Technological Evaluation of Mineral Sequestration of CO$_2$ by Carbonation

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ABSTRACT

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Increase in CO_2 emissions has led to development of various mitigation technologies for avoiding CO_2 building up in the atmosphere. One of CO_2 sequestration technologies is mineral sequestration, a way of permanent storage of CO_2 in solid minerals. This technology attracts the attention of many investigators to study and develop various carbonation approaches.

The chemistry and thermodynamic studies show that mineral carbonation reactions with silicate minerals are spontaneous and exothermic. A variety of measures are needed to enhance the carbonation kinetics. The main minerals used for mineral sequestration are serpentine and olivine, which exist in vast quantities worldwide. Implementation of mineral sequestration needs to address related energy consumption and environmental consequences.

The mineral sequestration approaches include chloride based mineral sequestration, direct dry carbonation, direct carbonation in aqueous solutions, integrated carbonation, *in-situ* carbonation in geologic formations, biomineralization with fly ash, and zero emission coal alliance (ZECA) process. Among all the mineral sequestration approaches, direct carbonation in aqueous solutions is the most promising method. Under optimal conditions, 78% stiochiometric conversion of silicate to carbonate was achieved in 30 minutes.

ACKNOWLEDGEMENTS

DEDICATION

To my parents

for

their love to my brother, my sisters and me

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CHAPTER 1   INTRODUCTION

Carbon dioxide is known as a "greenhouse gas", which can trap heat in the earth's atmosphere, preventing it from escaping into space and keeping the earth warm. The principal anthropogenic sources of CO_2 are combustion of fossil fuels, cement manufacture and deforestation. It is estimated that the total anthropogenic CO_2 emissions are 6 GtC/year from the usage of fossil fuel alone (Freund and Ormerod, 1997; DOE, 1999). Currently, fossil fuels supply over 85% of the global energy demand (Herzog, 2000), and fossil fuel usage is likely to continue to be the main energy source either in industrialized or less-developed countries.

Steady increase in CO_2 emissions and uprising of CO_2 concentration in the atmosphere have aroused the general public attention and legitimate concern about global warming and the global carbon cycle (Ramanathan 1988; Herzog, 2001). During the United Nations Earth Summit at Rio de Janeiro in 1992, 154 states signed the Framework Convention on Climate Change (UNFCCC) to promote climate stabilization through control of greenhouse gas emissions. During the conference in Kyoto in 1997, participating countries negotiated a set of greenhouse gas emissions targets for the years 2008 through 2012 and agreed in principle to various so-called "flexibility" mechanisms that countries can use to help meet the targets. This agreement is known as the Kyoto Protocol.

These concerns and agreements have resulted in various studies on the mitigation technologies for avoiding CO_2 building up in the atmosphere. In general, there are three

approaches to carbon management (DOE, 1999). The first approach is to increase the efficiency of primary energy conversion and end use so that fewer units of primary fossil energy are required to provide the same energy service. The second approach is to substitute lower-carbon or carbon-free energy sources for our current sources. This strategy might involve, for example, substituting low-carbon fossil fuels such as gas for coal and oil, using renewable energy supplies such as solar, wind or biomass, or increasing the use of nuclear power. Carbon sequestration, the third approach, refers to the removal of carbon dioxide (CO_2) from either manmade emissions or the atmosphere and the safe, essentially permanent storage of CO_2 or other carbon compounds (DOE, 2002). The objective can be achieved by keeping the carbon emissions from reaching the atmosphere through capture and secure storage, or removing carbon from the atmosphere by various means and fixing it.

Many nations, international organizations and commercial organizations have initiated and sponsored numerous research projects of carbon sequestration worldwide. These studies aim to explore the scientific understanding of carbon sequestration, and to find the feasible options to implement the environmentally acceptable sequestration to reduce the CO_2 concentration in the atmosphere. Most carbon sequestration research and development is concentrated in the following aspects:

- Sequestration in geologic formations such as depleted oil fields, coalbeds, gas fields and saline aquifers;
- Ocean sequestration, such as direct injection into the deep sea, or oceanic fertilization;

- Terrestrial sequestration, such as forest sinks and agricultural sinks;

- Conversion and utilization such as chemical & biological processes, and mineral sequestration.

Among all the technological options above, mineral sequestration refers to the processes by reacting minerals with CO_2 to form the thermodynamically stable and environmentally benign carbonates, i.e. mineral carbonation, thus a permanent and risk free storage of CO_2 is achieved. Mineral sequestration has many unique advantages (Goldberg *et al*., 2001). Most notably is the fact that carbonates have a lower energy state than CO_2, which is why mineral carbonation is thermodynamically favorable and occurs naturally. Secondly, the raw materials such as magnesium based minerals are abundant. Finally, the produced carbonates are unarguably stable and thus re-release of CO_2 into the atmosphere is not an issue, which, however, is a big concern to other carbon dioxide storage methods, such as ocean injection and geologic sequestration.

The objective of this study is 1) to review and summarize into a knowledge base for mineral sequestration, including the mineral sources, the carbonation mechanism and routes, the pathways to enhance the carbonation, and the related sequestration costs; 2) with the availability of the knowledge base for CO_2 mineral sequestration, its technological status, sequestration potential, advantage and disadvantage/limitations can be evaluated.

CHAPTER 2   CHEMISTRY AND THERMODYNAMICS IN MINERAL SEQUESTRATION

2.1 Natural carbonation process

Mineral sequestration process, binding CO_2 in carbonate solids as an approach to mitigate the CO_2 emissions, is an innovative research attempt. However, the process itself is not new at all. Mineral carbonation occurs naturally in nature every moment as weathering of rocks to form calcium and/or magnesium carbonates. On geologic time scales mineral carbonation happens spontaneously and represents an important part in the overall carbon cycle (Lackner *et al*., 1998).

Carbonate rocks in the nature are largely formed from the interaction of aqueous fluids with silicate rocks enriched in calcium and magnesium, either through weathering, ground water flow, or hydrothermal activities. Each of these fluid–rock interactions can lead, essentially, to the release of the alkaline-earth metals from the silicates via dissolution, leaching, or other mineral-alteration reactions (Guthrie *et al*., 2001). Once the alkaline-earth metals are released to the aqueous fluid, they can react with dissolved CO_2 to precipitate carbonates. The net result is the conversion of carbon dioxide to a thermodynamically stable and immobile solid form.

2.2 Chemistry and thermodynamics

Carbon chemistry is important to understand the process and to explore new routes to enhance the carbonation process. People used to think that CO_2 is the more stable state of carbon. Table 2-1 lists the free energy of formation of some carbon containing compounds and related species under standard conditions. It can be seen that the energy state of CO_2 is relatively high and carbonates are the more stable state of carbon. Also, as show in Figure 2-1, the energy state of carbonate is 60-180 kJ/mole (14-43 kcal/mole) lower than that of carbon dioxide (Schmidt and Romanosky, 2001), and the end energy state of carbon is mineral carbonate not CO_2. This indicates CO_2 is not the unavoidable end product of fossil fuel combustion.

Table 2-1 Free Energy of Formation of Selected Species

Species	$\Delta G_f°$(kcal/mole)
$C_{(s)}$, graphite	0
$H_2O_{(g)}$	-57.80
$H_2O_{(l)}$	-68.32
$CO_{2(g)}$	-94.26
$CO_{2(aq)}$	-92.31
$CO_3^{2-}{}_{(aq)}$	-126.22
$HCO_3^-{}_{(aq)}$	-140.31
$H_2CO_{3(aq)}$	-149.00
$SiO_{2(s)}$	-204.66
$MgCO_{3(s)}$	-246.05
$CaCO_{3(s)}$	-269.78
$Mg_2SiO_{4(s)}$ Forsterite (Olivine family)	-490.28
$Mg_3Si_2O_5(OH)_{4(s)}$ Serpentine	-964.16

Source: Soneyink and Jenkins, 1995; Wendt *et al.*, 1998b.
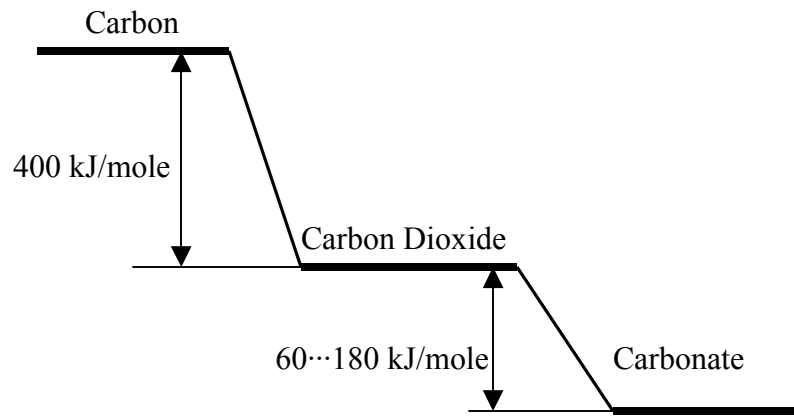
Figure 2-1 Energy State of Carbon (Source: Schmidt and Romanosky, 2001)

The chemical reactions concerning the mineral sequestration approaches are summarized as follows (Goldberg *et al*., 2001; O'Cannor *et al*., 2000c; McKelvy, 2001):

$$(Mg, Ca)_xSi_yO_{x+2y+z}H_{2z} + xCO_2 \longrightarrow x(Mg,Ca)CO_3 + ySiO_2 + zH_2O \qquad (1)$$

$$1/3\ Mg_3Si_2O_5(OH)_4 + CO_2 \longrightarrow MgCO_3 + 2/3\ SiO_2 + 2/3\ H_2O \qquad (2)$$

   (serpentine)

$$1/2\ Mg_2SiO_4 + CO_2 \longrightarrow MgCO_3 + 1/2\ SiO_2 \qquad (3)$$
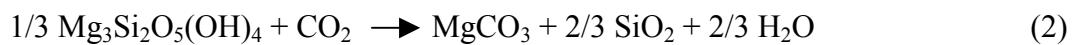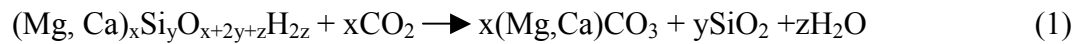
   (forsterite, one mineral of olivine family)

The family of general carbonation reactions of (Ca, Mg) silicates can be represented by Reaction 1, which illustrates the conversion of naturally occurring silicate minerals into geologically stable carbonate minerals and silica. This process emulates natural chemical transformations such as weathering of rocks to form carbonates over geologic time periods. Specifically, Reaction 2 illustrates the carbonation of serpentine (the common magnesium bearing silicate mineral) and CO_2 into magnesite ($MgCO_3$), silica and water. Below is the thermodynamic calculation for this reaction.

	Species	$\Delta G_f°$(kcal/mole)
Reactants	$Mg_3Si_2O5(OH)_4$	-964.16
	$CO_2(aq)$	-92.31
Products	$MgCO_3(s)$	-246.05
	$SiO_2(s)$	-204.66
	$H_2O(l)$	-68.32

$$\Delta G°=(-246.05-2/3*204.66-2/3*68.32)-(-1/3*964.16-92.31)$$

$$=-14.34 \text{ (kcal/mole)}$$

The negative value of ΔG indicates the reaction may proceed spontaneously as written. Also, this reaction is exothermic and the energy release is 14.34 kcal/mole of CO_2. Approximately, one ton of serpentine can dispose of half ton of CO_2. Reaction 3 illustrates the carbonation of forsterite, which is a member of olivine series minerals. The thermodynamic calculation for this reaction is as follows:

	Species	ΔG_f°(kcal/mole)
Reactants {	$Mg_2SiO_4(s)$	-490.28
	$CO_2(aq)$	-92.31
Products {	$MgCO_3(s)$	-246.05
	$SiO_2(s)$	-204.66

$$\Delta G^\circ = (-246.05 - 1/2 * 204.66) - (-1/2 * 490.28 - 92.31)$$

$$= -10.93 \text{ (kcal/mole)}$$

This is also a spontaneous reaction with an exothermic energy of 10.93 kcal/mole of CO_2. One ton of olivine can absorb approximately two-thirds of a ton of CO_2. The above calculations confirm that the mineral sequestration reactions are exothermic processes, which theoretically do not require energy input. Thus, mineral sequestration has the potential to cover the energy consumption associated with implementation of the carbonation process.

