CARBON DIOXIDE SEQUESTRATION: 
CHEMICAL AND PHYSICAL ACTIVATION OF AQUEOUS CARBONATION 
OF Mg-BEARING MINERALS AND pH SWING PROCESS

DISSERTATION

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By

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ABSTRACT

According to the United States Environmental Protection Agency (US EPA), carbon dioxide, the key greenhouse gas, was emitted to the atmosphere from fossil fuel combustion in the United States at nearly 5,788 MMT in 2003, amounting to more than 80% of the total CO₂ emission in the country. The United States is also the world’s largest emitter of carbon dioxide, releasing nearly 25% of worldwide CO₂ emissions. Although policy-makers and the media frequently claim that the effects of elevated atmospheric carbon dioxide levels on global warming are uncertain, there is enough scientific evidence being mounted to support the claim that anthropogenic greenhouse gas emissions are heating the Earth’s surface. In their recent report, the National Academy of Sciences Committee testified that human activities are causing increases in surface air temperatures and subsurface ocean temperature. Thus, to ensure the continued use of fossil fuels, it is essential to reduce CO₂ emissions from fossil fuel conversion plants and stabilize CO₂ levels in the atmosphere. The containment of carbon dioxide involves several steps including CO₂ separation, transportation, and sequestration. This study addresses the sequestration step, employing mineral carbonation. Specifically, mechanistic and kinetic characteristics of aqueous
carbonation of Mg-bearing minerals, which underline the methodology development for mineral sequestration of CO2, were explored.

Mineral carbonation is achieved through mimicry of natural inorganic chemical transformation of CO2, such as the weathering of rocks and dissolution of CO2 in seawater/saline waters to form bicarbonates. This sequestration process presents a safe and permanent method of CO2 containment that is based on chemical fixation of CO2 in the form of geologically and thermodynamically stable mineral carbonates. The total accessible amounts of the Mg-bearing minerals were estimated to significantly exceed the worldwide coal reserves. However, little has been known regarding the fundamental characteristics of CO2-mineral reactions to allow a viable CO2 mineral sequestration technology to be developed.

Screening of mineral samples for their application in the CO2 mineral sequestration scheme identified both olivine and serpentine to be the viable candidates. According to the experimental results, the chemically enhanced aqueous carbonation of serpentine showed promising results. From the investigation of serpentine dissolution in various solvents, it was found that a mixture of 1 vol% orthophosphoric acid, 0.9 wt% of oxalic acid, and 0.1 wt% EDTA greatly enhanced the Mg leaching process of ground serpentine while preventing the precipitation of Fe(III) on the surface of the mineral particles. When this acidic solvent was used for the aqueous mineral carbonation, the overall process was limited by the rates of dissolution of CO2 and dissociation of carbonic acid, rather than the dissolution rate of the mineral.
Next, the effect of the physical activation on the dissolution of serpentine was investigated and a pH swing scheme was developed to improve the overall conversion of the CO₂ mineral sequestration process. Various methods of the surface agitation such as ultrasound, acoustic, and internal grinding were examined for their effectiveness in removing the diffusion limiting SiO₂ layer in order to promote further dissolution of the inner Mg layer of serpentine. It was found that the fluidization of the serpentine slurry with glass beads was most effective in refreshing the surface of the serpentine particles during the dissolution process. Compared to the external attrition grinding, this method is much less energy intensive. It was also found that the mechanical agitation via the internal grinding alone did not enhance the dissolution of serpentine, while the combination of the internal grinding and Mg-leaching solvent resulted in rapid serpentine dissolution.

Using the proposed pH swing scheme, the overall conversion of the mineral carbonation was radically improved. By controlling the pH of the system, three solid products were generated: SiO₂-rich solids, iron oxide and MgCO₃·3H₂O. Since the iron oxide and magnesium carbonate produced were highly pure, these value-added products could eventually reduce the overall cost of the carbon sequestration process. In addition, it was found that the Mg-rich solution prepared during the pH swing process was also effective at removing SO₂ from flue gas. Consequently, there is a potential application of this process for a multi-pollutant control system.

Finally, in order to completely evaluate the proposed mineral carbonation process for the CO₂ sequestration, a life-cycle assessment (LCA) was performed using
an appropriate system boundary. According to the LCA results, a lower reaction temperature is desired, since most of the energy requirement came from heating the reactor. In addition, it was important to identify and ensure the use of three valuable byproducts in order to carry out the proposed carbon sequestration process as a net consumer of carbon dioxide.
To my parents and brothers for their love and support
I would like to express my sincere gratitude to my adviser, Professor Liang-Shih Fan, for his priceless guidance, encouragement, and support throughout this work. His enthusiasm and drive has been a constant source of inspiration. His patience and indulgence gave me ample time and space to mature not only as a researcher but also as an individual. As I stand at the starting point of my career, I truly appreciate experiencing his passion for research and love for his students. I will always carry the pride in my heart knowing I was a member of Professor Fan’s research group.

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CHAPTER 1

INTRODUCTION

Although policy-makers and the media often assert that the effects of increased carbon dioxide levels on global climate are uncertain, there is enough scientific evidence being mounted to support the claim that human activities are heating the Earth’s surface (Oreskes, 2004). According to the National Academy of Sciences report, *Climate Change Science: An Analysis of Some Key Questions*, anthropogenic greenhouse gas emissions are causing increase in surface air temperatures and subsurface ocean temperature (National Academy of Sciences Committee, 2001). Since fossil fuels will remain the main source of energy production for the foreseeable future, it is crucial to reduce carbon dioxide emissions in order to stabilize atmospheric CO$_2$ levels. Geological sequestration, ocean disposal, and biological fixation have been extensively reported in the literature, while mineral carbonation is a relatively new and less explored method of sequestering CO$_2$ – a disposal option that has great potential due to the availability of large quantities of mineral materials.

Predictions of global energy usage trends suggest a continued increase in carbon emissions and rising concentrations of carbon dioxide in the atmosphere unless major
changes are incorporated in the way energy is produced and used. Based on the current trends in CO₂ emissions, it is predicted that future global CO₂ emissions will increase from 7.4 billion tons of carbon (GtC) per year in 1997 to nearly 26 GtC per year by 2100 (US DOE, 2002). The atmospheric concentration of CO₂ rose from 280 ppm in 1800 to 370 ppm in 2000 mainly due to the consumption of fossil fuels (Fankhauser et al., 2001).

One of the more obvious effects of drastic increase of CO₂ in our atmosphere is the greenhouse effect. Greenhouse effect is the warming of earth’s surface from heat trapped in the atmosphere. The principal greenhouse gases resulting from human activities are carbon dioxide, methane, and nitrous oxides. The increased presence of CO₂ along with other greenhouse gases in the atmosphere traps heat radiated by the earth and keeps it from escaping from the earth’s atmosphere resulting in a gradual increase of earth’s surface temperature. Some researchers argue that increased warming of the earth’s surface could lead to the melting of the polar ice caps, which will result in raised water levels and unpredictable climate changes. Even though the effects of increased CO₂ levels in the atmosphere on global climate are uncertain, there is a general consensus that a doubling of CO₂ content could have a variety of serious environmental and ecological consequences in the next century. For example, doubling the CO₂ concentration in the atmosphere reduces the rate of calcium carbonate deposition in coral reefs by 30 to 40 % (Langdon et al., 2000). Most of this rise occurred over the last few decades, and, unless actions are taken, the projected growth over the twenty first century could lead to a doubling or tripling of the pre-industrial
level of CO$_2$ (Lackner, 2003). Unlike for SO$_2$ emission, the total accumulation of CO$_2$
matters rather than the rate of CO$_2$ emission. Oceanic uptake of CO$_2$ can compensate
for some emissions (Archer et al., 1997), but this uptake will collapse once CO$_2$
concentrations in the air are held constant. Oceanic uptake depends on a concentration
gradient in the surface ocean maintained by the currently rising CO$_2$ concentration in
air. At an increased CO$_2$ level in air, the ocean uptake rate will be decreased and with it
the world’s annual emission allowance. In order to stabilize the atmospheric CO$_2$ level,
emissions have to be reduced by several factors. As a result, the world’s per capita
emission would have to be a factor of ten to thirty smaller than current per capita levels
in industrial countries (Schimel et al., 1995). Stabilization of CO$_2$ concentrations in the
atmosphere either requires abandoning fossil energy or capturing and storing most, if
not all, CO$_2$ produced.

A large amount of anthropogenic carbon dioxide emission into the atmosphere
results from the combustion of fossil fuels for the production of energy. Use and
production of coal is the second leading source of carbon dioxide emission to the
atmosphere, contributing nearly 33% of the overall anthropogenic carbon emissions,
and is second only to petroleum products (EIA, 2000). Specifically, in the United
States coal accounts for nearly 52% of the electricity that is generated and about 81%
of electricity-related carbon emissions, as illustrated in Figure 1.1.

Two widely used scenarios, a “business as usual” and an atmospheric
stabilization scenario, are compared in Figure 1.2. The difference between the two
scenarios, 1 GtC per year in 2025 and 4 GtC per year in 2050, gives an estimate of the
CO₂ reductions required to reach atmospheric stabilization. Given the magnitude of carbon emission reductions required to bridge the gap between the two scenarios, a multi-faceted carbon management strategy is essential. One way to manage carbon is to use and produce energy more efficiently to reduce our need for major energy and carbon source – fossil fuel combustion. Another approach would involve increasing our dependence on low-carbon or carbon-free fuels and technologies, such as nuclear power and renewable sources of fuel, for global energy demands. Both these approaches would require, to some extent, educating consumers and adjustments to our present day lifestyle. Therefore, a more immediate, direct solution is a necessity.

Considering the importance of fossil fuels to the health of the global economy, there is an urgent need to develop an effective approach to carbon management, which requires capturing and securely storing carbon emitted from global energy systems – a process known as “carbon sequestration.” The term “sequestration” refers to “putting aside and locking up” carbon that is freed in the extraction of fossil fuels. Among some researchers the term sequestration has become synonymous with biological sequestration, i.e., the growth of biomass to capture and store CO₂ (Harvey, 2004). Here the term is used more broadly: sequestration refers to any storage scheme that can keep CO₂ out of the atmosphere. Carbon sequestration schemes can be ranked by capacity and permanence of storage, by environmental consequences, and by cost of implementation.

