$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{HCl(aq)} + 13\text{H}_2\text{O} \rightarrow 3(\text{MgCl}_2·6\text{H}_2\text{O}) + 2\text{SiO}_2 \quad (2)$$
By heating the solution and distilling off water and HCl according to the series of reactions defined in Table 1, solid Mg(OH)Cl is produced. Adding water to react with this solid, we then precipitate out Mg(OH)\textsubscript{2} in MgCl\textsubscript{2}·6H\textsubscript{2}O solution. In the laboratory, we can do this in essentially a two step process as follows:

\[
\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{220\degree C} \text{MgCl(OH)} + \text{HCl} + 5\text{H}_2\text{O}
\] (3)

followed by:

\[
2\text{MgCl(OH)} \xrightarrow{\text{H}_2\text{O}} \text{Mg(OH)}_2 + \text{MgCl}_2
\] (4)

The Mg(OH)\textsubscript{2} is easily filtered from the solution for carbonation, whereas the HCl and MgCl\textsubscript{2} are recycled to the first step.

The thermodynamics of the extraction and carbonation processes are simplistically but illustratively presented in Fig. 2. As serpentine is dissolved into hydrochloric acid, the reaction is exothermic and proceeds spontaneously, producing low quality heat. The product of this reaction, MgCl\textsubscript{2}·6H\textsubscript{2}O, is then heated to evolve HCl and H\textsubscript{2}O in an endothermic reaction as described above. Thus, substantial energy must be provided the system in order to produce Mg(OH)\textsubscript{2} from MgCl\textsubscript{2}·6H\textsubscript{2}O. The final step, the direct carbonation of Mg(OH)\textsubscript{2}, is exothermic, but as will be discussed below, the reaction is rather sluggish at atmospheric pressure. It is evident from Fig. 2, that the net reaction is exothermic in going from serpentine to MgCO\textsubscript{3}. In order to avoid the largest cost penalty associated with the endothermic step that yields Mg(OH)\textsubscript{2}, we are currently investigating means for dissolving serpentine in magnesium chloride solutions that are effectively starved of water. Thus, the extraction process could be done more economically at higher temperatures and most likely higher pressures. Consequently, our research is currently aimed at molten salt extraction of magnesium. When better quantified, these results will be reported at some future date.

**Figure 2.** Schema of relative free energy associated with changing the chemical state of magnesium through the reactions outlined above and in Table 1, using serpentine as the reference state. The solid line represents the proven path of extraction and carbonation. The dashed line represents one possible path for the process that we are exploring and that would be less energy intensive if implemented. Note that material is being added and removed from the system and the temperature is being changed in going from one step to another. Thus, this diagram is not unambiguous without comparison to the steps defined in table 1.
THERMODYNAMICS AND KINETICS OF DIRECT CARBONATION OF Mg(OH)$_2$

A limited number of studies of the carbonation kinetics of Mg(OH)$_2$ have been completed under atmospheric conditions and more recently at 30 to 440 atmospheres. The results generally follow trends predicted from thermodynamics. However, the processes can be quite complicated and the mechanisms are not fully understood at this point. Understanding the mechanisms could lead to significant improvements in the efficiency of the process. Figure 3, which was calculated from thermodynamic data, shows the effect of pressure on the dissociation temperatures of MgCO$_3$ and Mg(OH)$_2$. It is apparent that the dissociation temperatures of both the carbonate and hydroxide increase significantly with pressure. Thus, the carbonation of Mg(OH)$_2$ is inherently limited by the dissociation temperature, which is a function of the pressure of carbon dioxide. Above the dissociation temperature, which is near 410°C at atmospheric pressure, the carbonate will decompose according to the reaction:

$$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2(g)$$  \hfill (5)

