12.085 Seminar in Environmental Science
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<center>Sequestering Carbon Dioxide in Carbonates</center>

Introduction

Sequestering carbon dioxide in synthesized carbonates is a long-term solution to global warming that will keep CO_2 out of the atmosphere on geologic timescales. The principle of carbonate sequestration is based on a natural process: when Mg and Ca silicates are weathered, they react with CO_2 in the air to form carbonates that are deposited on the ocean floor. These carbonate deposits are stable for thousands or millions of years; compared to other geoengineering ideas such as iron fertilization of the oceans, carbonate sequestration offers a solution that is essentially permanent (Keith, 2000).

In theory, carbonate synthesis is simple: Mg and Ca oxides found in many silicate rocks are reacted with CO_2 to produce carbonates:

$$CaO + CO_2 \rightarrow CaCO_3 + 179 \text{ kJ/mol}$$
$$MgO + CO_2 \rightarrow MgCO_3 + 118 \text{ kJ/mol}$$

In practice, however, there are many challenges to consider. Problems associated with carbonate geoengineering include finding a reliable method of extracting CO_2, increasing mining operations, energy, and reaction kinetics. The solution can only be effective if it succeeds on a large scale—a commonly-cited goal is to lower CO_2 to twice that of pre-industrial levels, which will require 25 billion tons of CO_2 removal (The Earth Institute at Columbia University, 2007)—and there are challenges associated with designing an industrial process that can operate efficiently at those scales.

Carbon capture from the air

The first obstacle is to find a reliable source of CO_2. Power plants can provide continuous streams of CO_2, but this means that carbonate synthesis must occur close to the power plants. An alternative is to capture CO_2 from the air. There are several advantages to this approach. First of all, current CO_2-mitigation projects are focused on power plants and other stationary, concentrated CO_2-emitters. Despite the fact that cars and other vehicles emit a significant portion of the world's total CO_2, it is difficult to design on-board technologies to capture their CO_2. Other mitigation ideas such as switching to hydrogen fuel require enormous changes in the car industry's infrastructure, but trapping CO_2 from the air would account for vehicular emissions. In addition, the collected CO_2 could be used for enhanced oil recovery or sequestered underground in sealed aquifers (Lackner et al., 2001).

The CO_2-collector is based on a wind turbine designed for the desert: it is a bell-shaped tower about 300m high, whose top is 115m in diameter (Fig. 1). A pipe in the center pumps cold water to the top. The water cools the surrounding air, and the denser, colder air sinks down to power wind turbines surrounding the base of the tower (the potential energy of the falling air is much greater than the energy needed to pump the water to the tower's top) (Bishop, 1993). For CO_2-capture, the sinking air will flow over sorbents (such as $Ca(OH)_2$) instead of wind turbines; the CO_2 is then released in a stream to react with oxides and form carbonates. Ideally, the sorbent would then be recycled and used again to capture more CO_2.

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Figure 1: the basic design for a CO_2-collector. Water is pumped to the top of the tower, where it cools the air. As the air cools, it falls to the bottom where it is captured by CO_2-sorbents (Lackner et al., 2001).

Since the towers were for designed for desert use, it is unclear if they will work in other environments—the downdrafts depend on the cooling of hot air, so their use may be limited to dry, warm climates. And due to their size, these towers will be expensive to build.

But the main challenge lies in the question of scale: the estimated capacity of each tower is 9,500 tons CO_2/day. In comparison, total CO_2 emissions from the US in 2006 was 7.8 billion tons. This means that it would take 1,000 towers over two years to capture the CO_2 from one year (Lackner et al., 2001). A prototype of these towers was created by Global Research Technologies, LLC (Fig. 2). It operates on an even smaller scale, with a capacity of 1,000 tons CO_2/year (The Earth Institute at Columbia University, 2007). Although carbon-capture from the air shows promise, current technologies are not efficient enough for the large scales needed.

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Figure 2: an artist's drawing of CO_2-collection towers created by Global Research Technologies, LLC (The Earth Institute at Columbia University, 2007).

Mg and Ca oxides in rocks

Different rocks have varying amounts of MgO and CaO. Table 1 lists the MgO and CaO content of different rocks. The most important factor is the rock:CO_2 mass ratio, which is a measure of the effectiveness of each rock in sequestering CO_2. Dunite is clearly the best choice; only 1.8 tons of dunite is needed to react with each ton of CO_2, compared to 4.7 tons for gabbro or 7.1 tons for basalt.

Table 1: a chart of MgO and CaO content in rocks. Rocks such as limestone or dolomite have been left out; they are already carbonates and it would be counterproductive to mine them for CO_2 sequestration.

Rock	Rock: CO_2 mass ratio for sequestration
Dunite (peridotite)	1.8
Serpentinite	2.3
Gabbro	4.7
Basalt	7.1

The rocks are not the limiting factor in carbonate sequestration—Lackner et al. (1995) estimate that ample reserves of these rocks exist in ophiolite suites, more than enough to react with the world's carbon emissions.

