

## CO<sub>2</sub> Mineral Sequestration Studies in US

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### Abstract

Carbon sequestration by reacting naturally occurring Mg and Ca containing minerals with CO<sub>2</sub> to form carbonates has many unique advantages. Most notably is the fact that carbonates have a lower energy state than CO<sub>2</sub>, which is why mineral carbonation is thermodynamically favorable and occurs naturally (e.g., the weathering of rock over geologic time periods). Secondly, the raw materials such as magnesium based minerals are abundant. Finally, the produced carbonates are unarguably stable and thus re-release of CO<sub>2</sub> into the atmosphere is not an issue. However, conventional carbonation pathways are slow under ambient temperatures and pressures. The significant challenge being addressed by this effort is to identify an industrially and environmentally viable carbonation route that will allow mineral sequestration to be implemented with acceptable economics.

Under the sponsorship of the U.S. Dept of Energy, a team of researchers from the National Energy Technology Laboratory, Albany Research Center, the Los Alamos National Laboratory, and Arizona State University was formed in the summer 1998 to investigate and improve the carbonation process. This paper discusses significant progress achieved by the team in searching for faster reaction methods using: magnesium silicates, supercritical CO<sub>2</sub>, water, and additives; in searching for pretreatment methods to enhance mineral reactivity; and in analyzing the structural changes to identify reaction paths and potential barriers. The paper also discusses plans to construct larger scale operating units (up to several MWe) in order to validate the method as a viable sequestration tool at industrially relevant scales.

Keywords: carbon sequestration, global climate change, mineral carbonation, olivine, serpentine.

## Introduction

Fossil fuels, which account for 80 - 85% of the total of world energy use today are an important energy source. Fossil fuels have many advantages including abundant supply, high energy density, ease of use and storage, existing infrastructure, and most importantly, their low cost. The use of this important energy source is facing a challenge due to the vast amounts of CO<sub>2</sub> released into the atmosphere as a result of combustion. The level of CO<sub>2</sub> in the atmosphere has increased by roughly 30% since the industrial revolution, with much of this rise being attributed to the increased use of fossil fuels such as coal, oil and natural gas (1,2). Since 1800, the CO<sub>2</sub> content of the atmosphere has risen from a stable level of 280 ppm to above 365 ppm today. While the observation that the atmospheric CO<sub>2</sub> level has increased significantly is generally not at issue, the consequences arising from this increase are the subject of vigorous debate. Given that CO<sub>2</sub> is a greenhouse gas, such large and increasing atmospheric CO<sub>2</sub> levels will have climatic consequences. Unless action is taken, the emissions of CO<sub>2</sub> will continue to increase as the world economy grows, resulting in exponential growth of the level of atmospheric CO<sub>2</sub>. We are not likely to fully understand the actual consequences of increased levels of atmospheric CO<sub>2</sub> for some time. Should action be required, source control would likely be favored since it would be much more difficult and more expensive to retract dispersed CO<sub>2</sub> from the atmosphere than to gather it from large concentrated sources. Consequently, the USDOE is actively pursuing solutions that offer the potential to reduce atmospheric CO<sub>2</sub> emissions.

Historically, per capita energy consumption and wealth, as reflected by Gross Domestic Product (GDP), are nearly proportional. The U.S., followed closely by other highly industrialized nations, has a relatively high per capita energy consumption which is roughly equivalent to five times the global average. It is important to note that it is the U.S.'s high per capita energy consumption that is directly responsible for its high standard of living. As the standard of living continues to rise globally and in developing countries in particular, it is not difficult to imagine that in the not too distant future the world will be using energy (and emitting CO<sub>2</sub>) at many times today's rate. Over the 30-year period ending in 2020, projections made by the U.S. Energy Information Agency indicate global increase in energy use will increase worldwide emissions of CO<sub>2</sub> to  $38 \times 10^9$  tons per year or an increase of 80% compared to 1990 levels (3).