In practice, the above reactions do not necessarily proceed in one single step. For instance, Reaction 2 may include the three substeps below (O'connor *et al.*, 2001a). First, CO_2 is dissolved in water, so that carbonic acid (H_2CO_3) is formed. Carbonic acid then dissociates to form H^+ and HCO_3^-. Second, olivine is hydrolyzed by H^+, giving off Mg^{2+} cations and forming silicic acid or free silica and water. Then, the produced free Mg^{2+} cations react with the bicarbonate ions to form the carbonate solids.

$$CO_2 + H_2O \longrightarrow H_2CO_3 \longrightarrow H^+ + HCO_3^- \tag{4}$$

$$Mg_2SiO_4 + 4H^+ \longrightarrow 2Mg^{2+} + H_4SiO_4 \text{ or } SiO_2 + 2H_2O \tag{5}$$

$$Mg2+ + HCO_3^- \longrightarrow MgCO_3 + H^+ \tag{6}$$
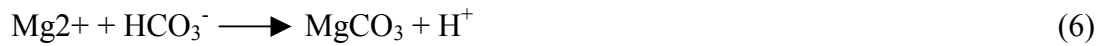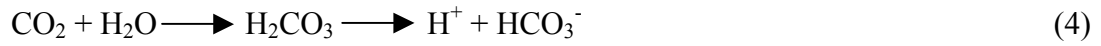
It is to note that, according to the entropy, enthalpy and free energy theories, the thermodynamically favored reaction, or theoretically spontaneous reaction, does not guarantee that a practical process will happen. For any commercial chemical process, reaction kinetics is more important with respect to the efficacy and capacity of the process. In fact, the natural carbonation rate, such as the weathering of rocks, is extremely slow. Thus, the most critical task for all current mineral sequestration attempts is to enhance the carbonation rate, so that an economically acceptable process with a considerably large production capacity can be expected.

CHAPTER 3   MINERAL RESOURCES FOR MINERAL FIXATION

The idea of mineral sequestration was first proposed by Seifritz (1990) to store CO_2 captured from the burning of fossil fuels. Since then, many carbonation approaches are proposed, tested and studied, and some methods have made great progress in term of the carbonation rate, extent of carbonation and the technological feasibility. Calcium and magnesium carbonates are common minerals of some rocks and keep stable in the natural environment, which means they are good end products of mineral sequestration of CO_2. Therefore, magnesium and calcium bearing minerals, mainly their silicates, are most commonly used in all the mineral sequestration methods. The mineral sources of calcium and magnesium minerals include naturally occurring minerals and industrial byproducts.

3.1 Industrial byproducts

Since mineral sequestration needs calcium and magnesium bearing minerals to bind CO_2, fly ash, scrubber sludge and other byproducts from industrial combustion system, which contain metal-rich oxides, are good candidate sources for mineral carbonation. Using industrial byproducts to sequester CO_2 has double environmental credits since it treats two products, carbon dioxide and fly ash, in one process. However, the total amount of CO_2 emission is enormous while the amount of industrial byproducts that can be used in mineral carbonation is relatively small. For instance, only 400 million tonnes of total coal ash were produced

worldwide in 1989 (Malhotra, 1999). Industrious byproducts can be considered as raw materials for mineral sequestration to address the regional or local CO_2 emission problem.

3.2 Naturally occurring minerals

Mg and Ca comprise about 2.0 to 2.1 %-mol of the earth's crust, respectively, primarily bound in silicate minerals (Brownlow, 1979). Although molar abundances are similar, Mg silicates contain more reactive material per ton of rock due to the lower molecular weight of Mg (Goff and Lackner, 1998a). Moreover, magnesium bearing rocks are more active than calcium silicates, which are usually very chemically stable. Therefore, so far all most all mineral sequestration studies are using magnesium bearing minerals.

Various magnesium bearing minerals, such as serpentine and olivine, were considered for mineral sequestration. These minerals occur in ultramafic complexes. They contain MgO in the form of serpentine or olivine. Generally, the nominal content of MgO in the rocks is in the range of 35% to 45% by weight. Lackner (1998) estimated that to bind one ton of CO_2 requires 2 to 2.6 tons of rocks. One should keep in mind that CO_2 emissions are huge in amount, so that carbon dioxide sequestration must be carried out in large scale. Thus, the minerals with low abundance in the earth do not deserve systematic investigation for the purpose of carbon sequestration. Till now, serpentine and olivine are the two main naturally occurring minerals utilized by mineral sequestration researchers, although these mineral samples vary in some mineralogical properties from different locations.

3.3 Mineralogical description of serpentine and olivine minerals

Serpentine, (Mg, Fe, Ni)$_3$Si$_2$O$_5$(OH)$_4$ (Berry *et al.*, 1983)

Serpentine as a mineral name applies to a group of minerals including chrysotile, antigorite and lizardite. The structures of the diverse polytypes are similar to those of minerals of the kaolinite group. The physical properties of chrysotile and antigorite are very similar, but antigorite generally has a lamellar or platy structure whereas most chrysotile is fibrous (serpentine asbestos is chrysotile). The crystal system of serpentine is monoclinic. Other properties include no observable cleavage, hardness 4-6, density 2.5-2.6, white streak and waxy or greasy luster etc.

Olivine (Mg, Fe)$_2$SiO$_4$ (Berry *et al.*, 1983)

The olivine series is an example, albeit imperfect, of continuous solid solution of two components, Mg$_2$SiO$_4$ and FeSiO$_4$. Three names are used currently: forsterite for pure or nearly pure Mg$_2$SiO$_4$, fayalite for pure or nearly pure Fe$_2$SiO$_4$, and olivine for the common intermediate varieties. Crystal system is orthorhombic. Other properties include {001} indistinct cleavage, hardness 6.5, specific gravity 3.3-3.4 olive-green, white or brown streak and vitreous luster.

Mineralogical properties of the main Ca, Mg bearing minerals are list in Table 3-1 (Golf *et al.*, 2000).

Table 3-1 Summary of Dominant Mineralogy in Serpentinite, Peridotite and Associated Rocks (Source: Golf *et al*., 2000)

Mineral Group	Mineral Species	Ideal Formula	Rock Type(s) Typically Found In
serpentine	chrysotile	$Mg_3Si_2O_5(OH)_4$	serpentinite; altered peridotite
serpentine	lizardite	$Mg_3Si_2O_5(OH)_4$	serpentinite; altered peridotite
serpentine	antigorite	$Mg_3Si_2O_5(OH)_4$	dunite; peridotite
olivine	forsterite	Mg_2SiO_4	high-grade serpentinite; altered peridotite
orthopyroxene	enstatite	Mg_2SiO_4	peridotite
clinopyroxene	diopside	$CaMgSi_2O_6$	peridotite
amphibole	anthophyllite	$Mg_2Mg_5Si_8O_{22}(OH)_2$	high-grade serpentinite
amphibole	tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	high-grade serpentinite
spinel	magnetite	Fe_2FeO_4	serpentinite, peridotite, dunite
spinel	chromite	Cr_2FeO_4	serpentinite, peridotite
carbonate	magnesite	$MgCO_3$	altered serpentinite
carbonate	dolomite	$CaMg(CO_3)_2$	altered serpentinite
silica	quartz, chalcedony	SiO_2	altered serpentinite
silica	opal	$SiO_2 \cdot nH_2O$	altered serpentinite

3.4 Resources of serpentine and olivine

According to Goldberg *et al*. (2001), raw materials which can bind CO_2 in solids exist in vast quantities worldwide and readily accessible deposits even exceed the most optimistic estimate of coal reserves. The candidate ore bodies of serpentine and olivine minerals to sequester CO_2 are distributed throughout the world. Figure 3-1 shows the worldwide locations of the ore bodies which are rich in serpentine and olivine (Lackner *et al*., 1998). Specifically in the US, Goff *et al*. (1998b) reported the distribution and geochemistry of

ultramafic deposits, estimation of the CO_2 sequestration potential of some US resources, and analysis some industrial and environmental impacts that would result from large-scale ultramafic rock mining. Their study shows that many states have the considerable amount of the ultramafic rocks that can be used for mineral sequestration, such as Washington, Oregon, Vermont, Maryland, California and Montana. The CO_2 mineral sequestration potential of some ultramafic bodies is summarized in Table 3-2.

From Table 3-2, it can be seen that the mineral sequestration potential is very huge. Even some small ultramafic bodies have considerable sequestration potential. For example, the ultramafic body at Belvidere Mt., VT can sequester the equivalent of 0.55 year of present total US CO_2 emissions. Base on the data in Table 3-2, the eight ore bodies of US have the potential to sequester the equivalent of approximately 11 years of current world CO_2 total emissions. Therefore, the mineral resources are definitely huge for mineral sequestration to handle the CO_2 emissions.

3.5 Mining of serpentine and olivine

Currently, olivine is produced only in North Carolina and Washington from dunite and perioditite deposits (Kramer, 2001). The application of olivine includes foundry sands, refractory, metallurgical fluxes, abrasives and soil conditioning. The current production of olivine is less than 100,000 metric tons each year in US. Serpentinite can be mined for the usage of crusted stone for roadbed aggregates, and it can also be mined for its asbestos content.
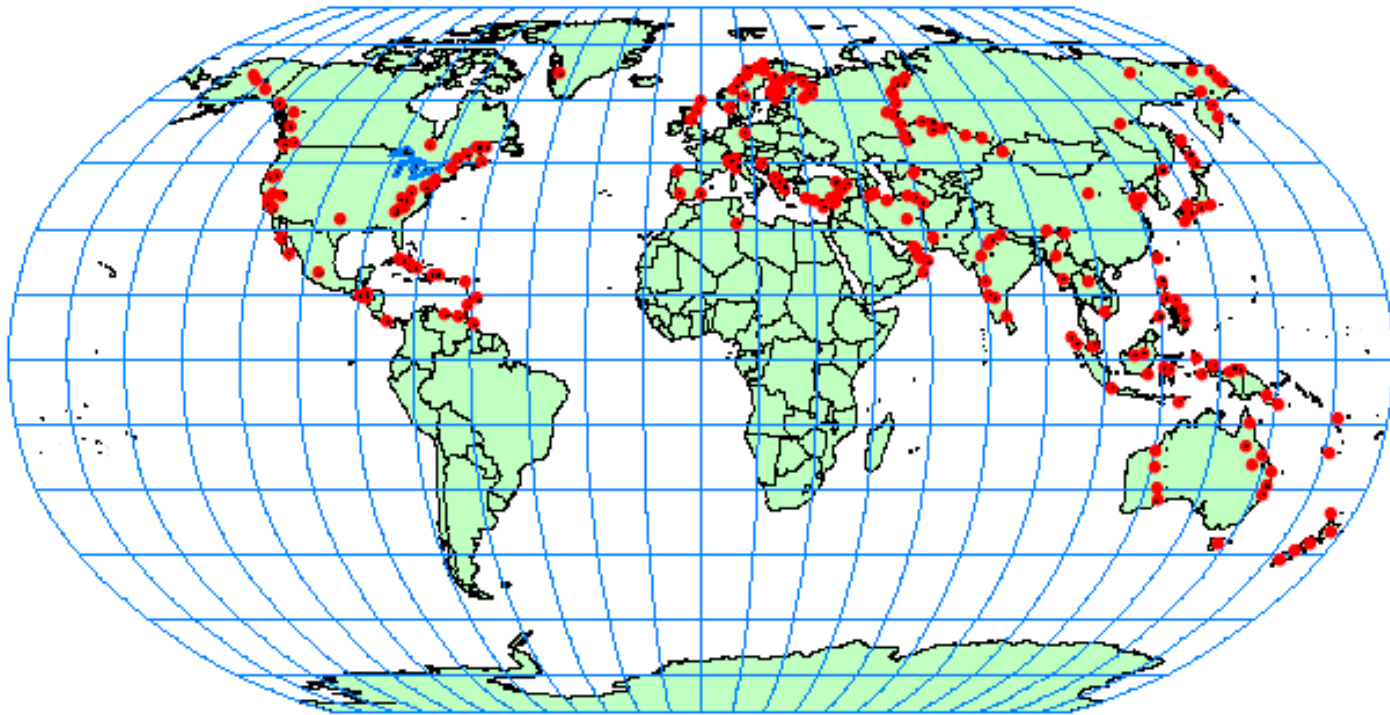
Figure 3-1 Location of Known Peridotite or Serpentinite Ore Bodies Worldwide (Source: Lackner *et al*., 1998)

Table 3-2 Physical-chemical and CO_2-sequestering Properties of Example Peridotite/Serpentinite Bodies (Source: Golf *et al*., 1998a)

	Twin Sisters WA	Vulcan Peak OR	Del Puerdo CA	Belvedere Mtn. VT	Wilbur Springs CA	Baltimore Complex MD	San Mateo CA	Stillwater MT
Volume density								
Area (km^2)	91	16	40	2.3	200	100	4?	26
Depth (km)	0.6	0.5	0.3	≤ 1	≥ 0.2	0.3	0.25	0.5
Est. Vol. (km^3)	54	8	12	2	40	30	1	13
Density (g/cm^3)	3.3	3.2	2.8	2.9	2.65	2.7	2.6	3.1
Wt-% Mg								
Peridotite	29.9	27.4	27.2	29.1	-	-	-	17.5
Serpentinite	-[a]	-	20.9	23.1	21.8	21.2	19.9	-
Combined	29	27	23	26	21	21	20	17
Sequestering Properties								
R(CO_2)[b]	1.91	2.05	2.40	2.13	2.63	2.61	2.76	3.25
Mg (10^9 tons)	52.0	6.91	7.73	1.5	22.3	17.0	0.5	6.85
CO_2 (10^9 tons)	94.1	12.5	14.0	2.7	40.3	30.8	0.9	12.4
USA (yr)[c]	18.8	2.50	2.80	0.55	8.05	6.15	0.18	2.48
World (yr)[c]	4.95	0.66	0.74	0.14	2.12	1.62	0.048	0.65

[a](-): not significant.
[b]R(CO_2) is the calculated mass ratio of rock processed to CO_2 disposed.
[c]Assumes annual USA and World CO_2 emission rates of ~5 ×10^9 and ~19 × 10^9 tons/yr respectively.