Mining: scale

The challenges associated with mining the required amount of rock are significant. Table 2 lists statistics for US mining and total CO_2 emissions in 2000. Using

the 1.8 ratio of dunite:CO_2, it would take 10.4 billion tons of dunite to store 5.8 billion

tons of CO_2. This is an order of magnitude above the US production of crushed rock, and

more than twice the total output from US mining (U.S. Department of Energy, 2000).

Table 2: Mining statistics for 2000 (U.S. Department of Energy, 2000):

	Billions of tons
US CO_2 emissions	5.8
US crushed rocks mining production	1.8
US mining total production	4.1

In effect, US mining would have to double or triple to reach the scale needed for

carbonate storage. Not only is this infeasible in terms of cost, resources, and logistics, it

creates additional environmental problems such as increased air pollution and water

contamination.

When considering global CO_2 emissions, the problem becomes even more

daunting. 26 billion tons of CO_2 were emitted worldwide in 2000; it would require 46.8

billion tons of mined rock to sequester the CO_2, or ten times the total US mining

production from that year (Energy Information Administration, 2007).

Energy

Another factor in feasibility is the amount of energy needed for mining

operations. The energy used depends on the amount of material excavated; copper

mining, for example, is less efficient and produces much more waste than mining for

crushed rocks. The energy required for limestone mining can be used as an analogy,

because limestone is often finely crushed after mining, and the rocks for carbonate

sequestration must be similarly processed to ensure reasonable reaction rates.

Below are the US limestone mining statistics from 2000:

Table 3: limestone mining statistics in 2000 (U.S. Department of Energy, 2000a; U.S. Department of Energy, 2000b).

Percent recovery (from ore)	93%
Amount of limestone mined	1.7 billion tons
Estimate of energy used for each ton of mined limestone	33500 Btu (average) 54000 Btu (for finely ground limestone)

The key data are the estimates of energy needed for mining limestone. The 54,000 Btu figure is more applicable because the rocks mined for carbonate synthesis will require extensive grinding and crushing—the rocks are generally ground to micron-scale particles to speed up reaction rates. Using this number of 54,000 Btu/ton of mined rock, 10.4 billion tons would require 561.6 trillion Btu. Here are more statistics for comparison (Energy Information Administration, 2006):

US energy consumption in 2000 (fossil fuels only)	84.733 quadrillion Btu (84733 trillion Btu)
US energy consumption in 2000 (wind energy only)	.057 quadrillion Btu (57 trillion Btu)
US energy consumption in 2000 (geothermal only)	.317 quadrillion Btu (317 trillion Btu)

561.6 trillion Btu is about 0.66% of the total fossil fuel use in 2000, ten times the energy produced by wind power, and nearly twice that from geothermal power. In reality, these numbers are underestimates because the rocks of interest are less than 50% MgO or CaO (Lackner et al., 1995). This lowers the percent recovery from 93% (for limestone) to 50% maximum, and raises the amount of energy used to at least 1% of total fossil fuel consumption in 2000. Even so, increasing energy use by 1-2% is a reasonable price to pay for sequestering a year's worth of CO_2 from fossil fuels—energy use is not a limiting factor for CO_2 sequestration in carbonates.

Direct carbonation: theory

The basic chemistry behind direct carbonation is simple: rocks with MgO or CaO content are crushed and mixed with a stream of CO_2. This one-step reaction is all that is required to synthesize carbonates:

$$CaO + CO_2 \rightarrow CaCO_3 + 179 \text{ kJ/mol}$$
$$MgO + CO_2 \rightarrow MgCO_3 + 118 \text{ kJ/mol}$$

However, the reactions as they occur in nature operate too slowly to be of use for CO_2 sequestration.

Increasing the temperature will speed up the reactions, but at a certain point, the reactants will be favored over the products. The key is to find the maximum temperature where carbonation is still favored. The carbonates' free energy of formation—$\Delta G(T,P)$—can be calculated (using $CaCO_3$ as an example) by

$$\Delta G = \Delta G_0 + RT\log([CaCO_3]/([CaO]*[CO_2]))$$

where $\Delta G_0(T)$ is the standard free energy change at 1 bar. At a given temperature, if the ΔG of reaction is negative, then the products will be favored over the reactants. The maximum temperature (T_{max}) is found when the reactants' free energy of formation equals that of the products. Higher pressures allow for higher temperatures and therefore faster reaction rates. For instance, T_{max} of CaO carbonation is 1160 K at 1 bar and 1670 at 200 bars.

The above applies for pure CaO or MgO, but using minerals with CaO or MgO content can present complications. Partial carbonation, as in the case of forsterite,

$$Mg_2SiO_4 + CO_2 \rightarrow MgSiO_3 + MgCO_3$$
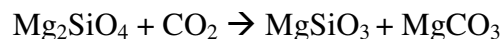
creates enstatite in addition to $MgCO_3$, so the carbonation reaction is less favorable thermodynamically (Lacker et al., 1995). On the other hand, serpentine (containing MgO)
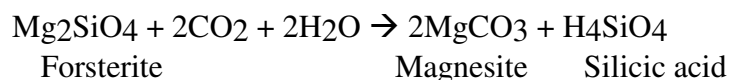
reacts readily with CO_2 once the water is driven off. Dehydrated serpentine is metastable, amorphous, and non-crystalline, so its enhanced chemical reactivity makes it an ideal reactant for carbonation (Barnes et al., 1950).