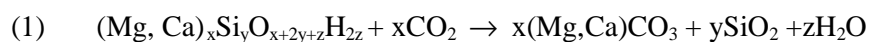
Given the public mandate to maintain economic growth, fossil fuels will remain a dominant energy source over the next century, as no alternative energy supply is poised to significantly replace fossil energy without causing other major problems. Therefore, developing effective CO<sub>2</sub> sequestration is one of the critical components in addressing global climate change. Note that improving the efficiency of energy production and utilization, and developing renewable energy sources will certainly play a very important role in reducing CO<sub>2</sub> emissions, however these measures alone cannot address the greenhouse emissions issue mainly because world energy consumption will increase significantly as the living standard improves in many parts of the world.

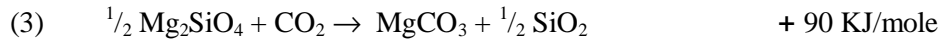
The Department of Energy is conducting various CO<sub>2</sub> sequestration and recycling studies including underground storage (seabed- or land-based), ocean sequestration, biomass utilization, and using CO<sub>2</sub> as feed material to produce various environmentally benign products (4). Challenges to any solution include technical feasibility, economic viability, environmental soundness and long term sustainability. A balanced research portfolio exploring a number of both short and long term mitigation methods is therefore essential to ensure appropriate technology for individual circumstances. This paper focuses on research on one method of CO<sub>2</sub> sequestration: permanent CO<sub>2</sub> fixation as environmentally benign carbonate minerals. The Mineral Sequestration Program is being managed by the National Energy Technology Laboratory (NETL) and is supported by USDOE/Fossil Energy's Power Systems Advanced Research and Advanced Metallurgical Processes programs. The activities of the working group are being coordinated by the CUS program. Related work is also being supported by internal funding at Los Alamos National Laboratory.

### What is Mineral Sequestration

Mineral sequestration involves the reaction of CO<sub>2</sub> with minerals to form geologically stable carbonates, i.e. mineral carbonation. This idea was first proposed by Seifritz (6) in 1990. There have been several methods suggested to achieve carbonation: an aqueous scheme by Kojima (7); an underground injection scheme by Gunter *et al.* (8); the processes via mineral derived Mg(OH)<sub>2</sub> suggested by Lackner *et al.* (9); and most recently, the carbonic acid process using olivine and serpentine directly proposed by O'Connor *et al* (10).

Mineral carbonation reactions are known to geologists and occur spontaneously on geological time scales. For example, the reaction of CO<sub>2</sub> with common mineral silicates to form carbonates like magnesite or calcite is exothermic and thermodynamically favored. For illustrative purposes, general and specific global mineral carbonation reaction pathways are shown below. The family of reactions represented by Reaction 1 has the potential to convert naturally occurring silicate minerals to geologically stable carbonate minerals and silica. This process emulates natural chemical transformations such as weathering of rocks to form carbonates over geologic time periods. Reaction 2 illustrates the transformation of the common silicate mineral serpentine, Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, and CO<sub>2</sub> into magnesite, MgCO<sub>3</sub>, silica and water. Using this ideal case, one ton of serpentine can dispose of approximately one-half ton of CO<sub>2</sub>. Reaction 3 illustrates the transformation of forsterite, which is the end member of the common silicate mineral olivine. One ton of olivine can dispose of approximately two-thirds of a ton of CO<sub>2</sub>. Again, the reaction is exothermic and releases 90 KJ/mole of CO<sub>2</sub>.