Since sequestering of one ton of CO_2 by mineral carbonation demands 2 to 2.6 tons of ultramafic rocks, the mining operation needs to be very large in order to make the sequestration process economically acceptable. According to Lackner *et al*. (1998), any mining operation that does not achieve 50,000 t/day is probably too small to take the advantage of the available economies of scale, considering the size of modern mining equipment. Also, in order to save the cost of transportation of either CO_2 or ultramafic rocks, the deposits that are near the large CO_2 sources have the high priority to be mined. From Figure 3-1, we can see many of the major deposit sites are located relatively close to the large population centers near the East and West Coasts in US.

CHAPTER 4   APPROACHES OF MINERAL SEQUESTRATION

After the proposal of mineral carbonation to store CO_2 captured from the burning of fossil fuels by Seifritz in 1990, Dumsmore (1992) further discussed this scheme from geologic perspective. Lackner *et al*. (1995) explored this scheme in details towards an industrial carbonation process and suggested that naturally occurring magnesium silicates, derived from ultramafic rocks, would provide an abundant and thermodynamically favored resource for the production of magnesite ($MgCO_3$). Recently, with the increase of concern of CO_2 effects on the atmosphere temperature, many organizations and governmental agencies, such as International Energy Agency (IEA) and US Department of Energy (DOE), initiates and supports various research and development programs to explore the pathways to sequester CO_2. Due to these efforts, several mineral sequestration approaches are proposed and studied. In general, these approaches include:

- Chloride based mineral carbonation;

- Direct dry carbonation;

- Direct carbonation in aqueous solutions;

- Integrated carbonation;

- *In-situ* carbonation in geologic formations;

- Biomineralization with fly ash;

- Zero Emission Coal Alliance (ZECA) process.

4.1 Chloride based mineral carbonation

Most research work of chloride based mineral carbonation was done in Los Alamos National Laboratory (LANL), US Department of Energy (Lackner *et al*., 1995, 1997, 1998; Wendt *et al*., 1998a, b, c). Their work includes development of the whole process scheme, calculation of thermodynamics, study of the pathways to enhance the carbonation process, proposal of the plant design, investigation of the Mg-rich ultramafic rock resources and economic estimates of the process.

The overall process for the chloride based mineral sequestration to disposal of 24 kt/day CO_2 is shown in Figure 4-1(Lackner *et al*., 1998). The upper branch shows the carbon flow from energy source (coal mine) through the power plant and the sequestration unit. It is assumed that the CO_2 gas is delivered to the mineral sequestration site through a pipeline. The lower part of the diagram represents the mineral carbonation process. First, the ultramafic rocks must be mined, crushed and fineground to powders in order to achieve better carbonation performance. To improve the carbonation kinetics, magnesium is extracted from the rocks with the formation of magnesium hydroxide. It is well known that serpentine and olivine dissolve readily in hydrochloric acid. The extraction is accomplished with HCl, which dissolves the ultramafic rocks forming magnesium chloride ($MgCl_2$) and silica. Silica is readily precipitated along with iron oxide, which is present in the original ultramafic rocks. The magnesium extraction reactions are as follows:

For serpentine

$$2HCl + 1/3Mg_3Si_2O_5(OH)_4 \longrightarrow MgCl_2 + 5/3H_2O + 2/3SiO_2 \qquad (7)$$
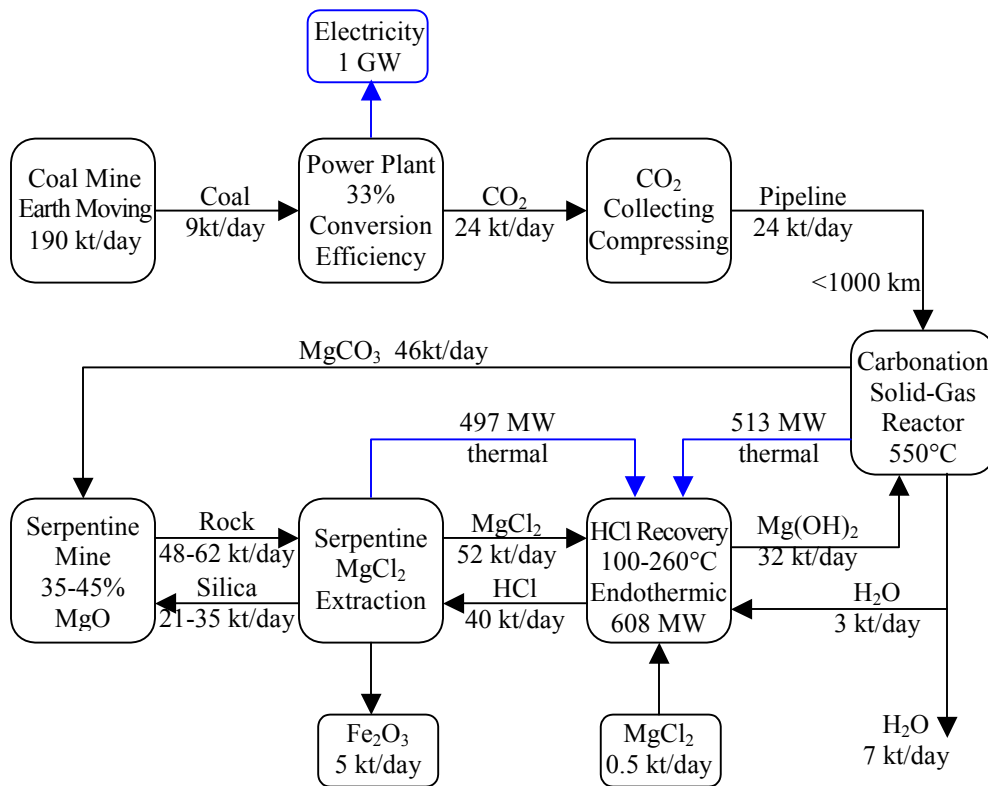
Figure 4-1 Processing Stream for CO_2 Disposal (Source: Lackner *et al.,* 1998)

For olivine

$$2HCl + 1/2Mg_2SiO_4 \longrightarrow MgCl_2 + H_2O + 1/2SiO_2 \qquad (8)$$

The resulting $MgCl_2$, which is always hydrated, can be hydrolyzed at 200 to 250 °C to form $Mg(OH)Cl$ and HCl.

$$MgCl_2 + H_2O \longrightarrow Mg(OH)Cl + HCl \qquad (9)$$

In water, $Mg(OH)Cl$ dissociates into $Mg(OH)_2$ and $MgCl_2$, which is sent through the cycle again.

$$2Mg(OH)Cl \longrightarrow Mg(OH)_2 + MgCl_2 \qquad (10)$$

Then, $Mg(OH)_2$ will react with CO_2 in the carbonation reactors:

$$Mg(OH)_2 + CO_2 \longrightarrow H_2O + MgCO_3 \qquad (11)$$
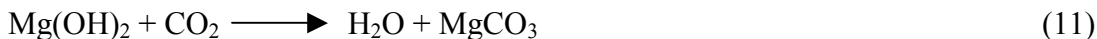
In this cycle, energy consumption in the process of HCl recovery and loss of the HCl are important issues. In principle, the carbonation reaction is quite exothermic and can provide all energy necessary to recovery the HCl. To harness this energy, the carbonation is performed in a gas-solid reaction between $Mg(OH)_2$ and CO_2. The reaction rate can be faster in the aqueous carbonation process. However, because of the high degree of dilution, the heat of reaction would be lost for practical purpose. As for the HCl loss, since alkali content of olivine and serpentine rocks is very low, the loss of HCl would not be a very serious problem because formation of alkali chlorides is the main mechanism of HCl loss.

According to Goff and Lackner (1998a), this process has demonstrated experimentally that the gas-solid carbonation of $Mg(OH)_2$ proceeds rapidly and the carbonation will be virtually completed in less than 30 min at pressure of 50 bar and temperatures of 500 to 600 °C. Based on their further work, they conclude that the carbonation of $Mg(OH)_2$ is a viable process that requires fine powders (precipitates), pressures in the range of 6 to 30 bars, temperatures between 400 and 550°C, and that can be accomplished in 30 minutes or less(Lackner *et al.*, 1998).

Based on the thermodynamic analysis and calculation, LANL researchers developed a thermodynamic description of the $MgCl_2 + n\ H_2O$ melts for the chloride based processes (Lackner *et al.*, 1998; Wendt *et al.*, 1998a,b). Typical values of n are between n=1 and n=4. As the water content of the melt is reduced, the HCl pressure over the melt increases, due to the reaction below:

$$MgCl_2 + H_2O \longrightarrow Mg(OH)Cl + HCl \qquad\qquad (12)$$

If water content is very low, the resulting HCl partial pressure is nearly enough to dissolve serpentine and olivine directly in the melt without adding additional HCl. Minor pretreatment of the serpentine may be sufficient to make this reaction work. There are other options to raise the acidity of the melt. Even if HCl would have to be recycled through the process, it constitutes a major improvement because its lowered water content would have greatly reduced the heat inputs and outputs associated with evaporating and condensing steam. An obstacle to this implementation lies in the fact that $Mg(OH)Cl$ is stable against repartitioning

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unless the surrounding melt of $MgCl_2$ + n H_2O contains at least 6 moles of water per mole of magnesium chloride (n=6). Partition reaction is as follow:

$$2Mg(OH)Cl \longrightarrow Mg(OH)_2 + MgCl_2 \qquad (13)$$
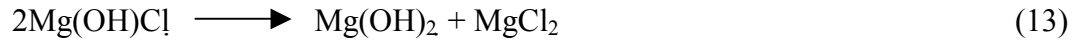
This obstacle can be overcome by reacting $Mg(OH)Cl$ directly with CO_2:

$$Mg(OH)Cl + CO_2 \longrightarrow MgCO_3 + HCl \qquad (14)$$

This reaction is favored in a chloride melt of any water content and CO_2 pressures on the order of a few bars. In addition, LANL researchers found that the presence of CO_2 over the chloride melt can raise the HCl partial pressure to a level that exceeds the spontaneous reaction level. The additional HCl pressure arises from the reaction:

$$MgCl_2 + CO_2 + H_2O \longrightarrow MgCO_3 + 2HCl \qquad (15)$$
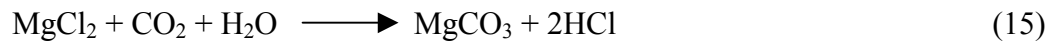
In a water poor chloride melt, the thermodynamic equilibrium favors a small amount of carbonate in the melt. At 20 to 30 bar of CO_2 pressure, the calculated HCl partial pressure for this reaction is sufficient to dissolve serpentine or olivine. This dissolution reaction in turn consumes the HCl and thus causes further precipitation of $MgCO_3$. In summary, a process starts in which magnesium from the mineral is dissolved and subsequently precipitated as carbonate from the melt. In this situation the chloride melt is used to speed up the reaction by providing additional reaction paths to the net carbonate reaction and is not consumed by the

reaction. The last option would lead to single step process which, if proven feasible, would provide the simplification necessary to make mineral carbonation cost effective and viable.

With regard to the overall process design, LANL researchers investigated the cost of mining, crushing, and milling the material and found this cost well within a reasonable cost budget. According to their estimation, they consider these processes appear economically viable. The mineral sequestration cost of \$15/ton of CO_2 (0.8 to 1.5 cents/kWh), excluding CO_2 capture and transportation, is a reasonable goal to this chloride based process, as the mining, crushing and milling operation is estimated at about \$8/ton of CO_2 (Lackner *et al.*, 1998).