Any viable system for sequestering carbon must meet the following requirements: (1) effective and cost-competitive, (2) stable for long-term storage, and
(3) environmentally benign (U.S. DOE, 2004). In addition, it is essential that the option of mineral CO₂ sequestration be economically competitive with other sequestration options when performed on a massive scale in order to make a significant impact compared with CO₂ production rates. Using the current technologies, the sequestration cost is estimated to be $69 to $300 / ton of carbon sequestered (U.S. DOE, 2004; Penner, et al., 2003). Thus, to achieve $10 or less per net ton of carbon sequestered by 2015, a goal of the U.S. Department of Energy, further research and development on carbon sequestration techniques are deemed necessary. An enhancement of the understanding of the science and an investigation of the potential impact and economic viability of all carbon management-related processes should be key considerations when trying to achieve the goal of sequestering a significant amount of CO₂.

Various schemes have been devised to reduce CO₂ emissions to the atmosphere such as geological sequestration, ocean disposal, mineral carbonation, and biological fixation. The focus of this study is on mineral sequestration, which is the reaction of CO₂ with non-carbonate minerals to form geologically and thermodynamically stable mineral carbonates. Mineral carbonation is a relatively new and less studied method of sequestration that has a good potential to sequester a substantial amount of CO₂. The reaction underlying mineral carbonation mimics natural chemical transformations of CO₂, such as the weathering of rocks to form calcium or magnesium carbonates. This sequestration process provides a safe and permanent method of CO₂ disposal. As CO₂ is chemically incorporated into the mineral and immobilized, there is little likelihood that an accidental release of CO₂ from the disposal site will occur. Furthermore, the
reactions that bind CO₂ to the mineral are exothermic and, if integrated efficiently, could result in CO₂ disposal processes that are net energy gains, yielding a high economic viability (Lackner et al., 1995).

Unfortunately, very little systematic effort has occurred when studying the carbonation of Mg-bearing minerals. This has led to some contradictory results reported among CO₂ mineral sequestration researchers. Particularly, many researchers have disputed the fate of the dissolving species (i.e. Mg, Si and Fe) and the process of magnesium carbonate precipitation in the presence of complex ions, but no concrete answers have yet been suggested. The challenge is to design and identify conditions of temperature, pressure, reaction medium, and reactor configuration that would allow these mineral carbonation reactions to be carried out at a sufficiently rapid rate with economic feasibility.

In this study, the aqueous reaction of CO₂ with the Mg-bearing mineral (i.e. serpentine) has been investigated in order to design more effective mineral sequestration processes that can convert captured and separated CO₂ to products amenable for long-term, environmentally benign, and unmonitored storage. The following delineates the organization of the subject matter into different chapters and their significance/relevance.

Chapter 2 provides the background information regarding various carbon sequestration schemes. The advantages and disadvantages of each of the CO₂ disposal methods are described with their estimated sequestration capacity. In-depth discussion
on the methods that can be visualized for binding gaseous CO₂ to the mineral matrix is also presented to set the basis for the design of the subsequent experimental studies.

In Chapter 3 information regarding the availability of Mg-bearing minerals and the physical and chemical characteristics of the procured Mg-bearing mineral samples are presented in detail. A battery of analytical techniques such as BET, SEM, XRD, flame-AAS and TGA, are used for the measurements. Once the mineral samples are characterized, the feasibility of the direct (gas-solid) carbonation process for the application of carbon sequestration is evaluated.

Chapter 4 is devoted to thermodynamic equilibrium studies for the proposed CO₂-mineral-water systems under various operating conditions. The simulation results are presented to illustrate the effects of the pH, temperature, CO₂ partial pressure, and ionic strength on dissolution of serpentine. In this work, Visual MINTEQ, a program that employs a free equilibrium speciation model, is used to calculate chemical equilibria in each proposed aqueous system. Using this program, ion speciation using equilibrium constants from the MINTEQA2 database is also simulated. The results from Chapter 4 lay the foundation for the experimental studies discussed in Chapter 5.

Chapter 5 illustrates how the dissolution of serpentine is chemically enhanced by various chemical additives. First, a geochemical model of the mineral carbonation process is developed to break down the complex, multi-step reaction into a more manageable scale. The reaction mechanisms are then proposed for the aqueous dissolution of serpentine with and without chelating agents. A series of bench-scale experiments are carried out to identify the mechanism of each individual reaction step.
and the fate of each species during reactions. This chapter identifies various factors that contribute to the dissolution of serpentine. Particularly, the evolution of the surface structure during the dissolution of serpentine particles is illustrated to provide an insight into the subsequent termination for further dissolution of serpentine.

Chapter 6 is devoted to studying the effect of physical activation for dissolution of serpentine. According to the results given in Chapter 5, in a solvent containing a mixture of weak acids and chelating agents, the dissolution of serpentine is terminated due to the precipitation of either SiO$_2$ or MgCO$_3$ on the surface of serpentine particles. Therefore, study of the physical activation proposed to remove the diffusion limiting SiO$_2$ layer form the backbone of this chapter. Various methods of the surface agitation such as ultrasound, acoustic, and internal grinding are examined for their effectiveness in refreshing the surface of serpentine particles during the dissolution process in order to further promote dissolution of the inner Mg layer of serpentine.

Based on the findings from Chapters 5 and 6, a pH swing process is developed to improve the overall conversion of the CO$_2$ mineral sequestration process while also producing value-added by-products. The details of this patented process is illustrated in Chapter 7. Since the bicarbonate and carbonate ions are predominant at high pHs, the amount of carbonated Mg is dramatically increased at pH level higher than 9.5 by increased concentration of carbonate ions in the liquid phase. By carefully controlling the pH, three solid products are generated from the mineral carbonation process: SiO$_2$-rich solids, iron oxide, and MgCO$_3$·3H$_2$O. Since the iron oxide and magnesium carbonate produced are highly pure, these value-added products can eventually reduce
the overall cost of the carbon sequestration process. In addition, the potential multi-
pollutant control characteristic of the Mg-rich solution that is prepared during the pH
swing process is also recognized in this chapter.

Finally, conclusions and contributions of this research work are delineated in
Chapter 8. Some recommendations for future work are also suggested in this chapter.

In Appendix A, special emphasis is placed on conducting a life cycle assessment
for the proposed pH swing process described in Chapter 7. In order to completely
evaluate the proposed mineral carbonation process for the CO\textsubscript{2} sequestration, a life-
cycle assessment (LCA) is performed using an appropriate system boundary.
Accounting for the LCA results, the energy sink in the overall process is identified and
the operating conditions that are more economically feasible are suggested. In addition,
the important value of the three byproducts in carrying out the proposed carbon
sequestration process as a net consumer of CO\textsubscript{2} and keeping the net change in the global
warming potential negative is portrayed.
Figure 1.1: Carbon dioxide emissions from the electric power sector by fuel, 1990 – 2025 (EIA, 2004).
Figure 1.2: Representation of reduction in CO₂ that would be necessary to reach atmospheric stabilization. Comparison between “business as usual” scenario (solid line) with “stabilized atmospheric” CO₂ concentration of 550 ppm (Wigley et al., 1996).
CHAPTER 2

CO₂ DISPOSAL OPTIONS: BACKGROUND

Most of the contents of this chapter will be published as an entry in Encyclopedia of Chemical Processing (with K. S. Lackner and L.-S. Fan, “Carbon Dioxide Capture and Disposal: Carbon Sequestration,” Encyclopedia of Chemical Processing, Ed. K. B. Kim, Marcel Dekker, Inc., (In Print)).

Fossil fuels provide a large, affordable source of energy that is limited by environmental impacts rather than resource constraints. A major concern in using fossil fuels is the emission of CO₂ to the atmosphere. Carbon dioxide is a potent greenhouse gas and the dominant contributor to anthropogenic climate change. It is also an acid gas that changes the chemistry of the surface ocean that is in equilibrium with the atmosphere. Since CO₂ is physiologically active, in plants as well as animals, a change in CO₂ concentrations is likely to have wide-spread ecological effects even without climate change. In order to stabilize the level of CO₂ in the air, emissions have to be reduced by a factor of three or more. In general, carbon management scheme involves three steps – capture, transport and disposal.
The amount of carbon dioxide generated from burning of fossil fuels alone is enormous and it has become apparent that no single disposal or sequestration option would be sufficient. Therefore, various schemes have been devised to reduce CO₂ emissions while allowing continuous use of fossil fuels (Blok et al., 1992). In nearly all the major processes CO₂ would have to be pipelined to the disposal site from a power plant. Therefore, separation and transportation of CO₂ is similar for all CO₂ disposal methods. In the case of CO₂ transportation, due to the very large quantities of CO₂ required to be disposed, it would be prudent to compress the CO₂ prior to transportation (~ 110 atm) (Wallace, 2000). The current estimated cost of capture and compression of CO₂ to pipeline pressure is approximately $ 30 – 50 per ton CO₂. Transport of CO₂ adds $ 1 – 3 per ton per 100 km (Wallace, 2000).

Disposal costs vary, but in some cases they are quite low, e.g., $ 4 per ton of CO₂ for some forms of underground injection. Since CO₂ sequestration will raise the cost of energy, it is unlikely that sequestration would be introduced without regulatory pressure. The trade-off between ignoring the risk of climate change and paying for a carbon neutral energy infrastructure is easier if the cost of the carbon management can be held low. Sequestration will only be considered if it is cheaper than the alternatives for reducing CO₂ emissions. Alternative forms of energy including wind and nuclear energy limit the acceptable price of CO₂ sequestration.

In a recent draft report submitted to the United States Department of Energy (U.S. DOE, 1999), few attractive and viable options for large-scale CO₂ disposal and sequestration have been identified, such as geological sequestration, ocean disposal,
mineral carbonation, and biological fixation. Table 1 gives the worldwide CO₂ storage potential of various options.