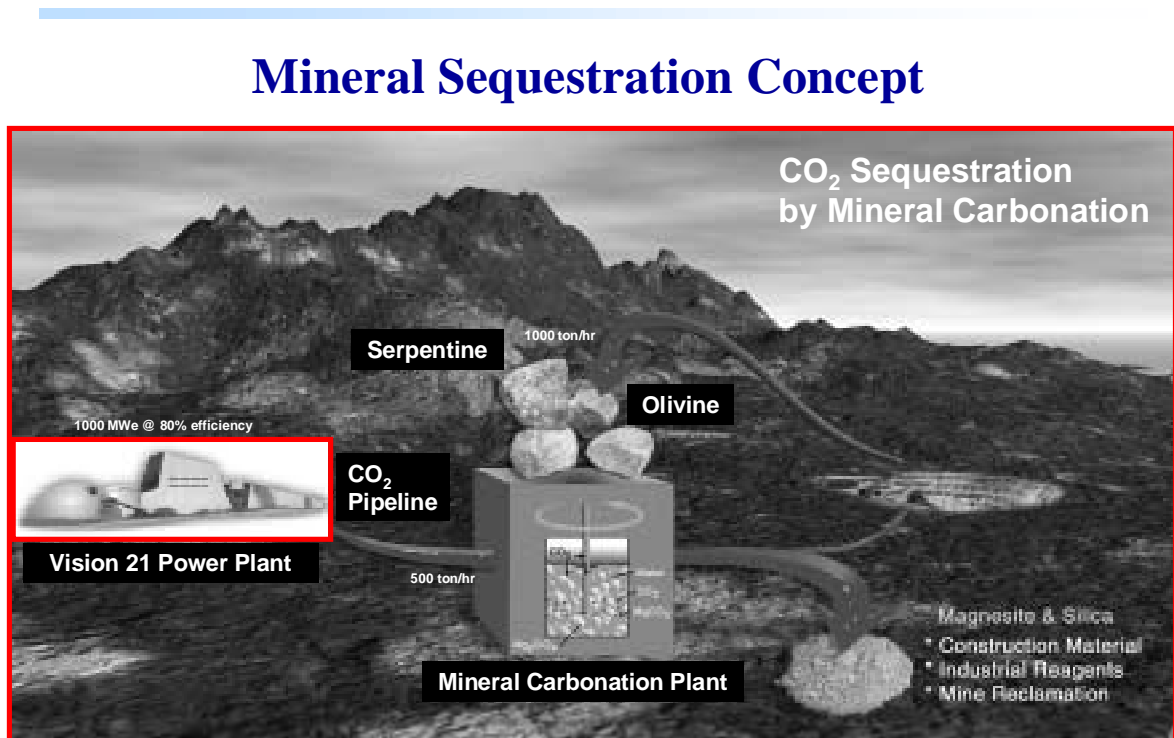




A conceptual illustration of the process is presented in Figure 1. As illustrated, CO<sub>2</sub> from one or more power plants is transported to a carbonation reactor, combined with crushed olivine or serpentine from a nearby mine and held at the appropriate reaction conditions until the desired degree of carbonation is reached. Then products of the reaction, which might be a slurry of carbonated minerals and residues in aqueous CO<sub>2</sub>, are separated. The CO<sub>2</sub> is recycled, useful materials are collected and the carbonated materials and residue are returned to the mine site.

There are adequate mineral deposits to support mineral sequestration. The tonnage of silicate mineral necessary to carbonate 100% of the CO<sub>2</sub> emissions from a single 500 MW coal-fired power plant can be estimated based on the following assumptions: 1) a mean magnesium oxide (MgO) content in the magnesium silicate ore mineral of 40 weight percent (wt pct); 2) 90% ore recovery; 3) 80% efficiency of the carbonation reaction; and 4) stoichiometry of equation 1. Based on these assumptions, a single 500 MW power plant, generating approximately 10,000 tons/day of CO<sub>2</sub>, would require just over 30,000 tons/day of magnesium silicate ore. Several ultramafic complexes in North America contain sufficient quantity of magnesium silicate mineral to provide raw materials for the mineral carbonation of all annual CO<sub>2</sub> emissions for many years (**14**).

Figure 1. Illustration of Mineral Sequestration Concept



Courtesy of Albany Research Center

## **Advantages of Mineral Sequestration**

The major advantages of CO<sub>2</sub> sequestration by mineral carbonation are:

*Long Term Stability* - Mineral carbonation is a natural process that is known to produce environmentally safe and stable material over geological time frames. The production of mineral carbonates insures a permanent fixation rather than temporary storage of the CO<sub>2</sub>, thereby guaranteeing no legacy issues for future generations.

*Vast Capacity* - Raw materials for binding the CO<sub>2</sub> exist in vast quantities across the globe. Readily accessible deposits exist in quantities that far exceed even the most optimistic estimate of coal reserves ( $\sim 10,000 \times 10^9$  tons) (5).

*Potential to be Economically Viable* - The overall process is exothermic and, hence, has the potential to be economically viable. In addition, its potential to produce value-added by-products during the carbonation process may further compensate its costs.