4.2 Direct dry carbonation

Among all the attempts in the study of mineral sequestration, most of them are looking into the wet method, i.e. aqueous carbonation. Only the research started in August 2000 at Helsinki University of Technology (Kohlmann 2001, 2002; Zevenhoven 2001, 2002) aims at dry methods and the researchers are still working on it. Their research concentration is to extract the reactive component MgO from the silicate minerals and to speed up the kinetics of the carbonation by dry method.

Experiments with serpentine

Kohlmann (2001, 2002) and Zevenhoven (2001, 2002) *et al*. conducted a few dry experiments to obtain some indication of the quality and reactivity of Finnish magnesium carbonates, using a serpentine that was mined near Kittilä north of Rovaniemi. The

serpentine used are fine powdered serpentine with the average particle size of about 50 microns. The carbonation was tested in a pressurized thermo gravimetric analyzer (PTGA). Their results show that at 200°C no detectable carbonation was measured after 3 hours, either at 1 bar in N_2/CO_2 85/15%-vol. and $N_2/CO_2/H_2O$ 80/15/5%vol., or at 15 bar in a N_2/CO_2 85/15%vol. gas mixture. The final CO_3 content of the samples was approximately 4.3%wt, which equals to the CO_3 content in the original serpentine sample before carbonation test. From this, it can be concluded that nothing had happened to the samples.

They also tested treatment of serpentine mineral at elevated temperatures, followed by carbonation at lower temperature. For this purpose a serpentine sample was heated at 50 °C/min to 1000°C, followed (after 10 minutes) by cooling at 10°C/min to 200°C, in the PTGA in a N_2/CO_2 85/15%vol. gas atmosphere. The results show a mass loss during heat-up which corresponds to ~110% of the water bound in the serpentine. Apparently this is due to the release of CO_2 present in the serpentine mineral as carbonate, probably $MgCO_3$. During the cool-down stage an increase of sample mass is seen until the temperature has decreased to ~400°C, corresponding to almost 3% uptake of CO_2 by MgO. Surprisingly, the mass of the sample appears to decrease again when lowering the temperature further to 200°C. The mass fraction of carbon bound as CO_3 in the final product is ~0.5%wt i.e. lower than in the starting material. Repeating this experiment at 15 bar resulted in a final CO_3 content of 0.8%wt.

They concluded that more work is needed to obtain a better understanding of the processes taking place during these tests. This includes especially a more detailed analysis of the

magnesium silicate minerals, also in order to get insight into the (possibly catalytic) effects of contaminations.

Experiment with magnesium hydroxide

Kohlmann (2001, 2002) and Zevenhoven (2001, 2002) *et al*. conducted the dry carbonation tests with a rather pure magnesium hydroxide sample, $Mg(OH)_2$. These tests involved heat up at 50 °C/min to 1000°C, followed (after 10 minutes) by cooling at 10°C/min to 100°C at 1 bar, 1) in an N_2/CO_2 85/15%vol. gas atmosphere, 2) in $N_2/CO_2/H_2O$ 80/15/5%vol., 3) in $N_2/CO_2/O_2$ 80/15/5%vol., and 4) in $N_2/CO_2/H_2O/O_2$ 75/15/5/5%vol. Also, the $Mg(OH)_2$ was mixed with 1%wt of NaCl, $NaHCO_3$ or Al_2O_3, respectively, as to investigate any catalytic effect of these chemicals.

Tests with a magnesium hydroxide sample showed a catalytic effect of H_2O, whilst no significant effect of O_2 is found, when added to a CO_2/N_2 mixture. A kinetics analysis showed, for this sample at a total pressure of 1 bar, a maximum conversion rate at a temperature around 350°C, above which thermodynamics become unfavorable, and below which the carbonation rate decreases. It is concluded that mineral carbonation should be carried out at this optimum temperature, which is slightly affected by the flue gas composition. If direct carbonation is possible with Finnish magnesium silicate minerals, it will certainly need a catalyst to reach reasonable conversions within a realistic timeframe. However, the first results with small amounts of NaCl, $NaHCO_3$ and Al_2O_3 added to $Mg(OH)_2$ did not show any improvement.

4.3 Direct carbonation in aqueous solutions

Direct mineral sequestration of CO_2 in aqueous solutions utilizes a slurry of water mixed with a magnesium silicate mineral, such as olivine (Mg_2SiO_4) or serpentine ($Mg_3Si_2O_5(OH)_4$). The mixed slurry is then reacted with sub- or supercritical carbon dioxide under some specific conditions. The CO_2 reacts with water to form carbonic acid (H_2CO_3), which dissociates to H^+ and HCO_3^-. Reaction of carbonic acid with magnesium bearing minerals consumes H^+ and liberates Mg^{2+}. Mg^{2+} cations react with the bicarbonate to form the solid mineral, magnesite ($MgCO_3$) (O'Connor, 2000b; Dahlin et $al.$, 2000).

In the aspect of aqueous carbonation, most of research work was done by Mineral Sequestration Working Group (MSWG) under the sponsorship of US DOE. This program is being managed by the National Energy Technology Laboratory (NETL) and performed by a multi-laboratory team, consisting of research teams from the National Energy Technology Laboratory (NETL), the Albany Research Center (ARC), Pennsylvania State University (PSU), Arizona State Univ. (ASU), and the Los Alamos National Laboratory (LANL). These teams conducted systematic research on the aqueous approach of mineral sequestration in searching for faster reaction methods using magnesium silicates, supercritical CO_2, 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 goal of the program is to develop the knowledge base necessary to design a commercial-scale mineral sequestration plant. In order to achieve this objective, members of the MSWG will develop and operate a family of flexible, pilot-scale mineral carbonation units that will enable second-order process refinements and engineering development on a commercially

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relevant scale. The program culminates with the design and construction of a 10MW equivalent demonstration plant with plant operation targeted to begin in FY2008 (Goldberg and Walters, 2002).

4.3.1 Aqueous mineral sequestration processes

Conceptually, the aqueous process is based on the raw magnesium bearing minerals being mined, crushed and cleaned if necessary, and then either a chemical or thermal pretreatment step applied to activate the feedstock. This activated feedstock is reacted in the carbonation reactor in an aqueous CO_2 solution and CO_2 is fixed as magnesite ($MgCO_3$). Optimally, the heat generated from the exothermic carbonation process is effectively utilized to offset energy input during the whole process, or integrated into the operation of a nearby power plant. In the post-treatment stage, the carbonated minerals, any salable by-products and residues are separated from the CO_2 slurry and sold or returned to the mine for long term storage (Goldberg *et al*., 2001, 2002; O'Connor *et al*., 2000a, 2001b). The proposed process flow diagram is shown in Figure 4-2.

4.3.2 Experiment results of aqueous carbonation

Materials

The materials used in the aqueous carbonation includes: naturally occurring olivine forsterite end member) and two varieties of naturally occurring serpentine, antigorite and lizardite. The magnesium oxide content in the materials varies around 40% (O'Connor *et al*., 2001a; Dahlin, 2000).
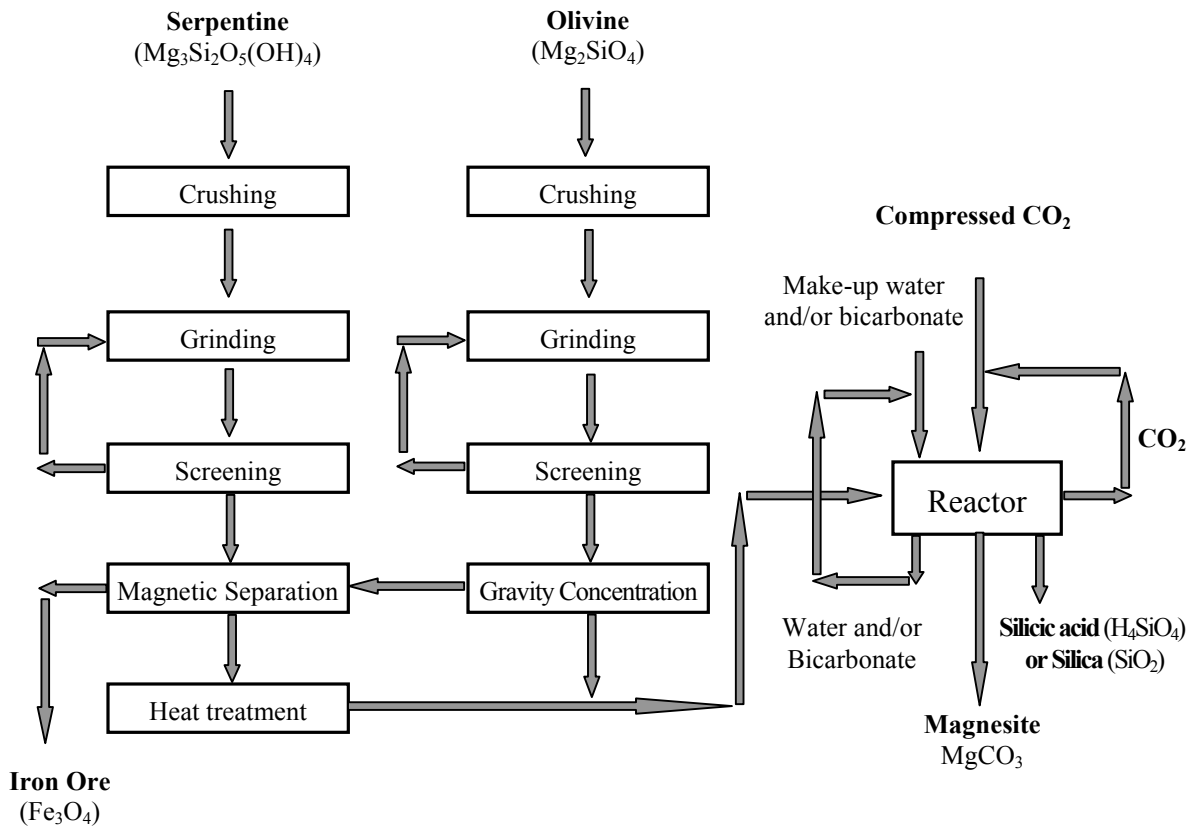
28

Figure 4-2 Process Flow Diagram for the Direct Aqueous Carbonation Process
(Source: O'Connor *et al*., 2000a)

Methods

The initial proof-of-concept tests were conducted with 5-g samples in 20 ml of distilled water in 45ml stainless steel autoclaves in an oil bath to maintain temperature and magnetic stir bars for agitation (Dahlin *et al*., 2000). The tests were then scaled up to use a 2-liter Hasteloy C autoclave with agitation, and process parameters were monitored and recorded continuously. In the carbonation test, a slurry of olivine or serpentine minerals along with certain amount of water and/or other additives are poured into the autoclave. The system was purged with CO_2 and agitated with mechanical stirrer. Then the autoclave was heated to the desired temperature (typically 185°C for olivine and 155°C for serpentine). After allowing some time for heat up to the operating temperature, CO_2 was injected for carbonation using a CO_2 gas booster pump. The pressure was continuously monitored and more CO_2 was injected if the pressure decreased either due to leaks or chemical reaction. At the end of the desired test time the stir rate was decreased and the slurry was cooled by running water through cooling coils in the solution. When the temperature fell below 85°C, the pressure was bled off and the slurry removed through a valve in the bottom of the autoclave. The slurry was filtered and dried at 105°C, weighed, and sampled for analysis (O'Connor, *et al*., 2000a, c, 2001b; Goldberg *et al*., 2002).

Carbonation results

In mineral sequestration, the most challenging task is to accelerate overall reaction rates. Since the foundation of MSWG in 1998, great progresses have been made in aqueous mineral sequestration rate. These progresses include pretreatment of minerals, enhancement

of carbonation reaction, understanding of reaction mechanism and engineering design assessment to achieve dramatically shortened carbonation reaction time.

At the initial development stage, tests conducted at ambient temperature (22°C) and subcritical CO_2 pressures (below 73 atm) resulted in an extremely slow carbonation or no carbonation (O'Connor et al., 2000a,c). When the temperature and pressure were increased to supercritical CO_2 condition, the rate of conversion to carbonate was increased. The process 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 size range of 75-100 micron (Goldberg, 2001). However, the carbonation rate is till very low in term of the possible commercial sequestration application. Then, MSWG researchers made careful control of solution chemistry (using a bicarbonate solution) and achieved roughly 83% conversion of heat treated serpentine and 84% conversion of olivine to the carbonate in 6 hours (O'Connor et al., 2000a). Later on, optimum results were achieved using heat pretreated serpentine feed material, with a surface area of roughly 19 m^2 per gram, and high partial pressure of CO_2 (P_{CO_2}). Specific conditions include temperature of 155°C, partial pressure of CO_2 185 atm and concentration of 15% solids. Under these conditions, 78% stoichiometric conversion of the silicate to the carbonate was achieved in 30 minutes (O'Connor 2001b). The details of the effects of the process parameters on the conversion from silicate to carbonate are discussed in Section 4.3.3.