2.1 GEOLOGICAL SEQUESTRATION

Underground storage in geological formations is a major option for disposing of CO₂ and is already practiced. Potential sites for geological storage are active oil fields, coal beds, depleted oil and gas reservoirs, deep saline aquifers, and mined salt domes and rock caverns (Herzog et al., 1993). In West Texas approximately 20 million tons of CO₂ are consumed in tertiary oil recovery (Ruether et al., 2002). These injections do not qualify as sequestration as the CO₂ has been extracted from underground wells about 500 miles away. However, these projects and similar projects in Canada demonstrate that the disposal of CO₂ is practically feasible. Nevertheless, the capacity of tertiary oil and gas recovery is quite limited. Estimates range from 20 to 60 GtC (Holloway, 2001). Displacing methane tied up in deep unmineable coal adds another small carbon sink to the portfolio of options. This method is attractive in the sense that most of the injected CO₂ will be immobilized by either physical or chemical absorption on the coal surface. On the other hand, in other reservoirs such as aquifers, the injected CO₂ will likely exist as a supercritical phase without being fully dissolved for thousands of years and that creates a potential problem of a higher leakage rate (Gale, 2004).

Beyond those examples where CO₂ can be utilized in the recovery of oil and gas large underground reservoirs, deep aquifers represent the best long-term underground geological storage option. Such aquifers are generally saline and are separated from shallower aquifers and surface water supplies. The estimated storage capacities of these
aquifers in the United States are 5 – 500 billion tons of CO$_2$ (Bergman and Winter, 1995). This technology has been demonstrated by Statoil at the Sleipner project in the North Sea. It shows that injection into deep aquifers is economically feasible (Herzog et al., 2000). This project is ultimately driven by a $50 per ton of CO$_2$ tax. Figure 2.1 shows the location of deep saline aquifers in the United States.

There are a number of additional projects underway or being brainstormed that will further outline the viability and long-term capacity of geological sequestration. The central question is long-term safety, long term leakage rate and ultimately the capacity of these projects. It is likely that there will a large number of sites where CO$_2$ can be stored safely and for all practical purposes permanently. While some proponents of the scheme have suggested storage capacities on the order of 300 GtC, the real number at this point is still very uncertain and may prove to be much larger. For the application of the geologic sequestration, both near surface and in depth monitoring systems should also be developed to minimize CO$_2$ leakage from underground.

2.2 OCEAN SEQUESTRATION

A large fraction of the emitted CO$_2$ will naturally be absorbed by the ocean. Therefore, non-action equates to partial ocean sequestration. In equilibrium, the partitioning of CO$_2$ between ocean and atmosphere is roughly 4 to 1 (Butler, 1991). As the partial pressure of CO$_2$ in the air rises, the ratio gradually moves toward a higher fraction of CO$_2$ remaining in the atmosphere. The CO$_2$ carrying capacity of the ocean is determined by its carbonate alkalinity, which is the charge weighted sum of ion concentrations, excluding protons, hydroxyl ions and bicarbonate and bicarbonate ions.
Charge neutrality demands that the alkalinity $A$ is equal to the sum of the ionic charge in these remaining ions,

$$A = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+].$$ \hfill (2.1)

For ocean water with a pH near 8, one can neglect protons and hydroxyl ions, thus

$$A \approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}].$$ \hfill (2.2)

At constant alkalinity, the ocean can absorb more CO$_2$ by replacing one CO$_3^{2-}$ with two HCO$_3^-$. Since 90% of all the inorganic CO$_2$ in the ocean is in the form of HCO$_3^-$, the uptake capacity of the ocean is far less than the 39,000 GtC present in the ocean. Eliminating all carbonate ions would reduce the pH to about 4 and store no more than 3500 GtC. In equilibrium with 550 ppm of CO$_2$ in the air, the pH of the ocean would drop by 0.3 and if stirred into the entire ocean it could pick up about 1000 to 1500 GtC. Without active interference, the approach to this equilibrium would take millennia (Lackner, 2002).

In spite of these limitations, estimates for ocean storage capacity in excess of 100,000 billion GtC have been cited (Herzog, 1997). Such numbers would only be feasible if alkalinity (i.e. NaOH) is added to the ocean to neutralize the corresponding amounts of the carbonic acid. Over thousands of years, the dissolution of calcerous oozes at the bottom of the ocean could provide such alkalinity (Archer et al., 1997; Broecker and Takahashi, 1978).

Ocean disposal options fall into several categories as illustrated in Figure 2.2. One is to dilute the dissolved CO$_2$ at a depth below the mixed layer. Carbon dioxide can be stored using this method for decades to centuries, while capacities are limited. Another approach is to form lakes of CO$_2$ at the bottom of the ocean. Below 2700 m
compressed CO₂ is denser than seawater and sinks to the bottom. In addition, CO₂ will react with seawater to form a clathrate, a cage structure with approximately six water molecules per CO₂ (Dendy and Sloan, 2003). Clathrates are solids that can form at temperatures slightly higher than the melting point of water and thus form spontaneously in the presence of liquid CO₂ near the bottom of the ocean. However, they are not stable and as a result, they dissolve into ocean water, once the CO₂ concentration in the water is dropped back to the normal levels. Since 1977, when Marchetti first introduced the concept of the direct ocean sequestration of CO₂ (Marchetti, 1977), significant research effort has taken place and now the cost for the direct disposal of CO₂ in the oceans is estimated to be as low as $ 1 – 6 per ton of CO₂ (Freund and Ormerod, 1997), to a more realistic estimate of $ 5 – 15 per ton of CO₂ (Herzog et al., 1995).

The environmental impact may be the most significant factor determining the acceptability of ocean storage, since the strategy is predicated on the notion that the impacts on the ocean will be less than the avoided impact of these emissions to the atmosphere. Environmental concerns in ocean sequestration focus on long term chronic issues of changing the ocean chemistry as well as on the local effects of low pH (as low as 4) and its effect on marine organisms (e.g. stunting coral growth). While it is true that the oceans will get acidified as well, if the problem is ignored, the need for dealing with elevated levels of CO₂ in the atmosphere may not be limited to climate change concerns but also to changes in the ocean water chemistry. It does not help to replace one environmental problem with another. In addition, there is the possibility of sudden release of the sequestered CO₂ due to thermal plumes and volcanic action in the ocean. It has been reported that when a lake in Africa erupted, an enormous amount of CO₂ was
discharged from the bottom of the lake killing thousands of animals and humans by asphyxiation (Slager, 1987).

2.3 BIOLOGICAL SEQUESTRATION

One of the largest natural carbon flows through the environment is driven by photosynthesis. Plants take up CO₂ and water and turn it into reduced carbon compounds such as starch and cellulose. Photosynthesis fixes about 100 Gt of carbon per year. Most of this is returned via respiration and decomposition, but it seems that over the last decade mid latitude forests have been net sinks for CO₂ (Houghton, 2003). Trees and other plants sequester CO₂ during periods of growth. Thus, forestation and agricultural fixation of carbon, either in biomass or soil carbon, can play a role in carbon sequestration. A mid-latitude forest stores about 60 tC/ha above ground and another 100 tC/ha below ground. Uptake rates can be as much as 3 – 10 tC/yr, but capacity is limited. Worldwide biomass amounts to 600 GtC and soil carbon to 1400 GtC (Griffin and Seemann, 1996). This defines the yardstick against which biological sequestration has to be measured. To match the CO₂ emission from a single GW coal plant, the forested area should be increased at a rate of one hectare (2.5 acres) per hour. Keeping up with a GW plant requires a growing forest of 370,000 ha (950,000 acres). Biological sequestration could make up for past deforestation, which is responsible for a small fraction of the increased atmospheric CO₂. Biological sequestration is most useful when it is the by-product of other societal goals. Environmental concerns would arise where monocultures for purposes of biomass fixation would replace less carbon efficient natural systems.
Another biological approach is ocean fertilization. This method spurs biomass growth in areas that are low in productivity due to lack of critical nutrients. It, too, is limited in capacity, and has raised environmental concerns over changes in the natural food chain. The cost of biomass conversion is often quite low. Planting forests in developing countries could be as low as $3 – 10 per ton of CO₂ captured (Paustian et al., 1998).

2.4 MINERAL SEQUESTRATION

As the amount of CO₂ stored increases, it becomes progressively more difficult to guarantee a physical barrier that prevents CO₂ from returning to the atmosphere. As shown in Figure 2.3, a chemical conversion to a thermodynamically lower state thus would be desirable and is indeed possible. CO₂ is the anhydrous form of carbonic acid and therefore can be used to displace weaker acids like silicic acid. The formation of carbonates from silicates is well known as geological weathering. Thermodynamically, CO₂ can be bound as a carbonate. In many instances these carbonates dissolve in water, but some, like magnesium or calcium carbonates, are remarkably stable as solids. Thus, mineral sequestration would provide a means of storing CO₂.

Mineral carbonation is a new and, consequently, less studied method of sequestration. Mineral resources are plentiful for storing all the carbon that could ever be released in the consumption of fossil fuels. This sequestration process offers a safe and permanent method of CO₂ disposal, since there is almost no possibility of accidental release of CO₂ from the disposal site, as CO₂ is chemically incorporated into the mineral and immobilized. Furthermore, the reactions that bind CO₂ to the mineral are exothermic.
in nature leading to the formation of thermodynamically stable carbonate forms (Lackner et al., 1995).

Minerals containing substantial quantities of Mg and Ca-oxide undergo carbonation in the presence of CO$_2$. The basic reactions can be given for the Mg and Ca-oxides as:

\[
\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 + 179 \text{ kJ/mol} \quad (2.3)
\]

\[
\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3 + 118 \text{ kJ/mol} \quad (2.4)
\]

Pure calcium and magnesium oxides are rare in nature, however, many minerals containing a chemical combination of these oxides can be found in nature in abundant quantities. Ultramafic igneous rocks (primarily peridotites and serpentinites) contain large amounts of MgO bound into a silicate structure. Dunite is a rock made up entirely of olivine (Mg$_2$SiO$_4$). More abundant ultramafic rock is serpentine (Mg$_3$Si$_2$O$_5$(OH)$_4$), which is hydrolyzed olivine. Peridotite and serpentinite rocks containing olivine and serpentine exist in amounts far exceeding fossil carbon resources and Figure 2.4 shows the map showing the world-wide locations of those deposits. There are large deposits in the United States and Puerto Rico (Goff and Lackner, 1998). There are also large deposits of these minerals in Canada and parts of Europe.