Our studies have shown that there is a strong interconnectivity between the dehydroxylation and carbonation reactions. As illustrated in Fig. 4, the rate of carbonation is most rapid very near the dissociation temperature of MgCO$_3$ (near 390°C at the altitude of our laboratory). Note that the carbonate fractions in Fig. 3 were determined by measuring the CO$_2$ evolved during reaction with 6M HCl. During carbonation of Mg(OH)$_2$, dehydroxylation occurs simultaneously. Thus, it is important to fully understand both the kinetics and mechanisms of each process. The kinetics and mechanisms of dehydroxylation of single crystal Mg(OH)$_2$ are relatively well understood. In the case of precipitated, polycrystalline Mg(OH)$_2$, the kinetics of dehydroxylation can vary significantly from one material to another. Also, the mechanism of dehydroxylation of precipitated Mg(OH)$_2$ has not been fully elucidated. The variations between the different studies appear to be real; that is, the kinetics are strongly dependent on purity, sample size, crystallite and agglomerate size, thermomechanical history, and environment. Despite these complications, we can still make some general statements about the process of simultaneous dehydroxylation and carbonation.

![Figure 3](image-url)  
*Figure 3.* Calculated thermodynamic dissociation temperatures for MgCO$_3$ and Mg(OH)$_2$ to MgO and CO$_2$ or H$_2$O, respectively. The arrows show how the efficiency of carbonation improves with pressure and temperature for a precipitated Mg(OH)$_2$ powder heat treated 30 minutes. Note the abscissa refers to the total CO$_2$ or H$_2$O pressures.
Results of isothermal carbonation experiments on two precipitated magnesium hydroxides are summarized in Fig. 4. As shown in Fig. 4, using a -35 μm or 75-150 μm precipitated Mg(OH)$_2$ powder, the carbonation reaction reached approximately 16% completion (8 wt% CO$_2$) in 30 minutes at atmospheric pressure. The kinetics of carbonation are most rapid very near the dissociation temperature of MgCO$_3$. As Fig. 4 helps to illustrate, particle size, and more importantly, crystallite size, strongly influence the kinetics of carbonation. That is, the material with a 1 μm crystallite size was relatively resistant to carbonation compared to that with a 100 nm crystallite size. Conversely, we have been able to get substantially more carbonation (approximately 50% completion) under the same conditions by grinding our powders to a finer particle size. However, the efficiency of carbonation at atmospheric pressure is relatively slow overall. This is due to the fact that the carbonate that forms is a barrier to both the outward diffusion of water, thus inhibiting dehydroxylation, and the inward diffusion of CO$_2$, thus inhibiting carbonation.

![Figure 4](image.png)

Figure 4. Measured weight percent CO$_2$ as a function of exposure temperature for two precipitated magnesium hydroxides. The LANL Mg(OH)$_2$ was comprised of -35 μm and 75-150 μm agglomerates of approximately 100 nm crystallites. The Chichibu Onoda Mg(OH)$_2$ was comprised of 250-500 μm agglomerates of approximately 1 μm crystallites. Tests were conducted for 30 minutes in 0.76 atm of CO$_2$.

Typically, the rate of a thermally activated reaction increases with temperature. As indicated in Fig. 3, by increasing the pressure of CO$_2$, we can substantially increase the temperature at which MgCO$_3$ dissociates. Therefore, by increasing the pressure of CO$_2$, we can increase the temperature at which we perform the carbonation step and presumably accelerate the carbonation rate. As Fig. 4 suggests, by increasing the dissociation temperature slightly, dramatic improvements in the carbonation kinetics might be expected. Subsequently, we evaluated the kinetics of carbonation at slightly elevated pressures and found that relatively modest increases in pressure give substantially more rapid rates of carbonation. For example, at 565°C and 52 atm, we have achieved 90% carbonation in 30 minutes using the powders described above. The final product is significantly different from that obtained at lower pressures and temperatures and is comprised of relatively pure, stable MgCO$_3$. The results of selected elevated pressure experiments are summarized in Fig. 5. It is apparent from this figure that the kinetics of reaction are relatively rapid after some initial induction period. This induction period is associated with a combination of effects related to both the experimental configuration, and the “catalytic” effects of water. In the case of experiments conducted in a static gas environment, the dehydroxylation process produces a backing gas pressure of H$_2$O, which inhibits the gaseous diffusion of CO$_2$. This can in part be blamed for the relatively long induction period observed during carbonation in the static gas environment. In addition,
we have a great deal of qualitative information that suggests that the presence of water is needed to provide reasonable carbonation kinetics. For example, we have found that the kinetics of carbonation are better in a slow flow of CO₂ compared with a slightly higher flow. These measurements, combined with studies of microstructural evolution, suggest that there is an intermediate state where magnesium oxide or hydroxide is more reactive and thus susceptible to carbonation.