According to Goldberg and Walters (2002), WSWG will complete Design of the 5 ton/hr Demonstration scale unit in FY 2006 and construction will begin. Construction of the

demonstration scale carbonation system should be completed in fiscal year 2007 and operation will begin. Data enabling full scale design will be collected and a performance assessment will be initiated. The MSWG scale of activities and the associated timeline and tasks are summarized in Table 4-1.

Table 4-1 MSWG Activities and Tasks Timeline (Goldberg and Walters, 2002)

Scale of Activity	Tasks	Timeline
Laboratory - Batch operation, gram quantities	Examine Kinetics, Mechanisms, Feedstocks, Role of impurities, and Pretreatment options	Fiscal Years 2003-2005
Bench – Continuous operation at 5lb/hr	Study multiple concepts, Semi-integrated pre- & post –processing, Materials issues, Heat transfer, and solid & liquid flow effects.	Fiscal Years 2003-2004
Engineering Development – Continuous operation at 500 lb/hr mineral input	Focus on system integration, concept validation, reliability, efficiency & cost characteristics.	Fiscal Years 2004-2005
Demonstration – Continuous operation at 5 tons/hr mineral input	Examine site issues, relevant reliability, byproduct handling and efficiency, and cost characteristics	Fiscal Years 2006-2008

4.3.3 Pathways to enhance mineral sequestration

Carbonation rate is the biggest challenge in mineral sequestration. It is not only the key to reduce the energy consumption, but also the necessity for this process to be commercialized. Thus, most research strives, including aqueous mineral sequestration, are concentrated in looking for the pathways to enhance the conversion of silicate minerals.

(a) Increasing the surface area of magnesium silicates

Basically, the mineral carbonation process is a liquid-solid reaction. Thus, the reaction rate not only depends upon the activity of species in the system and the reaction conditions, but also depends upon the surface area of the reactants. Large surface area of solids offers a high possibility of contact, and hence a high reaction rate. Therefore, the surface area, and thus the particle size, of the silicate minerals is recognized as a major factor determining the reaction rate and the extent of carbonation. The effect of particle size of olivine on the extent of reaction is shown in Figure 4-3 (O'Connor *et al.*, 2000a). It can be seen that the decreasing particle size dramatically improves extent of reaction. For minus 37 microns olivine feed, the extent of reaction is increased to over 90%.
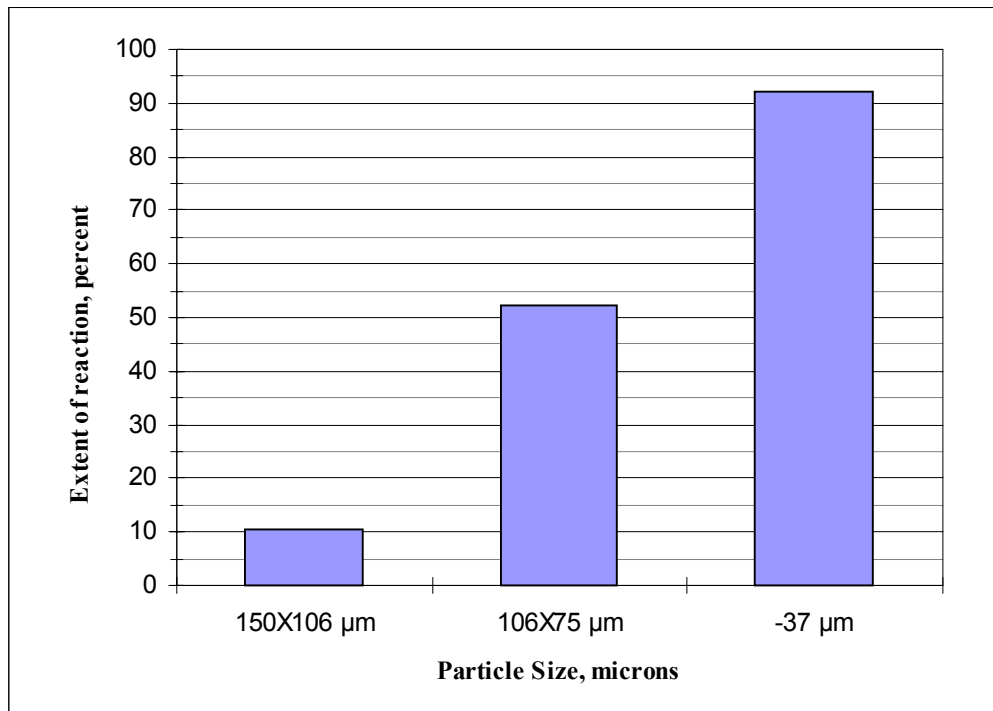

Figure 4-3 Effect of Particle Size on the Olivine Carbonation Reaction
(Source: O'Connor *et al.*, 2000a)

Fine particles are produced by grinding and/or ultrafine grinding processes with various comminution units. Gerdemann *et al*. (2002) studied the effect of particle size on the extent of reaction by using different grinding equipment, such as ball mill, attrition mill and METSO stirred media detritor (SMD). The carbonation results at 185 °C and P_{CO_2}=150 atm are listed in Table 4-2. It can be seen that smaller particle size greatly helps the conversion process. Also, we can see different grinding mechanisms have various effects. In terms of extent of reaction, attrition mill is better than METSO SMD mill and ball mill.

Table 4-2 A Comparison of the Extent of Reaction in One Hour[1]

(Source: Gerdemann *et al*., 2002)

	Size, μm	Extent of reaction[2] %
Head – Twin Sisters Olivine	-100	24
METSO SMD milled at 70 k.Wh/t	6.4	41
METSO SMD milled at 150 kAWh/t	3.1	57
Ball milled dry 1 hour	-	29
Ball milled wet 1 hour	-	42
Attritted dry 1 hour	4.3	77
Attritted wet 1 hour	1.9	83

1 Carbonation conditions: 185°C, P_{CO_2}=150 atm, 15% solids
2 Based on magnesium content

In fact, fine grinding not only creates large surface area, but increases the reactivity of ground powders, which is known as mechanochemical effects (Gutman, 1994). The grinding process can increase the imperfection of crystals or even produce a non-crystalline material, which is significantly more active (Gerdemann *et al*., 2002). The above improvement of carbonation performance cannot contribute solely to the size effect. Mechanochemical effect may also play a part. On the other hand, fine grinding means more energy consumption

during the pretreatment of silicate materials. However, this energy can be offset by the subsequent carbonation process. Therefore, compromise need to be made on the particle size and extent of carbonation concerning the whole sequestration process.

(b) Control of the process temperature

Another pathway to accelerate the carbonation rate is to control the temperature of reactor systems. Figure 4-4 shows the effect of temperature on the extent of reaction for olivine with one hour of carbonation time under similar conditions. It can be seen that the rise of temperature increases the extent of reaction when the temperature is lower than 185°C. Above 185°C, the extent of reaction decreases. From the viewpoint of energy saving, the temperature should be as low as possible. Thus, the appropriate temperature is below 185°C, which matches the temperature of 155°C of the optimum carbonation result (O'Connor, 2001b).
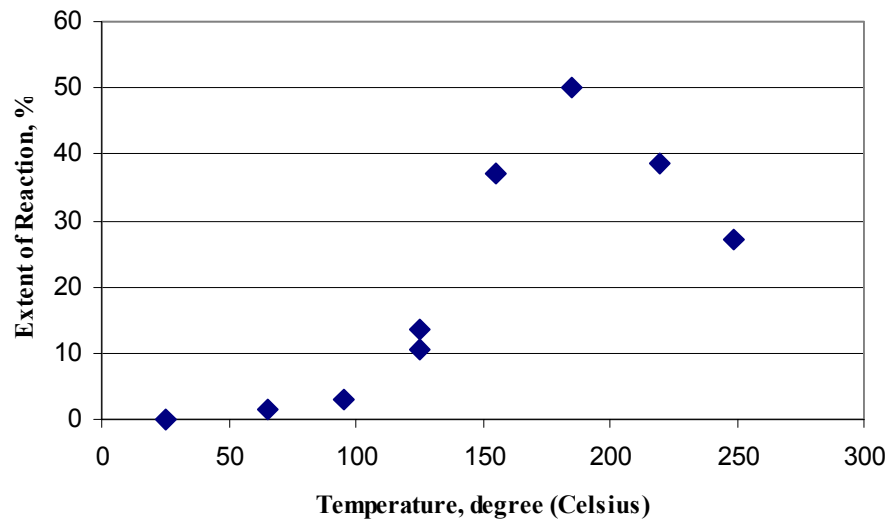
Figure 4-4 Effect of Temperature on Carbonation of Twin Sisters Olivine at 185°C
(Source: O'Connor, 2001b)

(c) Control of process pressure

From the perspective of chemical reaction, increasing pressure is expected to improve the extent of carbonation. Effect of pressure on the extent of reaction is shown in Figure 4-5 (Dahlin *et al.*, 2000). It indicates a high temperature does improve the reaction rate. The extent of reaction at 155°C is nearly the same in 30 minutes at P_{CO_2}=185 atm as it is in one hour at P_{CO_2}=150 atm. However, when P_{CO_2} is increased to 220 atm, no improvement is found in the extent of reaction. Pressure increase has the same problem as temperature for the mineral sequestration, i.e. the increase in the extent of reaction at higher pressures may not justify the additional costs that higher pressures imply.
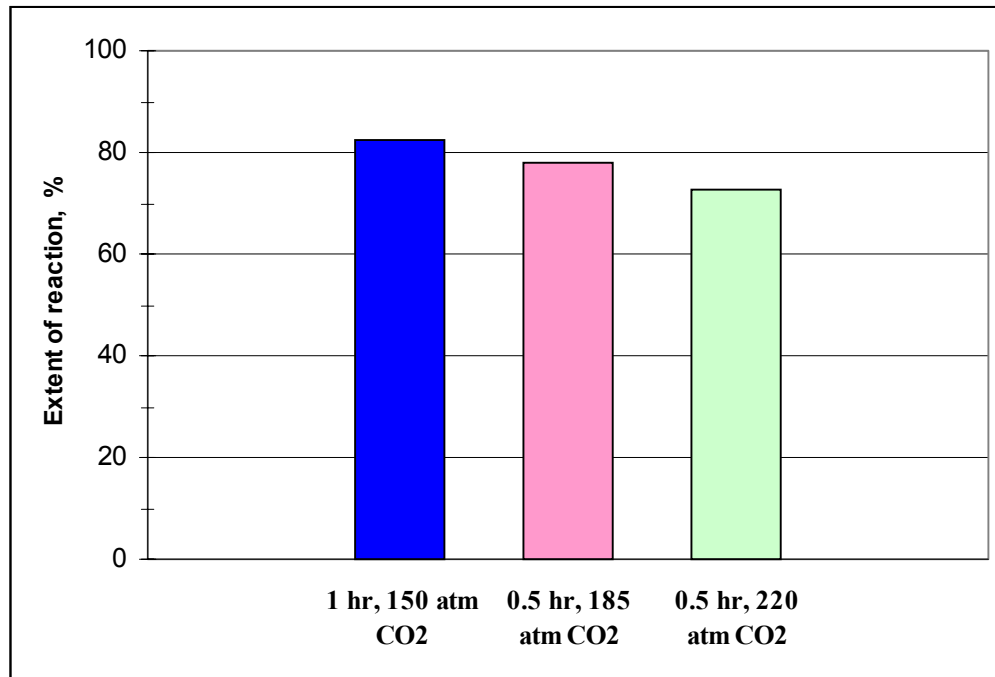
Figure 4-5 Effect of Pressure and Time on Extent of Reaction (Dahlin *et al.*, 2000)
(Tests were conducted at 155°C in 0.64M NaHCO$_3$/1M NaCl solution.)