Mineral sequestration can proceed in underground or industrial processes. In the first process, CO$_2$ could be injected into selected underground mineral deposits for carbonation (in-situ carbonation). This process envisions pumping CO$_2$ directly into an underground deposit of porous magnesium or calcium bearing rock. In contrast to permanent underground storage of CO$_2$ gas (as in aquifers and depleted oil/gas reservoirs), this process would result in chemically stable carbonates; it therefore poses
substantially lower long-term risk. The reaction would be aided by naturally high pressures (overburden) and could proceed more rapidly than mineral weathering on the earth’s surface.

Industrial processes could be based on gas-solid reactions, aqueous processes, or combinations of the two. Direct gas-solid carbonation process offers ease of energy integration as compared to aqueous phase reaction. This process involves the gas-solid reaction between finely ground minerals with CO₂ to form geologically stable carbonates. Magnesium and calcium containing silicate ores are identified to react with CO₂ to form stable carbonates by the generic reaction:

\[
(Mg, Ca)_{x}Si_{y}O_{x+2y+z}H_{2z} + xCO_{2} \rightarrow x(Mg, Ca)CO_{3} + ySiO_{2} + zH_{2}O \quad (2.5)
\]

For example, serpentine, a common silicate mineral, can be reacted with CO₂ to form a stable magnesite (MgCO₃), silica, and water by the reaction (2.6):

\[
Mg_{3}Si_{2}O_{5}(OH)_{4} + 3CO_{2} \rightarrow 3MgCO_{3} + 2SiO_{2} + 2H_{2}O \quad (2.6)
\]

The above stoichiometry indicates that one ton of serpentine can dispose of approximately one-half ton of CO₂.

Lackner et al. (1995) have researched in detail the basic chemistry and availability of some of the mineral deposits. They suggest that carbonation of magnesium and calcium silicates is promising method of CO₂ disposal. The direct reaction can be given in the case of forsterite as:

\[
1/2 Mg_{2}SiO_{4} + CO_{2} \rightarrow MgCO_{3} + 1/2 SiO_{2} + 95 \text{kJ/mol} \quad (2.7)
\]

and for serpentine as:

\[
1/3 Mg_{3}Si_{2}O_{5} + CO_{2} \rightarrow MgCO_{3} + 2/3 SiO_{2} + 2/3 H_{2}O + 64 \text{kJ/mol} \quad (2.8)
\]
As can be seen from equations (2.7) and (2.8), both reactions are exothermic and thermodynamically favored at low temperatures. For comparison, the combustion of carbon yields 394 kJ/mol.

\[ C + O_2 \rightarrow CO_2 + 394 \text{ kJ/mol} \quad (2.9) \]

These gas-solid reactions are very slow at room temperature, and their rates are accelerated at higher temperatures. However, at very high temperatures, the equilibrium shifts towards free CO₂ and the reaction does not take place. The Gibbs free energy of the reactions favors the formation of carbonates until at elevated temperatures (~ 400 °C, 1 atm) the equilibrium shifts towards free carbon dioxide (Lackner et al., 1997). Lackner et al. (1995) have carried out detailed thermodynamic calculations to find suitable range for temperature and pressure. By comparing the free energies of the reactants and the reaction products, they have estimated the highest allowable temperature for CO₂ binding. In the case of CaO at 1 atm of CO₂ pressure, they found that the free energy change is negative till 1160 K and therefore favors the carbonation reaction. At higher pressure of 200 atm, this temperature was calculated to be 1670 K. The corresponding equilibrium temperatures are lower for magnesium oxide (680 K at 1 atm and 930 K at 200 atm). For the direct carbonation of minerals containing Mg or Ca oxide, e.g., forsterite (Mg₂SiO₄), the equilibrium temperature is calculated as 515 K at 1 atm of CO₂. However, similar studies by Kojima et al. (1997) did not find any appreciable conversion at these conditions.

However, one of the main disadvantages of CO₂ disposal with this route is the slower rate of gas-solid reaction due to diffusional limitations. Some data exist in the literature, which give rough estimate of these rates. Lackner et al. (1997) were able to
partially carbonate samples of 100 µm radius to about 25 % of the stoichiometric maximum by treating the mineral with CO₂ at 340 atm and 500 °C for 2 hours. Researchers at Albany Research Center (ARC) have focused on the direct carbonation of olivine (Mg₂SiO₄) coupled with secondary carbonation of the serpentine formed. Initial results for olivine particles in the 75 – 100 µm range exposed to CO₂ and water at 150 – 250 °C and 85 – 125 atm for 24 hours indicate that 40 – 50 % of the stoichiometric maximum was carbonated.

Aqueous process has much higher reaction rates due to dissolution of Mg in the solution at higher temperatures and pressures, and will be the focus of the rest of the discussion here. Another type of process has also been studied in the literature, which leaches out Mg from minerals in the form of Mg(OH)₂ by use of HCl or MgCl₂ melt (Lackner et al., 1997). This Mg(OH)₂ can be either directly reacted with CO₂ as a gas-solid reaction, or reacted in the aqueous phase to form carbonate. Based on a detailed analysis of energy required and environmental impacts, these processes are found to be environmentally unacceptable (Haywood et al., 2001).

Another option is extracting the Mg-compounds in aqueous phase using suitable reagent, and then reacting with CO₂. This process is attractive because of the increased reaction rates. For example, serpentine can be dissolved in HCl, forming magnesium chloride and leaving behind silica gel (Blackburn and Nagamori, 1994):

\[
6 \text{HCl} + \text{Mg}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow 3\text{MgCl}_2 + 2\text{SiO}_2 + 5 \text{H}_2\text{O} \tag{2.10}
\]

Similarly, ground olivine decomposes in HCl while releasing enough heat to maintain boiling temperature. After the Mg (or Ca) ions are extracted in aqueous phase, they can be precipitated into respective carbonates by passing CO₂. In another process, calcium or
magnesium hydroxides could be precipitated, followed by dry carbonation of these hydroxides in a separate step. In this process, the carbonation step can be performed at a higher temperature and the heat released in the exothermic reaction can be used in the other steps of the processing chain (Lackner et al., 1995).

The acid used in the leaching step can be regenerated in a separate stage. After the Mg is extracted, the solution is boiled to drive off the water and excess acid. Heating to 150 °C results in decomposition of MgCl₂, regenerating the HCl.

\[ \text{MgCl}_2 \cdot 6\text{H}_2\text{O} (s) \rightarrow \text{Mg(OH)Cl} (s) + \text{HCl} (g) + 5\text{H}_2\text{O} (g) \]  \hspace{1cm} (2.11)

After dissolution in water, Mg(OH)Cl repartitions as follows:

\[ 2 \text{Mg(OH)Cl} (s) \rightarrow \text{Mg(OH)}_2 (s) + \text{MgCl}_2 (aq) \]  \hspace{1cm} (2.12)

The magnesium chloride is again recycled through the acid recovery step whereas the magnesium hydroxide precipitate is ready for carbonation. The carbonation of Mg(OH)₂ is carried out in a separate step, which releases substantial heat that could drive the other steps. The reaction is carried out at 680 K and releases substantial amount of heat.

The above-described aqueous process requires leaching of Ca and Mg ions in the solution using a complicated and costly acid dissolution method. Mg or Ca-bearing minerals can also be directly contacted with CO₂ in aqueous phase to convert the silicates and oxides into carbonates. This aqueous process mimics naturally occurring silicate weathering process (Holland et al., 1986). Formation of magnesite and silica in serpentinized ultramafic rocks is believed to take place by CO₂-rich fluids permeating the mineral deposits. The rates of these aqueous processes have been shown to be higher than direct carbonation process because of the dissolution of Mg and Ca-compounds in acidic water, formed by dissolution of CO₂ (Kojima et al., 1997). The mechanism of
aqueous processes is also quite different from the direct gas-solid carbonation process. In the latter case, diffusivity of gas and surface and structural properties of the solid determine the rate of reaction, whereas, in aqueous process the rates are determined by the solubility of CO₂ and minerals in water.

When CO₂ is contacted with water, it dissolves slightly forming hydrated oxide or [CO₂]. After the dissolution, a small proportion of the CO₂ reacts with water to form carbonic acid, H₂CO₃. This acid dissociates into carbonate [CO₃²⁻] and bicarbonate [HCO₃⁻] ions. Thus, when CO₂ is dissolved in water, equilibrium is established between protons [H⁺], carbonate [CO₃²⁻] and bicarbonate [HCO₃⁻] ions (Lower, 1999). Because of the presence of the protons, the solution becomes acidic and its pH decreases. The pH of saturated solution of carbon dioxide solutions varies from 3.7 at 1 atm to 3.2 at 23.4 atm (Pierantozzi, 1991). The pH of the solution, in turn, is a direct function of carbon dioxide solubility, which varies with temperature and pressure. At pressures below 200 atm, over the temperature range 273 – 398 K, the solubility decreases with increasing temperature and increases with pressure (Pierantozzi, 1991).

The above data indicates that CO₂ solubility in water at a particular temperature increases with pressure. This would in turn result in increased acidity of the solution. Increased acidity of the solution is advantageous for carbonation reaction, as acidic solutions are shown to be good solvents for the minerals. Once the active species are released in water the carbonation would proceed via ionic reactions (homogenous reaction) and the rate of ionic reactions are substantially higher than the rates of gas-solid reaction (heterogeneous reaction). However, the acidity produced by CO₂ dissolution in
In summary, aqueous phase carbonation of solids offers the advantage of higher reaction rates but depends on solubility of both the gas phase and solid phase in water. Slurry carbonation at elevated pressures would enhance the solubility of CO$_2$ in water leading to lowering of pH, which in turn would increase the dissolution of active species (Mg and Ca-oxides) from the solids. Once the active species are released in water the carbonation would proceed via ionic reactions (homogenous reaction) and the rate of ionic reactions are substantially higher than the rates of gas-solid reaction (heterogeneous reaction).

The economics for mineral carbonation has been discussed in detail by Lackner et al. (1995). It is argued that the total cost of the CO$_2$ fixation by minerals should be comparable to the cost required for purification and shipping of CO$_2$ produced by the fossil fuel combustion. In the case of the coal-fired power plants, this cost has been shown to be as low as 3¢/kWh. Considering 90 g of CO$_2$ per MJ of heat generated, and efficiency of 33%, the above cost can be transferred into $31 per ton of CO$_2$. For mineral carbonation using peridotite, 2 tonnes of rock are required per tonne of CO$_2$. This gives an estimated cost of $15 per ton of peridotite and would suggest a favorable economics for mineral carbonation.