At a single site and scale that is consistent with current industrial practice, the process can handle the output of one to several large power plants. It is directly applicable to advanced power plants such as zero-emissions Vision 21 system configurations being developed by DOE's Fossil Energy Program or to existing power plants, thereby providing an additional degree of flexibility for future implementation (5).

## **Technical Challenges and Program Goals**

The major technical challenge now hindering the use of minerals to sequester CO<sub>2</sub> is their slow reaction rate. Weathering of rock is extremely slow. The highest priority is given to identifying faster reaction pathways. Second, the optimized process has to be economical. Although many carbonation reactions are exothermic, it is generally very difficult to recover the low-grade heat while the long reaction time and demanding reaction conditions contribute to process expense. Clearly, the environmental impact from mining minerals and carbonation processes must be considered. The program goals are specifically designed to address these challenges, including

- i. identifying favored technical processes,
- ii. determining the economic feasibility of each sequestration process identified, and
- iii. determining the potential environmental impacts of each process.

## **Rapid Progress**

Although the program only has about two years of history, the working team consisting of Albany Research Center (ARC), the Los Alamos National Laboratory, the Arizona State University, and the National Energy Technology Laboratory has made significant progress.

In striving to accelerate overall reaction rates, the team has identified one very promising reaction pathway and succeeded in achieving dramatically shortened carbonation reaction times employing magnesium silicates such as olivine and serpentine.

For example, research at the Albany Research Center (*10,13*) has focused upon the direct carbonation of olivine. When the program first started, it took 24 hours to reach 40-50% completion of carbonation of olivine. The reaction required temperatures of 150-250 C, pressures of 85-125 bar, and mineral particles in the 75-100 micron size range. Careful control of solution chemistry yielded olivine conversions of 90% in 24 hrs and 83% within 6 hrs. The most recent results show further modifications of the same basic reaction can achieve 65% conversion in 1 hour and 83% conversion in 3 hours.

While the potential to utilize olivine to sequester CO<sub>2</sub> is clearly significant, there is approximately an order of magnitude more serpentine than olivine. Consequently, finding a way to use serpentine to scrub CO<sub>2</sub> will have greater practical impact than using olivine. Both minerals are valuable feedstocks and progress has been made in direct carbonation using serpentine also. When the program started, tests conducted at Los Alamos National Laboratory only achieved 25% conversion using 100 micron serpentine particles with CO<sub>2</sub> even at a very high pressure of 340 bars. Independently, researchers at ARC developed a successful carbonation process for serpentine that utilizes mineral heat pretreatment and carbonation in carbonic acid in aqueous solution. A recent literature review indicated that weak carbonic acid treatments had also been suggested for Mg extraction in the prior literature (*12*). Carbonation tests performed at ARC employing heat pretreated serpentine have resulted in up to 83 % conversion in 30 minutes under 115 bars (*13*)

Because the high pressure requirement of the carbonation reaction will certainly lead to high process costs, the team is modifying solution chemistry to allow reaction to proceed at a lower pressure and temperature. The research is guided by the idea that the concentration of HCO<sub>3</sub><sup>-</sup> in the solution is critical to the reaction rate. The high CO<sub>2</sub> pressure will lead increased CO<sub>2</sub> absorption in the solution and thus enhance the HCO<sub>3</sub><sup>-</sup> concentration. Adding bicarbonate such as sodium bicarbonate in the solution will significantly increase the HCO<sub>3</sub><sup>-</sup> concentration even at a relatively lower CO<sub>2</sub> pressure. Indeed, by increasing sodium bicarbonate concentration the carbonation reaction of serpentine can reach 62% completion under 50 bars.

To support laboratory carbonation tests, researchers at Arizona State are employing an Environmental-cell dynamic high- resolution transmission electron microscopy to directly image dehydroxylation of Mg(OH)<sub>2</sub>, an important step in Mg(OH)<sub>2</sub> carbonation reactions. They are extending this technique to study the solid gas reaction path using serpentine to provide insights into pretreatment and reaction issues.

In the process development area, the team has completed a feasibility study of a process originally proposed by Los Alamos National Laboratory (*9, 11*). This process uses HCl

solution reacting with serpentine to produce  $Mg(OH)_2$  which is subsequently used to sequester  $CO_2$ . Although the study found the process energy intensive and inappropriate for  $CO_2$  sequestration, the analyses of individual steps were useful for developing new processes. Los Alamos National Laboratory is currently pursuing reaction mechanisms that may allow the heat treatment step for serpentine to be bypassed.