(d) Control of solution chemistry

Aqueous carbonation is affected by solution chemistry and pH of the suspension. The extent of reaction is dramatically improved when a bicarbonate/salt solution was used instead of distilled water (O'Connor *et al*., 2001b; Dahlin *et al*., 2000). The effect of pH and ion species on the extent of reaction is shown in Figure 4-6 (Dahlin *et al*., 2000). It indicates that the solution with a pH value at in the range of weak alkaline (7<pH<11) has a better carbonation result. Acid systems and highly alkaline systems provide poor results. It also shows both sodium bicarbonate (NaHCO$_3$) and sodium chloride (NaCl) contribute to the improvement of reaction.
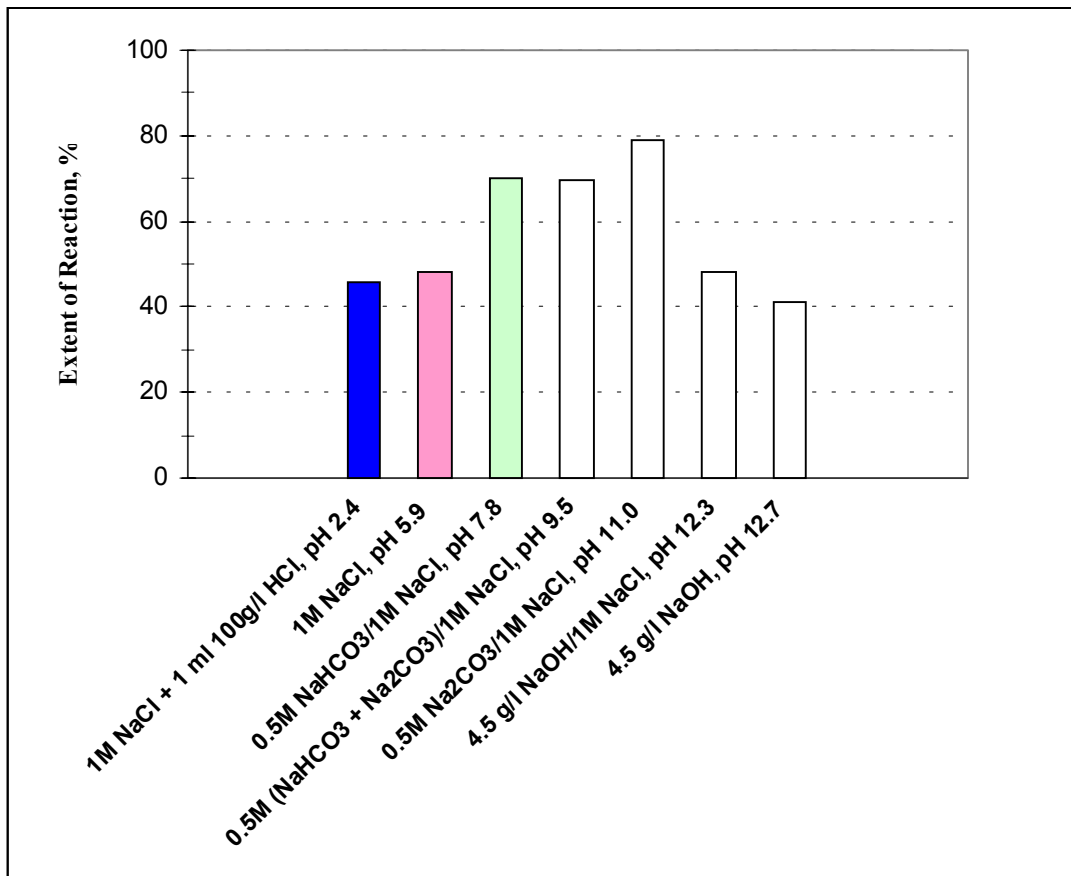
Figure 4-6 Effect of Solution Chemistry and pH on Extent of Reaction
(Tests were conducted for 3 hours at 185°C and 115 P$_{CO_2}$. Dahlin *et al*., 2000)

(e) Pretreatment

Pretreatment of magnesium bearing minerals has been tested by MSWG researchers to explore the rapid carbonation route. Figure 4-7 shows heat treatment in the air or in CO_2 improves the carbonation extent of serpentine (O'Connor *et al.*, 2001b). The effect of the heat treatment atmosphere on the serpentine carbonation reaction was minimal for the carbonation tests conducted in distilled water, although heat treatment in general improved the extent of reaction from 34% to over 57%. However, the effect of the heat treatment atmosphere was significant for the carbonation tests conducted in the modified solution chemistry (0.5 M $NaHCO_3$, 1 M NaCl). Extent of reaction increased to over 83% for the serpentine heat treated in CO_2, compared to 41% extent of reaction for the serpentine heat treated in air; both of these results were achieved in just 6 hours.

Figure 4-7 Effect of Heat Treatment on the Serpentine Carbonation Recation in Two Series: (1) 24h, T=185°C, P_{CO_2}=115 atm, in distilled water; (2) 6h, T=185°C, P_{CO_2}=115 atm, in 0.5M $NaHCO_3$ 1M NaCl. (Source: O'Connor *et al.*, 2001b)

4.4 Integrated carbonation

From the previous sections, it can be seen that current mineral carbonation studies using serpentine or olivine minerals require pulverization of the raw minerals, long reaction times and high partial pressures. Consequently, in order for mineral carbonation to become a vi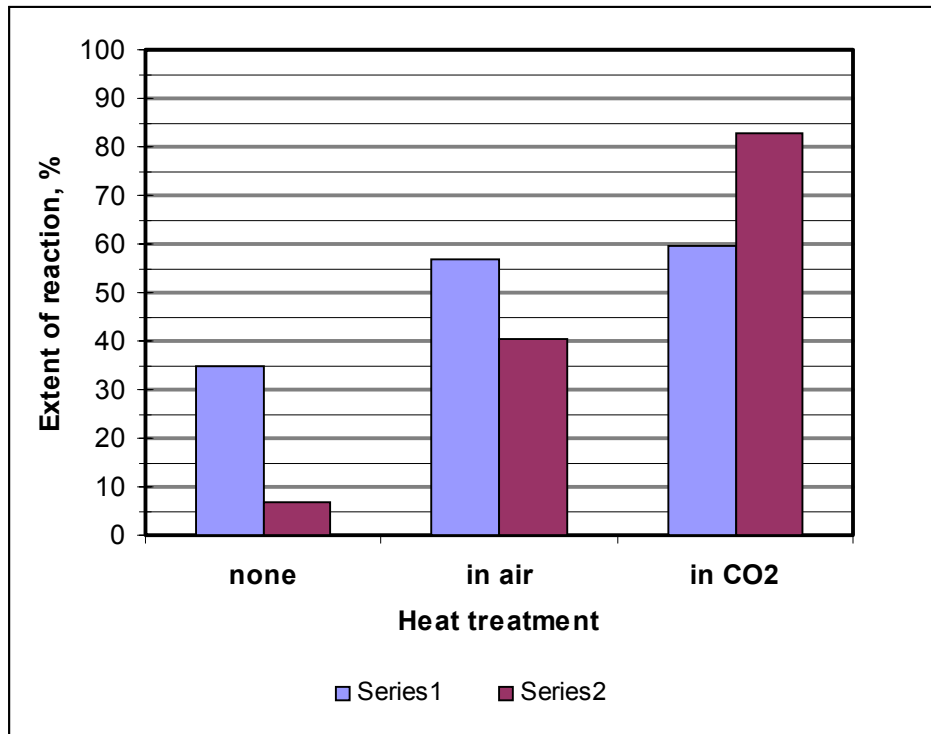able cost effective sequestration technology, it is necessary to explore innovative development of fast reaction routes in a continuous process. The studies of Maroto-Valer *et al*. (2001, 2002) at PSU are focused on the development of an active carbonation process that can promote and accelerate reaction rates and efficiencies through surface activation to the extent that extensive mineral particle communition and CO_2 capture from flue gases are not required prior to sequestration, which is called integrated carbonation. It combines the processes of pulverization, CO_2 capture, activation treatment and carbonation.

Experiment and results

Surface activation studies were conducted on a serpentine sample to promote its inherent carbonation reactivity via physical and chemical activations. The physical activations were performed using steam, while the chemical activations utilized various acids at room temperature over a time period of ~24 hours. The SEM studies show that the activated sample presents more needle-like particles than the raw material and the structure of the activated serpentine had been significantly altered. Maroto-Valer *et al*. (2002) concluded that it is possible to increase the surface area of the serpentine minerals to $330 m^2/g$, compared to only $~8 m^2/g$ for the raw serpentine. Chemical activation seems to be the preferred method to increase the surface area, while physical activation is the preferred

method to reduce the weight loss. However, no results on the carbonation experiments using the activated serpentines were reported yet.

4.5 *In-situ* carbonation in geologic formations

In all carbon sequestration approaches, storage of CO_2 in geologic formations, such as deep saline aquifers, is one of the most promising methods and is receiving considerable attention (van der Meer, 2002). One of the mechanisms of geologic formations to trap CO_2 is the carbonation process, which sequesters CO_2 in solid minerals. In the deep saline aquifer (>1000m), there are various solubles because of the mineral dissolution in the wall rocks. It can be expected that injection CO_2 into the huge water body can cause various geochemical reactions. These reactions may include the carbonation that forms the stable calcium, magnesium, and iron carbonates that are solids and will be stored permanently in the formations (DOE, 1999). The minerals necessary for the formation of these carbonates are abundant in saline brine formations, which are widely spread across the United States (Andresen *et al*., 2002). Thus, carbonation during geologic storage of CO_2 can be regarded as *in-situ* mineral sequestration.

Andresen *et al*. (2002) studied the kinetics of mineral carbonate formation using high-pressure thermogravimetric analysis that mimics the actual conditions found in saline brine formations. The transformation of gaseous CO_2 into stable carbonates was investigated at various pressures and temperatures. When pressures are between 200 and 600 psi and

temperatures are between 50 and 75°C, the uptake of CO_2 is about 0.9-1.1% of solids. The experiment conditions are common to the aquifers attainable for CO_2 injection.

McGrail *et al*. (2002) studied the mineral trapping in basalt formation for geologic sequestration. Basalt is rich in Ca, Mg, and Fe, and under the proper conditions of groundwater pH, temperature, and pressure, injected CO_2 will react with iron released from dissolution of primary minerals in the basalt to form stable carbonate minerals. Conversion of CO_2 into solids was confirmed in laboratory experiments with supercritical CO_2 in contact with basalt samples from Washington State.

Bruant Jr. *et al*. (2002) conducted the study on the effects of pressure, temperature, and aqueous solution chemistry on rates and mechanisms of silicate mineral dissolution and carbonate precipitation. A high pressure/high temperature flow-through reactor system is used for macroscopic determination of steady-state forsteritic olivine dissolution rates. The system allows continuous monitoring of temperature, pressure, and pH, and periodic sampling of effluent fluids for dissolved ion concentration determination. The extent of olivine dissolution in batch reactors increases with increasing temperature, P_{CO_2} (i.e., decreasing pH), and surface area.

4.6 Biomineralization with fly ash

Biomineralization processes utilize the biological process to sequester CO_2 in carbonate solids. Roh *et al*. (2001) at Oak Ridge National Laboratory (ORNL) conducted this study to examine biogeochemically facilitated carbonate precipitation processes using metal-rich fly

ash in the presence of different atmospheres (N_2, N_2-CO_2, and H_2-CO_2) as well as in HCO_3^- buffered media (30 - 210 mM).

The Fe(III)-reducing bacteria and metal-rich fly ashes were used to examine microbially facilitated precipitation and mineral formation into soluble carbonate minerals such as calcite ($CaCO_3$) and siderite ($FeCO_3$). Chemical analysis of water-soluble metals in the culture media with TOR-39 organisms after incubation and the control system is shown in Figure 4-8. TOR-39 organisms use glucose, lactate, formate as electron donor for growth. It reveals that the leaching of Ca and Fe from fly ash was significantly reduced in the presence of a H_2-CO_2 atmosphere (Roh *et al.*, 2001). XRD and SEM analysis verify the formation of carbonate minerals. Studies also show that the atmosphere and bicarbonate buffer concentration in conjunction with biomineralization processes have profound influences on the types of minerals and the rate of carbonate mineral precipitation.