While the cost of mining, mineral preparation and tailing disposal is well known in industry and relatively inexpensive; the chemical reaction process is still too expensive for a practical implementation (Lackner et al., 1997). The mining, grinding, separation and processing of concentrate are estimated to cost about $9 per ton of the ore and about
$6 for further chemical processing. The latter cost could be further lowered for CO₂ fixation if; the process could provide its own energy; it could employ lower temperature reactors; it requires only a single grinding operation; and it could achieve larger economies of scale (Lackner et al., 1995). The bottleneck of the chemical reaction process is the slow kinetics of the process and the high cost of accelerating the process by various means. Heat treatment of serpentine, external attrition grinding, acid dissolution have all been shown to work, but the cost of the process will still have to be reduced from current estimates of $69 per ton of CO₂ (Penner et al., 2003) to more acceptable numbers like $30 per ton (Lackner et al., 1995). Since carbonic acid has proven to be too weak to dissolve serpentine or olivine with sufficient speed, some of the more promising approaches are based on the use of mixtures of weak acids that enhance the dissolution of serpentine and olivine while still allowing for their recovery at minimal energy cost (Park et al., 2003).

Currently, there are few research groups investigating the CO₂ mineral sequestration using Mg-bearing minerals. Researchers at Helsinki University of Technology in Finland are examining direct dry mineral carbonation for CO₂ sequestration (i.e. gas-solid reaction), whereas most of researchers in the United States are studying direct aqueous carbonation reactions (i.e. gas-solid-liquid reaction). Until now, dry mineral carbonation has not been successful at achieving significant conversion. On the other hand, there has been a great advancement in the field of aqueous mineral carbonation during last five years. One of the most advanced groups is DOE Mineral Sequestration Study Group, which consists of Albany Research Laboratories (ARC), Los Alamos National Laboratory, National Energy Technology Laboratory, Arizona State
University, and Science Applications International Co. The group at ARC was able to achieve 80 % of stoichiometric conversion within 30 min at 185 °C and 150 atm for 30 % solid by either heat treating serpentine and attrition grinding olivine and serpentine (O’Connor et al., 2002). However, the energy requirements for these pretreatment options are extremely high, as a result, the search for the more practical treatment methods are desired. In spite of recent active research in this area of studies, considerable knowledge gaps and discrepancies remain for the reaction kinetics and mechanisms. CO₂ mineral sequestration is a wide-open research area that still requires new and advanced ideas.
<table>
<thead>
<tr>
<th>Storage/Disposal Option</th>
<th>Estimated/Theoretical Storage capacity (Billion tonnes of CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep Ocean</td>
<td>5,100 - &gt;100,000</td>
</tr>
<tr>
<td>Deep Aquifers</td>
<td>320 – 10,000</td>
</tr>
<tr>
<td>Depleted Gas Reservoirs</td>
<td>500 – 1,100</td>
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<tr>
<td>Biological Sequestration</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

Table 2.1: Worldwide storage potential for CO₂ (Herzog et al., 1997; Ormerod, 1994)
Figure 2.1: Saline aquifers in the U.S. based on U.S. Geological Survey (Holloway, 2001).
Figure 2.2: Ocean disposal of CO$_2$: five injection scenarios (Butler, 1991).
Figure 2.3: Qualitative illustration of thermodynamic stability of carbonated form of carbon (U.S. DOE, 1999).
Figure 2.4: World-wide distribution of magnesium-rich ultramafic rocks

(Lackner et al., 1995).
CHAPTER 3

PROCUREMENT AND CHARACTERIZATION OF SUITABLE MINERALS

3.1 AVAILABILITY OF Mg-BEARING MINERALS

Because of the large amounts of CO$_2$ to be disposed, the raw materials for CO$_2$ sequestration are required to be abundant in nature and contain a large fraction of reactive components such as Ca and Mg-oxides. Ultramafic igneous rocks (primarily peridotites and serpentinites) contain large amounts of MgO bound into a silicate structure. Dunite is a rock made up entirely of olivine ($\geq 90$ vol %) and it is the richest mineral containing about 50 % MgO by weight. The next in this category is serpentinite, which has MgO about 40 % by weight (Lackner et al., 1995). Peridotite, serpentinite, gabbro and basalt are all found in large amounts as components of ophiolite complexes. The total accessible amounts of peridotite and serpentinite are expected to significantly exceed the worldwide coal reserves, which are estimated to be 10,000 Gt (United Nations, 1993). Small ultramafic bodies (~1 km$^3$) can potentially sequester ~1 Gt of CO$_2$ or ~ 20 % of annual U.S. emissions. A single large deposit of dunite (~30 km$^3$) could dispose of nearly 20 years of current U.S. CO$_2$ emissions (Goff and Lackner, 1998). The most voluminous and widespread ultramafic rocks are the
alpine (“metamorphic”) peridotites that form the basal sequence of ophiolites, slabs of oceanic crust uplifted and eroded along subduction zones and plate boundaries. Within North America, ultramafic rock belts (especially, ophiolite) are found along the Appalachian mountain belt stretching from the southeast United States to Quebec and Newfoundland and along the Cordilleran mountain chain stretching from Alaska through British Columbia to California (Coleman, 1977). Rocks comprising solely of olivine and serpentine would make the best ores for CO₂ sequestration because of ease of reaction for these minerals.

As shown in Figure 3.1 Olivine (Mg₂SiO₄) and serpentine (Mg₃Si₂O₅(OH)₄) minerals exist in large amounts in the eastern United States and they have potential to sequester CO₂ emissions for many decades (Goff and Lackner, 1998; Goff et al., 2000). A recent report by a team of researchers at Los Alamos National Laboratories and US Geological Survey evaluated the ultramafic deposits in the eastern United States (Goff et al., 2000). Table 3.1 summaries the CO₂ sequestration potential of some ultramafic bodies found in Vermont, PA-MD-DC-region, and Western North Carolina. The average concentration of Mg in these deposits ranges from 22 to 28 wt%. Each of these mineral deposits can sequester CO₂ emissions from Ohio power plants for many decades.

In the United States, there are two major companies that produce olivine – Unimin Corp. and Olivine Corp. Unimin operates two mines, one in North Carolina and one in Washington, and processing plants in Indiana, North Carolina, and Washington, whereas Olivine Corp. is only based in Washington (Kramer, 2000).
Although olivine has higher MgO content, most quarries in the eastern United States mine serpentine. D.M. Stoltzfus & Son, Inc. located in Talmage, PA and Rockville Crushed Stone Inc. in Rockville, MD are the examples of the mines that produce crushed serpentine aggregates (Arnold, 2002; Lipin, 2002). They are mostly open-pit mines. According to the companies, they mine in quantity of millions tons per year and their deposit is massive. Their current prices of olivine and serpentine are $87.97 and $9.70 per metric ton, respectively (Pettit, 2002; Rockville Crushed Stone Inc., 2002). However, if these minerals are mined in massive quantities for the application in carbon sequestration processes, these costs will be reduced down to much smaller values (i.e. ~ $3 per metric ton).

3.2 CHARACTERIZATION OF PROCURED MINERALS

Minerals with high contents of Mg oxides from different regions were procured and characterized. Olivine and serpentine were chosen as the reactants for CO₂ mineral sequestration and were procured from Ward’s Natural Science Establishment, Inc. Olivine was from two different (Jackson County and Twin Sister Range) locations and serpentine was from Eden Mills, Vermont. Olivines were numbered 1 and 2, respectively indicating minerals from these two locations.

Olivine1 and olivine2 are forsterite and their chemical formula is Mg₂SiO₄. Olivine is usually in granular masses and as rounded grains and rarely in small equidimensional or tabular crystals. The color of olivine is generally olive-green, pale yellow-green, or white with vitreous luster. It is transparent to translucent, and has
white streaks. The vendor reported that olivine is richer in Mg than in Fe (fayalite). This common rock-forming mineral found in basic to ultrabasic igneous rocks is slowly soluble in hot HCl. Olivine is widely used to manufacture refractory bricks.

Serpentine’s chemical formula is Mg₃Si₂O₅(OH)₄. Serpentine is commonly massive and fine-grained. Its color is usually various shades of green, often variegated showing mottling, with white streaks. Also some serpentines have yellow, brown, reddish-brown, gray or white colors. Serpentine has greasy, waxlike luster in massive varieties and silky luster when fibrous. According to the vendor, serpentine refers a group of three common polymorphs: antigorite, lizardite, and chrysotile. Antigorite and lizardite are commonly massive and fine-grained, while chrysotile is a fibrous asbestos variety. It is a common mineral and widely distributed, usually formed as an alteration of magnesium silicates (i.e. olivine). Chrysotile is the principle asbestos mineral used in industry.

Both olivine samples supplied by Ward’s are raw, unprocessed, naturally – occurring materials and have no hazardous properties. However, serpentine is warned as fibrous substance by the vendor. Asbestos and related minerals of the serpentine groups, such as chrysotiles, are naturally occurring minerals, which possess fibers. In their natural state, they are generally safe to handle. However, breathing fibrous dust of these materials may pose a health hazard. It is strongly recommended that protective gloves and a filter mask be worn while handling these materials, and fibers not be allowed to collect on clothing. Hands should be washed thoroughly after handling and
examination of any asbestos-like mineral. Specimen materials must be kept sealed in protective bags and stored in the box provided when not in use.

Selected minerals: olivine1, olivine2 and serpentine, were analyzed for their chemical and physical properties. The minerals supplied by the vendor were in the forms of various sizes of rocks. Therefore, it was necessary to crush and grind them to produce mineral powders. The selected minerals were ground using an 8000M SPEX CertiPrep Mixer/Mill with an agate vial set to minimize the degree of contamination and sieved to obtain particles with a size of less than 75 µm. An optimization of the particle size will be necessary considering the grinding cost, but for the purpose of investigating reaction rates, this fine size has been used. Chemical composition of the minerals was determined using a battery of analytical techniques such as Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and X-ray Diffractometer (XRD). First, the samples were dissolved by LiBO₂ fusion. The analysis was done for seventy different elements to screen out the key elements. The analysis was semiquantitative based on calibration of five elements in order to speed up the process, and therefore, actual concentrations could vary up to factor of 5 of measured results. Next, the more accurate analysis was conducted for five elements, Mg, Si, Fe, Al, and Ni, that were identified as the key elements and they were accurately analyzed followed by the calibration on each element in interests. Table 3.2 summarizes the chemical composition of these elements in three different mineral samples. As reported in literature, Mg and Si were the major elements in the minerals. The average measured concentrations of Mg and Si for these minerals were approximately 30 and 22 wt %,
respectively. The concentration of calcium in the minerals was found to be insignificant. A measurable amount of Fe was also found from the tests (~5 wt %).