Progress has also been made in identifying sources of alternative minerals that can be used for  $CO_2$  sequestration. In addition to natural olivine and serpentine deposits, researchers at NETL are engaged in a study of using waste streams such as coal ash rich in calcium and magnesium as a potential mineral source to sequester  $CO_2$ .

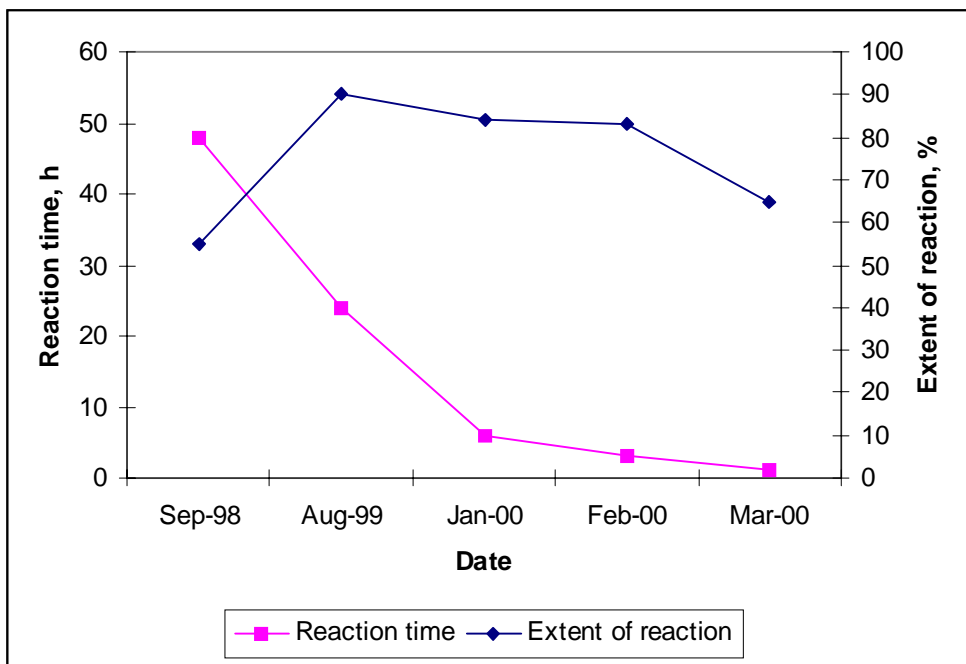


Figure 2. Reaction time of carbonic acid mineral carbonation has been reduced from 48 hrs to 1 hour over the period from Sept. 1998 to March 2000 at the Albany Research Center.

### Scale-up Plan for Next Several Years

Most of the past work has been summarized in a paper presented at Globe-Ex conference (15). Recently, the mineral sequestration team conducted an extensive review of its approach and achievement and drafted a scale-up plan. Our projective goal is to build a validated knowledge base necessary to construct a demonstration plant capable of effectively sequestering 5.5 ton/h  $CO_2$  (for a 10 MWe plant) in a time frame of around six

years. There are several stages of efforts to achieve such a goal. The team has identified critical issues at each stage. Table 1 listed a four-stage plan and critical issues to be addressed.

Table 1. Experimental Stages Employed to Address Critical Issues

<i>Stage</i>	<b>Operational Scale</b>	<b>Major Issues</b>
Laboratory	Batch operation using gram quantities	-Kinetics/Mechanisms/Feedstocks -Role of impurities -Pretreatment options
Bench	Continuous operation at 5 lb/hr mineral input	-Evaluation of multiple concepts -Semi-integrated pre- & post -processing -Materials issues -Heat transfer, solid & liquid flow effects
Engineering Development	Continuous operation at 500 lb/hr mineral input	-System integration -Concept validation -Relevant reliability, efficiency & cost data
Demonstration	Continuous operation at 5 tons/hr mineral input	-Site Issues -Relevant reliability, efficiency and cost data -Byproduct Handling

The critical issues can be further illustrated in their relation to the processing steps as shown in Figure 3.