4.7 Zero Emission Coal Alliance (ZECA) process

The Zero Emission Coal Alliance (ZECA) was formed in 2000 (Jia and Anthony, 2002) and it consists of 18 members from private industry and government agencies, mainly from Canadian and United States. The objective of ZECA was to pursue a novel technology concept for the generation of electricity and/or hydrogen from coal with zero atmospheric emissions and high efficiency, while producing a stream of high-purity CO_2 which would be sequestrated as a mineral carbonate (Ziock, 2001; Zoick and Lackner, 2000). The overall ZECA process is shown in Figure 4-9 (Jia and Anthony, 2002).
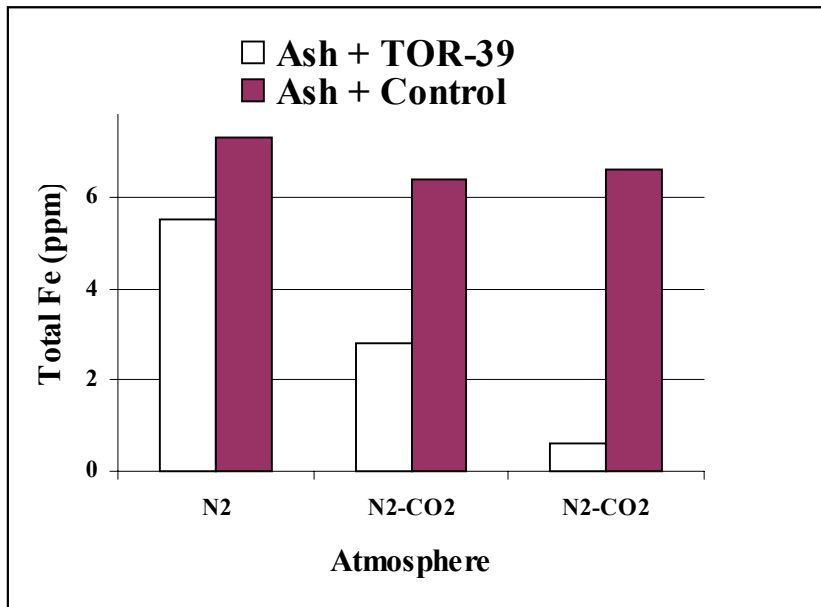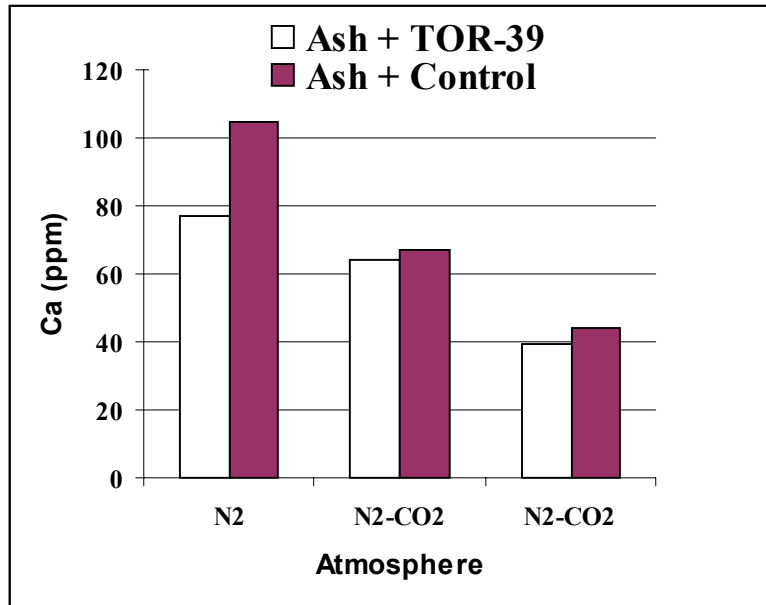
Figure 4-8 Water Soluble Ca and Fe after Microbial Precipitation and Mineralization Process Using Fly Ash (Above: ORNL steam plant fly ash (90%) + lime (5%); Below: Johnsonville fly ash) (Source: Roh *et al.*, 2001)
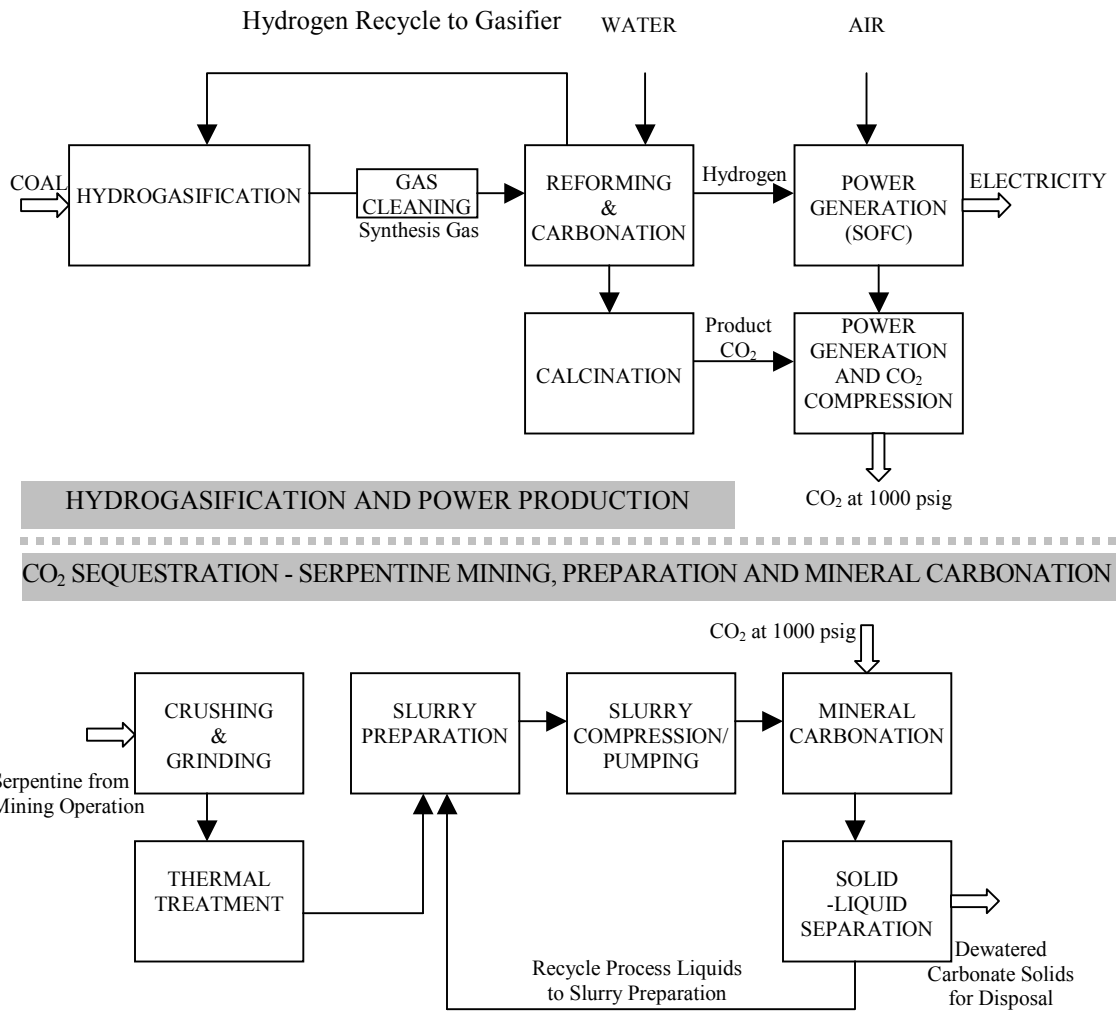
Figure 4-9 ZECA Process (Source: Jia and Anthony, 2002)

ZECA process combines the generation of electricity, capture and separation of CO_2, and mineral sequestration. It is made up of two main parts. The first part in Figure 4.9 includes coal gasification, CO_2 separation and power generation. The second is the mineral sequestration of captured CO_2. In this process large quantities of serpentine minerals are mined, finely ground and heat-treated (600°C, 30 min). Carbonation of the processed mineral is performed at high pressure, and results in finely precipitated solids, which are separated from the liquid. The liquid is returned to the process and the solids are sent to a final disposal area (Jia and Anthony, 2002).

It is to note that, basically, the mineral sequestration part in ZECA process in Figure 4-9 is the aqueous sequestration method. According to Jia and Anthony (2002), experiments were conducted to test a number of magnesium silicate rocks mined in Canada. Three methods were used to carbonate the minerals: pressurized thermal gravimetric analyzer (PTGA), pressure bomb (2 liters by Parr), and ultrasound irradiation.

Experiments indicate that carbonation of magnesium silicate minerals in gas-solid systems was extremely slow and application of ultrasound irradiation in mineral slurry does not accelerate the reaction to any significant level. Carbonation within pressure bomb in NaCl and NaCl/$NaHCO_3$ solutions can result in 40-80% Mg being converted to carbonate at pressure of 12 MPa (Table 4-3). Carbonation results also show that different types of magnesium silicate minerals carbonated very differently. In general serpentines were the easiest to react and peridotite was the most difficult to carbonate.

Table 4-3 Parr Bomb Experiment Results (temperature 155 °C)

(Source: Jia and Anthony, 2002)

Test	Sample	Solution	Pressure MPa	CO_2 wt%	Mg utilization, %
10201-1	Heat treated serpentine #1010	Water	6	3.08	5.95
10201-2	serpentine #1010	Water	6	1.83	4.09
10125-1	Heat treated serpentine #80F	Water	12	1.43	3.03
10208-2	Heat treated serpentine #1010	1 M NaCl	12	14.0	30.5
10214-1	Heat treated serpentine #80F	1 M NaCl	12	1.68	3.57
10221	serpentine #1010	1 M NaCl	12	5.3	12.30
10226	Heat treated serpentine #1010	1 M NaCl	12	28.5	74.59
10322	Heat treated serpentine #80F	1 M NaCl	12	17.8	45.57
10611	Heat treated serpentine #1010	1 M NaCl	12	4.47	12.17
20314	Heat treated serpentine #1010	1 M NaCl and 0.5 M $NaHCO_3$	12	27.66	78.48
20315	Heat treated serpentine #80F	1 M NaCl and 0.5 M $NaHCO_3$	12	17.83	45.60
20316	Heat treated serpentine #1010	1 M NaCl and 0.5 M $NaHCO_3$	12	30.12	85.81

CHAPTER 5   EVALUATION AND ASSESSMENT

5.1 Carbonation approach assessment

A variety of carbonation pathways have been proposed and tested for mineral sequestration with the aim to achieve the rapid carbonation and reasonable sequestration costs. A great amount of research work has been done and progresses have been made in various mineral sequestration approaches. All the mineral sequestration processes are in the stage of laboratory scale development. Toward the goal of commercialization of mineral sequestration, much more work is needed in every aspect, such as process improvement, scaling up, demonstration and pilot test etc.

5.1.1 Chloride based mineral sequestration

For the chloride based carbonation, thermodynamic calculation shows the process is possible and LANL conducted experiments to demonstrate the process. They concluded that carbonation would be virtually completed in less than 30 min at pressure of 50 bar and temperatures of 500 to 600 °C or at even lower temperature and pressure. Their economic estimation shows that \$15/ton CO_2 is a reasonable goal for the cost of the mineral sequestration (excluding CO_2 capture and transportation) (Lackner *et al*., 1998). However, compared with other methods, the chloride based carbonation process is complex. This process includes $MgCl_2$ extraction from magnesium silicates, HCl recovery and carbonation

etc. Thus, the operation of this process is more difficult than that of other methods. Also, this process involve corrosive conditions (mainly HCl), which may create materials issues that must be addressed prior to an industrial implementation (Guthrie *et al.*, 2001). Since the mineral sequestration must be carried out in large scale, it is reasonable to assume that the rocks for carbonation contain certain amount of impurities. These impurities are expected to increase the chlorine consumption in the reactions and take some chlorine (mainly as ions) away from the process in the final products. This means extra chlorine source is needed, and cause extra sequestration cost. Another issue concerning this process is its reaction conditions of high temperature and pressure. Unquestionably, this consumes more energy. Although the LANL claimed that heat emitted from exothermic reactions can be used for the process, how to collect the energy and how to use it in the process are uncertain.

5.1.2 Direct dry carbonation

Direct dry carbonation was developed at Helsinki University of Technology (Zevenhoven and Kohlmann, 2002). Zevenhoven and Kohlmann claimed that the only option of carbon sequestration for Finland appears to be mineral carbonation, because Finland does not have deep oceans or exhausted oil or gas fields, and improved forestry, biofixation and utilization of CO_2 also do not have enough capacity. However, their experimental results of this method are far from optimistic. Experiments with serpentine with direct dry method shows almost no carbonation occurs. Therefore, for this method, much more work is needed to understand this process and to test its feasibility. Because the process is straightforward, any breakthrough in the future can be expected to bring promise to this method.

5.1.3 Direct carbonation in aqueous solutions

This approach is the major focus of mineral sequestration in United States. Great progresses have been made by MSWG since 1998 (Goldberg and Walters, 2002). The systematic research work led to understanding of the process and the parameters affecting the carbonation rate. The pathways to enhance carbonation were explored, such as increasing the surface area of silicate minerals, control of temperature and pressure, solution chemistry control and pretreatment of reactants. The encouraging result is obtained at 78% conversion of silicates to carbonates within 30 minutes in bicarbonate solutions at 155°C and P_{CO_2} 185 atm with pretreatment serpentine. Thus, this process is the most promising mineral sequestration method.

However, there are still some challenges to be addressed in order to successfully develop and demonstrate a commercial process. The rapid carbonation rate is achieved by pretreatment of silicate minerals at high temperature and pressure for hours. Since heat treatment demands high energy consumption, it may make the subsequent rapid carbonation costly. Further research work is needed to reduce the mineral pretreatment severity, so that the energy requirement for the overall process will be lower and acceptable. Also, all the aqueous carbonation experiments were carried out at high pressures (150 atm). High pressure requires high energy input and the sequestration cost, and it causes difficulty in the process operation. Other issues may include how to use the heat emitted from the system during carbonation,

and the treatment of the carbonate products after reaction, such as dewatering or exploring their application to offset the carbonation costs.