Another experimental method used to identify the chemical compositions of minerals was XRD. The results from XRD runs are shown in Figures 3.2 (a) to (c). The XRD scans were compared ones from the JCPDS database to determine the chemical formula of the minerals. Olivine 1 and olivine 2 were identified as Mg$_2$SiO$_4$ (magnesium silicate / forsterite), whereas serpentine was found to be Mg$_3$Si$_2$O$_5$(OH)$_4$ (magnesium silicate hydroxide / antigorite). These results match the information given by the vendor. However, from XRD results, the concentrations of other traceable elements in the minerals cannot be found.

For physical analyses, surface and pore properties of procured solids were determined using low temperature N$_2$ adsorption BET apparatus (NOVA 2200). In addition, Scanning Electron Microscopy (SEM) was used to characterize the surface morphology. Table 3.3 summarizes the findings from BET experiments. The specific surface areas and pore volumes of olivine 1 were about twice higher than those of olivine 2. In the case of serpentine, its specific surface area was very similar to that of olivine 2, but the total pore volume was twice larger. As a result, it was easier to crush serpentine than olivine 2.

Scanning Electron Microscopy (SEM) and EDX were done for all three minerals to characterize the surface morphology, local chemical composition and hardness of all three mineral samples. As shown in Figures 3.3 (a), (b), and (c), the shapes of the ground particles were irregular. Particularly, the broken edges of olivine 1 and olivine 2
were very sharp and irregular (Figures 3.3 (a) and (b)), whereas Serpentine particles had smooth edges (Figure 3.3 (c)). The density measurement also indicates that olivine samples are denser than serpentine (Table 3.4). These results agree with the previous finding that it was easier to crush serpentine than olivine. In fact, the hardness of serpentine is only 3 – 4.5, whereas olivine’s hardness is 6.5 – 7. Therefore, the grinding cost is expected to be much lower for serpentine.

The Sauter mean particle diameters of mineral samples in Table 3.4 were then obtained from these sieve results using the following equation (Fan and Zhu, 1998).

$$\bar{d}_p = \frac{1}{\sum x_i \frac{d_{pi}}{d_{pi}}}$$

where $x_i$ is the mass fraction of particles within an average screen size of $d_{pi}$. Particle size distribution of the ground mineral samples were obtained from the sieve analysis carried out using a GilSonic AutoSiever (Model GA-1A & GA-6A) and the results are presented in Figure 3.4. As shown in the plot of cumulative particle size distributions, the particle size distributions were very wide for all three samples.

Next, thermal characterizations of minerals were performed using a Thermal Gravimetric Analyzer (TGA). These tests were carried out to find the thermal stability of the mineral as well as to find the calcination temperature. First, calcination reactions of $(\text{MgCO}_3)_4\text{Mg(OH)}_2\cdot5\text{H}_2\text{O}$ were done under $\text{N}_2$ or $\text{CO}_2$ flows at atmospheric pressure. Figure 3.5 shows the TGA plot for calcination reaction of $(\text{MgCO}_3)_4\text{Mg(OH)}_2\cdot5\text{H}_2\text{O}$ under $\text{N}_2$ flow. The first weight decrease was due to the losses of water. The weight loss at a higher temperature corresponds to the calcination of MgCO$_3$ in the sample.
The calcination temperature was at where the rate of weight loss increased significantly. As expected, the calcination temperature for \((\text{MgCO}_3)_4\text{Mg(OH)_2}\cdot5\text{H}_2\text{O}\) started around 350 °C, when the reaction was carried out in a flow of inert gas, N\(_2\). On the other hand, the calcination temperature was increased to 400 °C when the same calcination reaction was performed under CO\(_2\) flow.

These thermal characteristics of MgCO\(_3\) set the upper temperature limit for the CO\(_2\) mineral sequestration using direct carbonation method at atmospheric pressure. In addition, the weight change obtained using the analysis technique of TGA can now be applied to evaluate the extent of the carbonation of minerals.

The extent of carbonation of pure MgO at atmospheric pressure of CO\(_2\) was also investigated using TGA. As shown in Figure 3.6, the degree of the carbonation of pure MgO was almost insignificant. There was only about 0.3 % weight increase during carbonation process. Temperature was then increased further to perform the calcination reaction. The carbonation temperature was found to be about 160 °C, whereas the calcination temperature was around 320 °C. This experiment was then repeated using three mineral samples (< 125 \(\mu\)m in diameter). The extent of mineral carbonation at 1 atm under CO\(_2\) flow was insignificant (0.075 % weight increase), and olivine and serpentine minerals were found to be thermally stable till 500 °C under nitrogen flow. Therefore, it was proposed to apply high pressure for direct carbonation study. The increase in pressure also pushes the calcination temperature higher, so that the operating temperature for the reactor can be higher than that used at 1 atm operating pressure.
Next, the solubility of the mineral samples in aqueous solutions was investigated. Extraction fluids consisting of water and water buffering at a fixed acidic pH (100 ml) was originally proposed. HCl and HF were considered, however, due to their corrosive nature, an alternative method was tested instead. Theoretically, the bicarbonate ion reacts with the silicate, forming the carbonate, hydroxide (OH\(^-\)) ions, and free silica (SiO\(_2\)). There are many variables that would affect the solubility of Mg\(_2\)SiO\(_4\), such as the concentration of solid mineral samples and NaHCO\(_3\), and the operating temperature. First, the solid concentrations of ground olivine1, olivine2, and serpentine were varied. Then, at a fixed solid concentration, the NaHCO\(_3\) concentration was varied. After each batch reaction in a 100 ml flask, the concentration of dissolved Mg\(^{2+}\) in solution was determined through a simple titration technique. For each mole of Mg\(_2\)SiO\(_4\) dissolved, there was 2 mol of OH\(^-\) ion generated. The solution was titrated against 0.1 M HCl with phenolphthalein as the indicator. The end point color was pink (basic condition) to clear (acidic condition).

First, the solid concentrations were varied from 25 to 75 g/ml, while the temperature was kept at 29 °C and the concentration of NaHCO\(_3\) was 0.4 M. As shown in Figure 3.7, as expected the solubility of Mg ion increased as the solid concentration increased. When the concentration of NaHCO\(_3\) was varied from 0.4 M to 1 M, higher NaHCO\(_3\) concentration resulted in higher dissolved concentration of Mg\(^{2+}\) in solution. The experiments were performed at 60 °C and 25 g/ml solid concentration. The results are shown in Figure 3.8. These solubility test results are important since they provide information about the behavior of minerals under aqueous slurry conditions.
3.3  PRELIMINARY TESTING

The direct carbonation experiments were conducted under differential conditions
to eliminate external transport resistances. 200 mg of mineral powders were placed in a
differential reactor and were supported by glass wool padding. The schematic diagram
of the reactor is shown in Figure 3.9. The high pressure and temperature reactor
(HPTR) system is designed to withstand pressures up to 50 atm while operating at
temperatures up to 1000 °C. An internal diffusion furnace is used to heat the gas
mixtures. The gas flow rate was set at 5 slpm and the concentration of carbon dioxide
at the inlet was 99.999 %. Mass-flow meters calibrated for the appropriate ranges were
also incorporated into the reactor system.

Direct carbonations of the mineral powders were carried under differential
conditions with gas flow rate of 5 slpm with 99.999 % CO₂ at 350 °C and 1 and 25 atm
pressure for 24 and 8 hours, respectively. The reaction temperature was also varied
between ambient and 700 °C. Post-carbonation analysis of the minerals was carried out
to determine the extent of solid carbonation using TGA analysis for different reaction
times. From the experimental results, carbonation for all three mineral samples was
found to be negligible. Therefore, it was decided to carry out the mineral carbonation in
an aqueous system.

One of the issues related to the slow reaction kinetics could be the pore size of
the mineral particles. For example, according to the surface area distributions for pore
sizes given in Figure 3.10, most of the surface area of olivine corresponded to pore sizes
between 20 to 50 Å. In other words, more of pores were in near microporous range and
as a result, they were plugged up very fast at the beginning of the reaction resulting very low conversion. Therefore, it could be beneficial to investigate methods that can increase the pore sizes.

Various researchers (Wei et al., 1997; Agnihotri et al., 1999) have shown that the rate of carbonation reaction of oxides of alkaline earth elements is significantly higher when water is used as the reaction media (i.e. aqueous phase reactions). Bubbling CO$_2$ through an aqueous suspension of these minerals could enhance the formation with subsequent precipitation of carbonates. In this part of the work, carbonation of minerals was studied in a high pressure and temperature slurry bubble column reactor (HPSR) with water as the reaction medium. The detailed schematic of the reactor and experimental setup are shown in Figures 3.11 and 3.12. The maximum operating temperature and pressure for the HPSR system are 200 $^\circ$C and 210 atm, respectively. The unique viewing windows described in Figure 3.11 are made of quartz and allow the visualization of the carbonation process under high pressure and temperature conditions. The gas exiting from the column went through a back-pressure regulator and was vented into an exhaustion system. The back-pressure regulator controlled the system pressure. Carbonation of minerals in the aqueous phase was expected to be strongly influenced by CO$_2$ partial pressure, since the solubility of CO$_2$ in water increases drastically with pressure, thus making the solution highly acidic. The lowered pH would then increase the solubility of minerals into the aqueous phase. Since the high purity carbon dioxide that is transferred from the power plant to the sequestration site is usually pressurized up to 110 atm, the utilization of this pressure
will be important. Therefore, an air driven, single-stage, dual acting gas booster pump (Model AGD-152) made by Haskel was installed to provide high pressure CO₂ to this reactor system. The maximum outlet pressure of the booster pump is 1,360 atm and it requires a minimum inlet pressure of 13 atm.