Even with progress made so far, to develop an economical method to sequester CO<sub>2</sub> with minerals is still a challenging task, because the process is still relatively slow, and most reactions require high pressure and moderately elevated temperature. The number one priority is still to develop faster reaction conditions that require a lower pressure. In order to achieve this goal, the team is not only testing at different conditions, but also working to improve fundamental understanding of reaction paths. At the same time for scale-up purpose, a system study has been initiated at the Albany Research Center and the National Energy Technology Laboratory to evaluate a potential realization using conceptual designs and known reaction conditions. Issues to be addressed in the system study include capital and operating costs, and environmental impacts. The study will also prioritize future research needs.



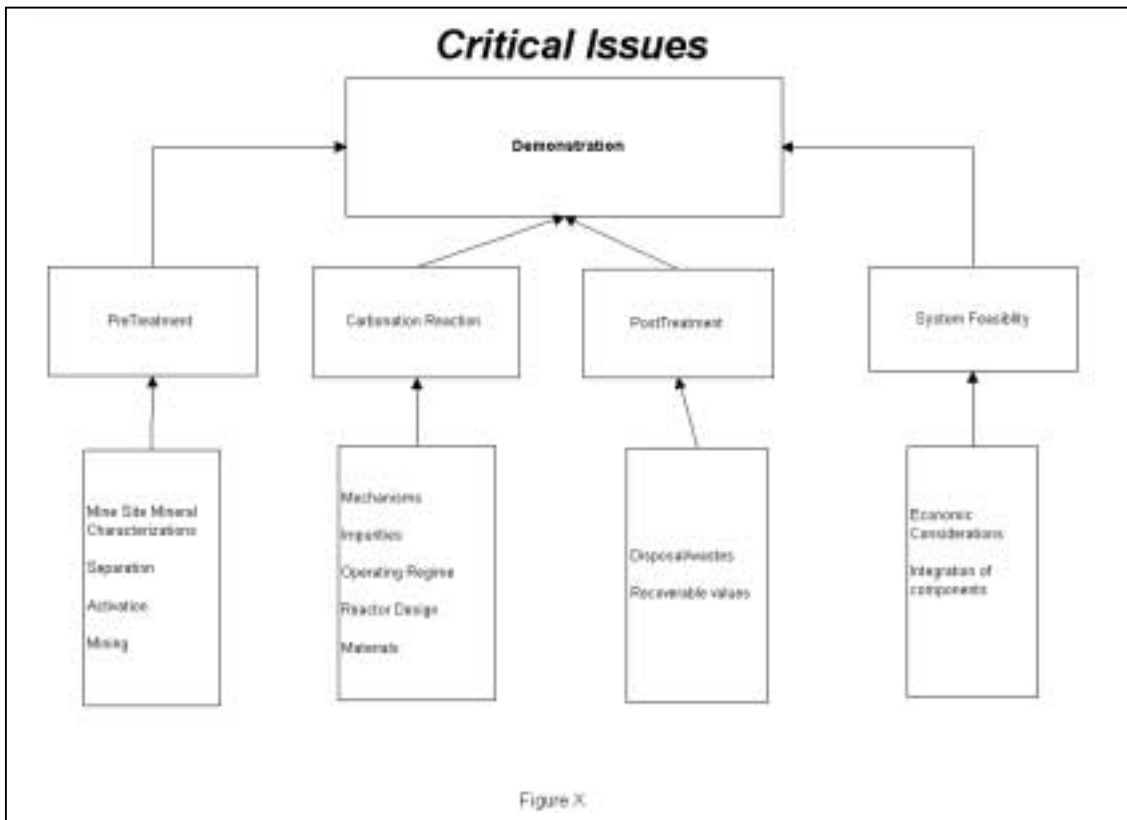


Figure 3. Critical Issues listed by Processing Step

Because of many fundamental advantages, such as long-term stability, large capacity, and favorable thermodynamics discussed in this paper, using minerals to sequester CO<sub>2</sub> appears attractive. Although currently a practical process is still yet to be developed, we have significantly reduced reaction times since the inception of the program. We also identified many critical areas to be studied. Additional support and industrial participation is welcomed so that progress can be accelerated and an early small-scale sequestration testing can be built.

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