Direct carbonation: experiments

A preliminary study conducted by the Finnish Pulp and Paper Industry yielded results that were both puzzling and discouraging. Small-scale experiments were set up with MgO (280 mg total, with a particle size of 20 μm) and a stream of CO_2 gas. The experiments were conducted over a range of pressures (1, 5, 12, 20, and 35 bars). At the end of the experiment, the percent conversion from MgO to $MgCO_3$ was only 1.19-5.57%. Surprisingly, the highest yields occurred for the lowest pressure (Teir et al., 2003), which is the exact opposite of what was expected. Teir et al. were unable to explain this trend.

Another study from O'Connor et al. (2000) yielded more promising results. Their experiment was conducted at a larger scale (Fig. 3): 100 grams of olivine were combined in a slurry with water, then reacted with supercritical CO_2:

$$Mg_2SiO_4 + 2CO_2 + 2H_2O \rightarrow 2MgCO_3 + H_4SiO_4$$
$$\text{Forsterite} \qquad\qquad\qquad \text{Magnesite} \quad \text{Silicic acid}$$

O'Connor et al. obtained high conversion rates for magnesite synthesis. Under high temperature and pressure (185°C, 115 atm), and with continuous stirring of the slurry, a 90% conversion rate was reached within 24 hours. These results are much more promising than those obtained by Teir et al. One possible explanation is that Teir et al. used a maximum pressure of 35 bars (nearly 35 atm), whereas O'Connor et al. conducted their experiment at 115 atm—higher pressures are generally correlated with faster reaction rates, although Teir et al. obtained better results at 1 bar than at 35 bars.

In addition to olivine, serpentine was also used as an alternative reactant. Barnes et al. proposed that dehydrated serpentine would have enhanced reactivity, but the heat pretreatment required for serpentine dehydration adds an extra step to the reaction process. Even after heat pretreatment, serpentine and olivine resulted in the same conversion rates, so it is more practical to just use olivine.

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Figure 3: a diagram of carbonation reactions used by O'Connor et al.

Particle size was a determining factor for reaction rates. Over 90% of the reactants were converted to products by reducing the particle size down (from over 100 microns) to 37 microns. O'Connor et al. also proposed future research into catalysis as another possible way of speeding up the reactions.
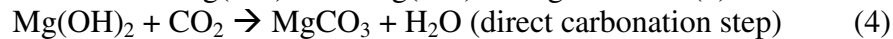
Carbonation: aqueous chemistry

Another approach to synthesizing carbonates is to use aqueous chemistry rather than direct carbonation. Although there are more steps involved in this method, the

kinetics are more favorable. The basic principle is to extract Mg or Ca from rocks using acid:

$$6HCl + Mg_3Si_2O_5(OH)_4 \rightarrow 3MgCl_2 + 2SiO_2 + 5H_2O \quad (1)$$

Magnesium chloride exists in solution, and is decomposed (through heating) to regenerate HCl:

$$MgCl_2 \cdot 6H_2O \rightarrow Mg(OH)Cl + HCl + 5H_2O \quad (2)$$
$$Mg(OH)Cl \rightarrow Mg(OH)_2 + MgCl_2 \quad (3)$$
$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O \text{ (direct carbonation step)} \quad (4)$$

In addition, the $MgCl_2$ generated from step 3 can be re-used in step 2 to recover HCl. One advantage of the process is that step 4 releases heat which can be cycled back to other steps of the overall reaction. Step 3 is also used industrially for producing $Mg(OH)_2$— since the infrastructure for this reaction already exists, there would be fewer problems associated with scaling up for CO_2 sequestration (Blackburn and Nagamori, 1994; Lackner et al., 1995).

One critique of the system is that step 2 is highly endothermic. A large energy input is required to release water in the reaction, but the step is necessary because it is not practical to use HCl continuously without recycling it. A solution has been proposed to use $MgCl_2(H_2O)$ instead of HCl for dissolving rocks; reducing the water content would speed up the process and decrease the energy needed to run the reaction. However, this solution is also flawed since $MgCl_2(H_2O)$ is less acidic than HCl, and may not be acidic enough to dissolve the rocks (Eliasson et al., 1999).

Conclusions

There are many issues that still need to be addressed for carbonate sequestration. First of all, where will the synthesized carbonates be stored? Can they be deposited in the

same sites where the rocks were mined from? There are also location constraints—to minimize transportation costs (in terms of money, energy, and labor), the carbonate sequestration plants should be located close to a reliable and large source of CO_2, as well as the area from which the rocks will be mined. Large amounts of water are also needed for reaction chemistry. However, the biggest challenge is the scale of operations required to sequester the required amount of CO_2. Proposals that are reasonable on smaller scales (such as the CO_2-capture towers) are limited by their inefficiency on global scales. Although there is no lack of raw materials, the amount of rock required far exceeds the current mining capacity. Ultimately, carbonation sequestration is not a viable form of geoengineering and cannot be used to solve the world's CO_2 crisis.

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