Carbonation of the solid was then carried in aqueous solution, and the concentration of the slurry was 10 wt %. The vigorous movement of bubbles provided a good mixing to the slurry. The superficial gas velocity (99.999% CO₂) was maintained at 5 cm/s at 15 atm pressure and the reaction temperature was kept constant at 100 °C. After 7 hours of carbonation reaction, approximately 2 % of the MgO in the mineral carbonated to MgCO₃. It was speculated that the dissolution rate of the mineral as too slow. Therefore, the mineral samples were further ground to 26 µm average size. Using 26 µm mineral powers and the operating conditions of 15 atm and 160 ºC, the conversion of 13 % was achieved for the same reaction time. The extent of carbonation was determined using TGA and the EDS plot shown in Figure 3.13 also supports the finding (Note the high C peak).

Since the overall conversion was still low, it was necessary to determine the rate limiting reaction in order to fully understand the problem. Thus, Mg(OH)₂ which is water soluble at low temperature was used to prepare a Mg ion rich solution. Using the same experimental setup, carbonation reaction was carried out by bubbling carbon dioxide through this solution. It was found that the conversions were 32 % and 90 % for 160 °C and 20 °C, respectively. In other words, as expected the rate of carbonation/precipitation was relatively fast. However, through the viewing windows
of the reactor it was observed that the reaction time was approximately 1 hour, which was still not sufficiently, fast enough. Therefore, the enhancement of the rate of carbonation/precipitation should also be studied.

From the solid product characterization, it was found that when olivine was used as the reactant, MgCO₃ was generated, whereas if magnesium hydroxide was used, MgCO₃·3H₂O was generated. The XRD plots are shown in Figures 3.14 (a) and (b).

### 3.4 CONCLUSIONS

Samples of olivine and serpentine all contained large amounts of magnesium, which is desired for the carbon sequestration process. From the preliminary testing, it was found that the reaction rate of the direct (gas-solid) carbonation of Mg-bearing minerals was not sufficient, whereas the aqueous carbonation process showed promising results. Therefore, the aqueous carbonation of Mg-bearing minerals was selected for the subsequent experimental studies. Serpentine was chosen among the mineral samples because of its availability in the eastern United States.
Table 3.1: Physical, chemical and CO₂ sequestrating properties of example ultramafic bodies from the eastern United States (Fraser et al., 2000).

<table>
<thead>
<tr>
<th></th>
<th>Belvidere Mtn</th>
<th>Vermont</th>
<th>East Dover</th>
<th>Mad River</th>
<th>PA–MD–DC–Region</th>
<th>Soldier's Del.</th>
<th>Hunting Hill</th>
<th>Rockville Quarry</th>
<th>Buck Creek</th>
<th>Day Book</th>
<th>All</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume-Density</td>
<td>2.75</td>
<td>2.70</td>
<td>0.064</td>
<td>6</td>
<td>0.003</td>
<td>7</td>
<td>1</td>
<td>0.01</td>
<td>0.29</td>
<td>0.013</td>
<td>7.5</td>
</tr>
<tr>
<td>Volume (km³)</td>
<td>2.75</td>
<td>2.70</td>
<td>0.064</td>
<td>6</td>
<td>0.003</td>
<td>7</td>
<td>1</td>
<td>0.01</td>
<td>0.29</td>
<td>0.013</td>
<td>7.5</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.9</td>
<td>2.97</td>
<td>2.7</td>
<td>2.5</td>
<td>2.5</td>
<td>2.4</td>
<td>2.5</td>
<td>2.5</td>
<td>3.17</td>
<td>3.17</td>
<td>3.17</td>
</tr>
<tr>
<td>Ore mass (tons)</td>
<td>8.0 x10⁶</td>
<td>7.8x10⁶</td>
<td>0.15x10⁸</td>
<td>15x10³</td>
<td>0.055x10³</td>
<td>17x10³</td>
<td>2.5x10³</td>
<td>0.16x10⁵</td>
<td>0.92x10⁴</td>
<td>0.040x10⁸</td>
<td>22x10⁶</td>
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<table>
<thead>
<tr>
<th>Rock-Mg Content</th>
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<th></th>
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<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt % Mg</td>
<td>26</td>
<td>26</td>
<td>22</td>
<td>24</td>
<td>24</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>28</td>
<td>28</td>
<td>26</td>
</tr>
</tbody>
</table>

| Sequestrating       |               |         |            |           |                 |               |             |                 |            |          |     |
| Properties          |               |         |            |           |                 |               |             |                 |            |          |     |
| R(CO₂)²             | 2.13          | 2.13    | 2.51       | 2.30      | 2.30            | 2.40          | 2.40        | 2.40            | 1.97       | 1.97     | 2.13 |
| Mg (10⁷ tons)       | 2.08          | 2.03    | 0.033      | 3.60      | 0.013           | 3.91          | 0.58        | 0.037           | 0.26       | 0.011    | 5.72 |
| CO₂ (10⁷ tons)      | 3.76          | 3.67    | 0.060      | 6.52      | 0.024           | 7.08          | 1.04        | 0.067           | 0.47       | 0.020    | 10.4 |
| Q-value¹            | 1             | 1       | 2          | 2         | 2               | 2             | 2           | 2               | 1          | 1        | 1 to 2|
| Yr/million people, US² | 200          | 190     | 3.2        | 350       | 1.3             | 380           | 57          | 3.5             | 25         | 1.1      | 570  |

¹ Calculated using a tonnage double that estimated by Hunter (1941) for all serpentinized dunites in the region.
² R(CO₂) is the calculated mass ratio of rock processed to CO₂ disposed.
³ Q-value is a semiquantitative evaluation of dissolution properties that considers ease of magnesium extraction and residual insoluble silicates. A Q-value of 1 is best and 3 is worst (see text).
⁴ Years per population center of one million people; assumes annual US CO₂ emission rate of about 5 x 10⁶ tons/year and present population of 270 million people.
Table 3.2: Measured weight percents of elements in mineral samples obtained using ICP-MS (Perkin-Elmer Sciex ELAN 6000 Inductively Coupled Plasma Mass Spectrometer).

<table>
<thead>
<tr>
<th>Element</th>
<th>Olivine1 [wt%]</th>
<th>Olivine2 [wt%]</th>
<th>Serpentine [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>31.4</td>
<td>30.8</td>
<td>27.1</td>
</tr>
<tr>
<td>Si</td>
<td>20.5</td>
<td>24.1</td>
<td>20.1</td>
</tr>
<tr>
<td>Fe</td>
<td>5.5</td>
<td>5.8</td>
<td>4.3</td>
</tr>
<tr>
<td>Al</td>
<td>0.1</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Ni</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Mineral</td>
<td>Specific Surface Area [m²/g]</td>
<td>Total Pore Volume [cm³/g]</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------</td>
<td>--------------------------</td>
<td></td>
</tr>
<tr>
<td>Olivine1</td>
<td>8.6</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>Olivine2</td>
<td>4.1</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Serpentine</td>
<td>4.6</td>
<td>0.013</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3: Specific surface areas and total pore volumes of Mg-bearing minerals.
Table 3.4: Sauter mean particle diameters and densities of Mg-bearing minerals.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$d_p$ [µm]</th>
<th>Density [g/ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine1</td>
<td>61.94</td>
<td>3.041</td>
</tr>
<tr>
<td>Olivine2</td>
<td>94.47</td>
<td>3.219</td>
</tr>
<tr>
<td>Serpentine</td>
<td>79.96</td>
<td>2.550</td>
</tr>
</tbody>
</table>
Figure 3.1: Deposits of olivine and serpentine in the United States
(a) Olivine1 (Mg$_2$SiO$_4$)

(b) Olivine2 (Mg$_2$SiO$_4$)

(c) Serpentine (Mg$_3$Si$_2$O$_5$(OH)$_4$)

Figure 3.2: XRD analysis of procured Mg-bearing minerals.
Figure 3.3: SEM photos of (a) Olivine1, (b) Olivine2 and (c) Serpentine.
Figure 3.4: Cumulative particle size distribution of mineral samples.
Figure 3.5: TGA plot for calcination reaction of $(\text{MgCO}_3)_4\text{Mg(OH)}_2\cdot5\text{H}_2\text{O}$ under N$_2$ flow.
Figure 3.6: TGA plot for carbonation reaction of MgO under CO₂ (99.999%) flow.
Figure 3.7: Effect of solid concentration on the amount of magnesium dissolved into the aqueous phase.
Figure 3.8: Effect of NaHCO$_3$ concentration on the solubility of Mg-bearing minerals.
Figure 3.9: Detailed schematic of high pressure and temperature reactor (HPTR).
Figure 3.10: Surface area distribution for pore sizes of Olivine2.
Figure 3.11: Detailed schematic of high pressure and temperature slurry bubble column reactor.
Figure 3.12: Experimental setup for aqueous carbonation studies.
Figure 3.13: EDS of solid product (operating conditions: 15 atm, 160 °C, \( d_p = 26 \, \mu m \), 10 wt\% solid).
Figure 3.14: XRD of solid products (a) conversion from Olivine to MgCO$_3$ and
(b) conversion from Mg(OH)$_2$ to MgCO$_3$·3H$_2$O.
CHAPTER 4

VISUAL MINTEQ SIMULATION

4.1 INTRODUCTION

Visual MINTEQ is a Windows version of MINTEQA2 ver 4.0, which was released by the United States Environmental Protection Agency (U.S. EPA) in 1999. It is a most widespread chemical equilibrium model for the thermodynamic calculations such as metal speciation and solubility equilibria, for natural waters. It is renowned for its stability. Visual MINTEQ is capable of (Gustafsson, 2004):

- **Ion speciation using equilibrium constants from the MINTEQA2 database, which has been updated using the most recent NIST data to contain > 3000 aqueous species and > 600 solids**
- **Solubility calculations involving solids phases**
- Adsorption calculations with five surface complexation models (Diffuse Layer, Constant Capacitance, Triple Layer, Basic Stern and Three Plane), with the 1-pK or 2-pK formalisms, and with the CD-MUSIC concept
- **Ion-exchange calculations using the Gaines-Thomas formalism**
- Calculations with redox couples and **gases (e.g. CO₂)***
• Metal-humic complexation can be simulated using either the Gaussian DOM or the Stockholm Humic Model.