Figure 5. Plot of the time dependence of carbonation of Mg(OH)₂ at mildly elevated temperatures in flowing and static CO₂.

Based on these results it appears that the final process will require the use of moderately high pressures of CO₂, with a relatively slow flow rate. We do not view this as a problem because CO₂ is typically transported under similar pressures, and its transport would be also required for most other sequestration methods, such as ocean disposal. Thus, there may be no need to add extra energy to the system since the pipeline will supply at least part of the required pressure. In addition, it will be important to carefully control the quality, i.e. microstructure and particle size, of the Mg(OH)₂ to ensure that the host substrate is intrinsically reactive.

CONCLUDING REMARKS

Regardless of one's view of the consequences of global warming, it would seem prudent for the U.S. and other countries to work towards better understanding of both the effects of and how to mitigate CO₂ emissions. Japan, for example, has recognized the importance of CO₂ mitigation and sequestration technologies and recently established the Research Institute of Innovative Technologies for the Earth (RITE) which is an organization largely dedicated to studying ways to collect, bind, and reuse CO₂. The political pressure to curb CO₂ emissions into the atmosphere is gradually rising as reflected in the UN conferences starting in Rio de Janeiro and ending with the most recent and highly publicized one in Kyoto where the U.S. agreed to the principal of reducing U.S. CO₂ emissions 7% below the 1990 rate by the year 2010. Currently, there is a strong political impetus within our government to limit greenhouse gas emissions as echoed in both the 1997 and 1998 State of the Union Addresses. This trend, regardless of its scientific merits, poses a risk to fossil fuel power and mining industries. However, many opportunities will inevitably be created as the market for mitigation technologies grows.

Our research, as partly summarized above, has been aimed at binding CO₂ in a thermodynamically stable solid, namely magnesium carbonate. In our laboratory we have
demonstrated the feasibility of extracting Mg(OH)$_2$ from common minerals, and that the Mg(OH)$_2$ can be converted by a direct thermal treatment to a stable carbonate for subsequent disposition using CO$_2$ pressures comparable to those used in its normal transportation. As with our method, there is often a cost penalty associated with any technology which can reduce global emissions by a large fraction. The economics of binding CO$_2$ in a solid form is strongly dependent on the kinetics of reactions between CO$_2$ and the host substrate. The kinetics of simultaneous thermal dehydroxylation and carbonation of precipitated Mg(OH)$_2$ has been studied in some detail. We demonstrated that during carbonation, carbonate precipitates on the surface of disrupted Mg(OH)$_2$ crystals acting as a kinetic barrier to both the outward diffusion of H$_2$O and the inward diffusion of CO$_2$. The kinetics can be overcome using slightly elevated CO$_2$ pressures and subsequently higher temperatures. Optimization of the means of extracting Mg(OH)$_2$ from ultramafic minerals will inevitably require the development of a new molten salt process. However, the thermodynamics of doing the extraction with less water and at higher temperatures appears to be quite favorable.

The processes that we have developed or outlined can be carried out on a massive scale, sufficient enough to bind in theory all anthropogenic CO$_2$. The quantity of useful minerals in the world, namely serpentinite and peridotites, are far in excess of what is needed to collect the CO$_2$ emissions from the remaining world’s supply of coal.$^{23}$ The kinetics of extraction and carbonation have yet to be optimized. Likewise, thermal management in the Mg(OH)$_2$ extraction process has yet to be optimized. Further research at both our laboratories (Los Alamos and Chichibu Onoda Cement Co.) is aimed at enhancing the reaction kinetics. However, we are nearing the stage where a pilot demonstration of the entire process can be justified. It is hoped that the first such system will be developed within the next few years.

REFERENCES