5.1.4 Integrated carbonation

The concept of this approach was proposed by Maroto-Valer *et al*. (2001, 2002). It is an innovative idea since it combines the processes of pulverization of mineral rocks, CO_2 capture, activation treatment and carbonation, and most of the processes are energy intensive. Only some basic experiments were conducted to test the effects of physical and chemical activations on the structure and surface of silicate minerals. No actual carbonation results were reported. Also, in the chemical activation method, Maroto-Valer *et al*. (2002) reported two acids were used, but they did not reveal the composition of the acids. Since mineral sequestration process is expected to have a relatively high capacity, the large amount of acid consumption of this approach could be high. So we can only say this approach is still in the conceptual stage.

5.1.5 *In-situ* carbonation in geologic formations

In the geologic formations, there are various soluble mineral species because of the mineral dissolution in the wall rocks. The carbonation in geologic formations is naturally occurring under some pressure and temperature conditions. The studies of *in-situ* mineral sequestration can help understand the geologic sequestration process, such as geochemical reactions and sequestration permanence, etc. In geologic sequestration of CO_2, one of the main concerns is

the possible leakage of CO_2. *In-situ* carbonation will converse CO_2 into calcium, magnesium and iron carbonates permanently in solids, thus it helps address the leakage problem. In the laboratory scale carbonation tests, the studies have verified this conversion under the conditions similar to the geologic formations. Whether *in-situ* carbonation will proceed forever depends on continuation of the dissolution of silicates from the wall rocks. It is observed that scales of calcium and magnesium carbonates are deposited on the wall of boiler after a period of operation using natural water from rivers or lakes. If the similar case happens in the geologic formations, it is reasonable to predict that, after certain period of time, there will be a layer of carbonate sediment coated over partial or the whole walls of geologic formations. This layer of carbonate sediment might prevent the silicate minerals from dissolution and thus prevent the further *in-situ* carbonation. Under this hypothesis, *in-situ* carbonation may be slowed down or may not be significant in the storage of CO_2 in geologic formations.

5.1.6 Biomineralization with fly ash

This approach deals with two industrial byproducts, CO_2 and fly ash, in one operation by the biological process, which makes it have double environmental credits. This characteristic makes it distinct from other mineral sequestration approaches. Preliminary tests using different Fe(III)-reducing bacteria show that formation of carbonate minerals occurs in 25°C at different cultures after 21-30 days of incubation. It is a promising method to converse silicates to carbonates. Clearly, however, more research work is needed to assess its carbonation rate, sequestration potential and related costs. Fly ash is the main solid byproduct

at power generation plants using fossil fuels such as coal. The biomineralization product can be disposed in the abandoned mines. This process can be an attractive option for the regional or local mitigation of CO_2 emissions.

5.1.7 Zero Emission Coal Alliance (ZECA) process

ZECA process is an all-around solution to the CO_2 emission and usage of fossil fuels as energy source by leading the development and demonstration of ultra-clean, highly efficient and competitive Zero Emission Technologies. It includes power general, CO_2 capture and mineral sequestration.

Basically the mineral sequestration in ZECA process is aqueous carbonation. Carbonation within pressure reactor in NaCl and NaCl/NaHCO$_3$ solutions can result in 40-80% Mg being converted to carbonate at pressure of 12 MPa. Other issues concerning aqueous carbonation have been discussed in the Section 5.1.3.

5.1.8 Summary

Clearly, all the attempts above have some advantages and limitations in the mineral sequestration technology. Although progress was made in some methods and some approaches have very good idea, none of the carbonation approaches has yet demonstrated sufficient technological basis for a commercial mineral carbonation process. *In-situ* carbonation may help geologic sequestration of CO_2. However, it is less likely that human

can interfere with the process in the geologic formations. More additional work is needed for all scenarios. Among them, direct carbonation in aqueous solutions (including the mineral sequestration part in the ZECA process) received more attention and was studied more sufficiently. It is the most promising approach and MSWG plans to design and construct a mineral sequestration demonstration plant in FY 2008, which can dispose of 5 ton/hr silicate minerals.

5.2 Mineral sequestration capacity and environmental issue

Mineral resources which can be used to sequester CO_2 in minerals are widely distributed globally. According to Goldberg *et al*. (2001), raw materials which can bind CO_2 in solids exist in vast quantities worldwide and readily accessible deposits even exceed the most optimistic estimate of coal reserves. In US, the eight example ore bodies have the potential to sequester the equivalent of approximately 11 years of current world CO_2 total emissions (See Section 3.4). Thus, many investigators claimed sufficient mineral reserve is one of the advantages of mineral sequestration (Goldberg *et al*., 2001; McKelvy *et al*., 2001).

However, sufficient mineral resources are only one side of the problem. As for the huge CO_2 emissions annually, many operations, including mining, crushing and grinding, transportation, pretreatment and carbonation operations, are necessary for completion of mineral sequestration. All these operations are energy-related, which may also create other related environmental problems.

In order to assess the potential of mineral sequestration and its related environmental concern, some calculations of mineral consumption are made. According to Energy Information Administration (EIA) of US DOE (EIA, 2001), the total CO_2 emissions from use of fossil fuels is 1,565 million metric tons carbon equivalent (1.565 GtC) in US in 2001. If 10% of this amount of CO_2 emission is to be sequestered each year by mineral sequestration with serpentine as raw material, according to Reaction (2) in Section 2.2, the theoretical serpentine consumption can be calculated based on the stoichiometric coefficient as follows:

Theoretical Consumption of Serpentine

$$= \frac{277.1g \, serpentine / mol \, serpentine}{44g \, CO_2 / mol \, CO_2} \times \frac{1mol \, serpetnine}{3mole \, CO_2} \times \frac{44g \, CO_2 / mol}{12g \, C / mol} \times 1.565 \text{GtC/year} \times 10\%$$

=1.205 Gt serpentine/year

The candidate serpentine deposits for mineral sequestration contains 35-45% MgO, which means the purity of serpentine ores is about 90%. According to current mining operation practice for similar ores, recovery of mining is selected at 90%. Based on current mineral sequestration studies, silicate conversion ratio of 80% can be achieved. According to these data, the actual serpentine consumption can be calculated as follows:

Actual Consumption of Serpentine

$$= \frac{1.205 \text{Gt Serpentine/year}}{(90\%)*(90\%)*(80\%)}$$

=1.860 Gt Serpentine /year

Considering the size of modern mining equipment and in order to take the advantage of the available economies of scale, the mining capacity of a serpentine mine is set at 50,000 ton/day (18.25 million ton/ year or 0.01825 Gt/year). Then the number of this kind of mines can be calculated to handle 1.860 Gt Serpentine /year.

$$\text{Number of serpentine mines}$$
$$= \frac{1.860\,\text{Gt serpentine/year}}{0.01825\,\text{Gt serpentine/year}}$$
$$= 102$$

The above calculations show that, to sequester 10% of CO_2 emissions from fossil fuels in US, 102 serpentine mines with a production capacity of 50,000 t/day must put into operation, especially for mineral sequestration. Considering the energy consumption in mining, grinding the ore into tens of microns, and transportation, a great amount of CO_2 emissions can be expected during the mineral preparation operations of mineral sequestration. These mines under operation might also cause other environmental problems, similar to those that current mining facilities are facing, such as landscape damage, erosion, noise, dust, possible heavy metallic ion exposure and water pollution etc. It is to note that the above calculations do not include the CO_2 capture and separation, which will cause extra CO_2 emissions. Therefore, sufficient mineral reserve does not necessarily mean a high sequestration potential. In order to fully exploit the potential of mineral sequestration, related environmental consequences should be addressed.

5.3 Thermodynamics versus full scale operation

The thermodynamic calculation shows that mineral sequestration reactions are exothermic and certain amount of energy will be released during carbonation process. However, thermodynamic calculation does not guarantee the practical process energy-favorable. For a full scale process, reaction kinetics is very important. Much more work is needed to explore the pathways to enhance the reaction rate for full scale process.

Also, since mineral sequestration reaction is exothermic, many investigators expected that it can proceed without an external supply of energy, or the energy released can be used for other purposes, so that it can save the energy consumption related to mineral sequestration. However, all of the studies show extra energy input is a necessity and no studies are reported on how to collect and utilize this released energy efficiently during carbonation yet. In fact, improving energy efficiency is a technological challenge for power generation in decades. The energy efficiency of power plants worldwide is around 31% and state-of-the-art coal fired plants operating on super-critical steam cycles have efficiencies of about 47% (Audus, 1999). According to Bauer (2001), the efficiencies of some new power generation systems, such as Integrated Gasification Combined Cycles (IGCC) and Natural Gas Combined Cycles (NGCC), are expected to reach 52% and 58% in 2010, respectively. Therefore, the energy released during carbonation might not be able to reuse to a very large extent. It means that the reduction of the energy demand and sequestration cost might not be significant as shown by theoretical analysis.

5.4 Mineral sequestration cost

Since currently there is no mineral sequestration plant in operation and the viable mineral carbonation approach is under investigation, it is difficult to make the cost estimate of mineral sequestration. However, a couple of estimates were reported based on some assumptions. Lackner *et al*. (1998) considered that $15/ton of CO_2 is a reasonable and realistic goal of mineral sequestration cost, excluding CO_2 capture and transportation. This estimation is based on assumption of a successful design that avoids the use of additional energy and a cost of $8/ton CO_2 of the mining, crushing and milling operations. Newall *et al*. (2000) reported the estimation of CO_2 mineral sequestration cost of IEA Greenhouse Gas R&D Program. They estimated that the cost is at $60-100/ton of CO_2 with current mineral sequestration processes. Therefore, the cost estimates are quite different. This is due to the different assumptions and prerequisites. However, the estimate of $60-100/ton of CO_2 is more practical since the assumption of no additional energy input into carbonation system is difficult to achieve for actual sequestration plant. It is to note that these estimates do not include the additional CO_2 emissions associated with implementation of mineral sequestration. Also, the costs of CO_2 capture, separation and transport are not included in these estimates. By comparison with the cost estimates of other carbon sequestration methods, about $15/ton of CO_2 avoided (the CO_2 emission during implementation is subtracted) for storage in saline aquifers (Herzog, 2000) and $5-15/ton of CO_2 for ocean injection (Herzog, 1997). It seems that mineral sequestration with current technology does not have cost advantage with current mineral sequestration technology. Progresses in carbonation are expected to reduce the costs of mineral sequestration.

CHAPTER 6 CONCLUSIONS

Mineral sequestration is a way of permanent storage of CO_2 in solid minerals, which attracts the attention of many investigators to development various carbonation approaches. Great progresses are made in terms of reaction rate, reaction extent and less strict reaction conditions. However, all studies in mineral sequestration are in the stage of laboratory scale. Much more research work is required towards the commercial implementation of mineral sequestration, including laboratory tests, bench continuous operations and demonstration plant. Among all the mineral sequestration approaches, direct carbonation in aqueous solutions is the most promising method.

Mineral sequestration mimics such a natural process as weathering of rocks to bind CO_2 in carbonates. Thermodynamic studies show that mineral carbonation reactions with silicates minerals are spontaneous and exothermic. Thus, mineral sequestration has the potential to be economically viable. However, with respect to a commercial process, a variety of measures are needed to enhance the carbonation kinetics. This is the key technical challenge for all mineral sequestration attempts.

The main minerals that can be used for mineral sequestration in a large scale are serpentine and olivine. Their mineral resources exist in vast quantities worldwide, which show mineral sequestration has sufficient sequestration capacity theoretically. However, calculation shows implementation of mineral sequestration needs a huge material preparation industry to

support, which must consume a large amount of energy and emit additional CO_2, and may cause other related environmental consequences. This might greatly discount the theoretical sequestration capacity.

The mineral sequestration approaches include chloride based mineral sequestration, direct dry carbonation, direct carbonation in aqueous solutions, integrated carbonation, *in-situ* carbonation in geologic formations, biomineralization with fly ash and zero emission coal alliance (ZECA) process. Among them, direct carbonation in aqueous solutions has been studied extentively. Under optimum operation conditions, 78% stiochiometric conversion of silicate to carbonate was achieved in 30 minutes. Various pathways to enhance carbonation include increasing surface area of silicates, controlling temperature and pressure, controlling solution chemistry and pretreatment.

Estimate of mineral sequestration cost based on assumptions differs greatly because no large scale mineral sequestration plant is in operation. However, compared to the cost estimates of other carbon sequestration methods, mineral sequestration with current technology does not have cost advantage.

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