• **Sweep runs in which one parameter is varied**, e.g. \( \text{pH} \) or the total concentration of component

• Titrations in which a titrant with a given composition is added in steps to the original solution

• Data import from Excel

• Presentation of results from Visual MINTEQ runs on separate output tables; export of results to EXCEL

• Management of Visual MINTEQ’s thermodynamic databases from within the program

The highlighted functions are the ones that mostly used in this study. Many of these functions were more related to the natural water system with a low ionic strength. For high concentration chemical systems, the model should be used with caution. First, known aqueous systems were simulated in order to verify the model.

4.2 **RESULTS AND DISCUSSION**

4.2.1 **Dissolution and Speciation of CO\(_2\)**

The speciation of the dissolved CO\(_2\) was calculated at various pH conditions using Visual MINTEQ. The following is the simplified instruction of the program inputs.
1. Gases → select CO$_2$(g) and input a desired partial pressure of CO$_2$

2. Multi-problem/Sweep → select Sweep and input number of problems, start and increment (e.g. 14 problems, start at pH 1, increment 1) and Choose species for sweep output → Save

3. Ionic strength → set to be calculated

4. Temperature can be changed

5. Add components → e.g. CO$_3^{2-}$ (obvious choice for CO$_2$ dissolution) and NO$_3^{-}$ (need this component to ensure the charge balance, choose ionic species that doesn’t interact with other species) → add to list (concentration can be zero – used as an initial guess)

Running the program was quite simple and fast. Once simulation results were obtained, the ionic strength and the charge difference were checked for each set of the solutions. If the ionic strength was greater than 1, the result was not reliable. For example, the Visual MINTEQ results of the speciation of the open CO$_2$ system at P$_{CO2} = 10$ atm were not reliable at pHs higher than 6. However, from the results obtained, one could extrapolate the values to the higher pH conditions. Finally, Figures 4.1 and 4.2 were generated using EXCEL.

As shown in Figure 4.1, under equilibrium, the amount of the dissolved CO$_2$ in water increased with the partial pressure of CO$_2$. On the other hand, as expected, an increase in temperature decreased the dissolution of CO$_2$. The speciation of CO$_2$ was a strong function of pH and the Visual MINTEQ results agreed very well with the plot in the literature. From Figures 4.1 and 4.2, it was found that the dissolution of carbon
dioxide was a stronger function of pressure than of temperature within the selected range ($P_{CO2} < 30$ atm and $T < 75$ °C). The maximum partial pressure of CO$_2$ for the simulation was set at 30 atm to ensure that the ionic strength of the system was always less than 1.

4.2.2 Dissolution of CaCO$_3$

Next, the dissolution of the infinite solid phase is simulated. Calcite (CaCO$_3$) is chosen as the solid phase and infinite amount of CaCO$_3$ is dissolved in water at a constant partial pressure of CO$_2$ ($10^{-3.5}$ atm) at 25 °C. The simulation results are then compared to the literature (Stumm, 1992) and as shown in Figure 4.3, the results matched the literature very well. The speciation of the dissolved CO$_2$ was very similar to the earlier case in Figures 4.1 and 4.2. As expected, the solubility of CaCO$_3$ was higher at lower pH conditions.

4.2.3 Dissolution of SiO$_2$

Solubility calculations involving another solid phase was performed. SiO$_2$ was selected as the infinite solid phase, since the study of the SiO$_2$ dissolution could be helpful for predicting the fate of the Si-oxide layer during the serpentine dissolution. The required program inputs were similar to the previous case of the CaCO$_3$ dissolution. As shown in Figures 4.4 (a) and (b), the Visual MINTEQ simulation results were very close to the literature values. But here another limitation of Visual MINTEQ was found. Since the aqueous species were auto-selected by the program based on its
database, there were some species in Figure 4.4 (b) that are not account for in Figure 4.4 (a) (e.g. Si₄O₆(OH)₆⁻²). Nevertheless, the overall trend for the equilibrium speciation was the same. As the pH of the aqueous system increased, the solubility of SiO₂ increased. Since the maximum pH that the CO₂ mineral sequestration process operated at was less than 10, it was concluded that the Si-oxide layer of serpentine would form SiO₂ and H₄SiO₄ during the mineral carbonation process.

### 4.2.4 Dissolution of Serpentine without CO₂(g)

Fortunately, chrysotile (mineral in serpentine group) was in the database of Visual MINTEQ. If not, one could also add a new solid as long as its thermodynamic data are available. The method of running the program was the same as before. Infinite amount of chrysotile was added to water at a given temperature.

First, no chemical was added and the program was ran without any CO₂(g) in the system. As shown in Figures 4.5 (a) and (b), at 25 °C, as pH decreased, the amount of the leached Mg increased and the amount of leached out Mg decreased as the pH of the aqueous phase increased. The major portion of Si was in the form of H₄SiO₄(aq), while at pH lower than 8.5, a significant amounts of Si exists as precipitated SiO₂. The output results were checked for any precipitation of the possible solids such as magnesium hydroxide. It was found that starting at pH 13, small amount of Mg(OH)₂ was precipitated. Since CO₂ was not available in the system at this point, no MgCO₃ was formed.
Next, the effect of the temperature on the serpentine dissolution was investigated, while letting the pH of the system be calculated from the equilibrium compositions. As a general observation, the solubilities of the ionic substances (about 95% of them) increase with increasing temperature. The same was observed for chrysotile. Figure 4.6 shows an increase in the concentration of each species at higher temperatures. The final pH of the serpentine-water system at 25, 50 and 75 ºC were 9.47, 8.88, and 8.38, respectively. Due to rather high pH conditions achieved by the equilibrium, the overall dissolved amount of the species was small and some portion of $\text{H}_4\text{SiO}_4$ was ionized as illustrated in Figure 4.4.

### 4.2.5 Dissolution of Serpentine with $\text{CO}_2$(g)

Next, $\text{CO}_2$(g) was added to the simulation, while varying the temperature and the partial pressure of $\text{CO}_2$. Again, the pH and the ionic strength of the aqueous system were calculated from the equilibrium compositions. Six sets of the simulations were performed ($P_{\text{CO}_2} = 1, 10$ and 30 atm at $T = 25, 50$ and 75 ºC). Figures 4.7 and 4.8 are the typical results obtained from the Visual MINTEQ simulations.

As shown in Figure 4.7, as temperature increased, the dissolution of serpentine decreased, which was opposite to the trend found in Figure 4.6. This was due to the lowered $\text{CO}_2$ dissolution at a higher temperature. Note that the magnitudes of the concentrations of the dissolved species were much higher than those reported in Figure 4.6. The acidic condition created by the dissolved $\text{CO}_2$ resulted in a greater extent of the serpentine dissolution, and therefore, it was concluded that the amount of the
dissolved CO$_2$ affected the chrysotile dissolution more than temperature within the
given operating conditions. At 25 ºC and 10 atm of P$_{CO2}$, a large amount of magnesite
(MgCO$_3$) was found to be precipitated. As temperature was increased to 50 ºC, the
amount of the precipitated magnesite decreased and at $T = 75$ ºC, magnesite was
reported to be undersaturated.

The next set of the simulations was carried out at different partial pressures of
CO$_2$. As shown in Figure 4.8, a higher partial pressure of CO$_2$ brought about a lower
pH of the aqueous system, and consequently, increased the dissolution of chrysotile.
Same results were obtained for temperatures of 25 and 50 ºC. However, at 75 ºC, even
at the maximum pressure ($P_{CO2} = 30$ atm), MgCO$_3$ was not precipitated. Although
significant amount of Mg was leached out, the concentration of CO$_3^{-2}$ was very small at
low pH conditions, and thus, unless the temperature was low enough (e.g. $T < 50$ ºC)
MgCO$_3$ was undersaturated.

4.2.6 Effect of Ionic Strength

The effect of the ionic strength on the serpentine dissolution was investigated
using Visual MINTEQ simulation. Since the ionic strength can be controlled with
inexpensive chemicals such as NaCl, controlling ionic strength might be a more
economical enhancement method than the addition of the ligands (e.g. EDTA). Like
pH, the ionic strength of the solution also influences the surface speciation of the
mineral and changes the dissolution rates (Casey and Bunker, 1990; Xie and Walther,
1992). However, these effects of the ionic strength are not clearly defined yet. In
simple solutions, in theory, the activity of the neutral species such as silica is increased as the ionic strength is increased. It means that the rate of the silica dissolution should decrease with the ionic strength due to the increase in the degree of saturation. However, in general, it has been reported that the increase in the ionic strength causes the increase in the quartz dissolution rates (Dove and Crerar, 1990; Bennett, 1991). The effect of the ionic strength can be varied by the electrolyte species in the solution and the nature of the surface reaction sites (Dove and Crerar, 1990). During the Visual MINTEQ simulation, it was found that the total amount of Mg dissolved increased as NaCl concentration increased, although the speciation of the dissolved Mg varied at the same time. The results are shown in Figure 4.9. These results would be used to set a basis for the future experimental studies.

4.3 CONCLUSIONS

Visual MINTEQ was used to simulate the equilibria of the reactions involved in the mineral sequestration. Visual MINTEQ is a free equilibrium speciation model, which calculates the chemical equilibria in the aqueous systems at a low ionic strength (I < 1). From the simulation results, it was found that the dissolution of CO$_2$ is a stronger function of the partial pressure of CO$_2$ than of temperature. A few examples of the chemical equilibria were examined to verify the model and to understand the limitation of the program. The simulation results agreed well with the experimental data in the literature as long as the ionic strength was less than 1. Finally, Visual MINTEQ was used to simulate the chemical equilibria of the serpentine-water and
serpentine-CO$_2$-water systems. According to the simulation results, the magnesium component in serpentine dissolves better in low pH (acidic) conditions, while the silica layer dissolved in greater quantity in high pH (basic) conditions. As expected, it was found that greater amount of serpentine was dissolved into the aqueous phase when the partial pressure of CO$_2$ was higher. Being an acid gas, as CO$_2$ is dissolved in water, the pH of the aqueous phase was lowered and this promoted the dissolution of serpentine. As temperature increases, the solubility of serpentine is decreased for the serpentine-water system, whereas the opposite trend was observed for the serpentine-CO$_2$-water system due to lower solubility of CO$_2$ gas at higher temperatures.
Figure 4.1: Effect of partial pressure of CO$_2$ on the speciation versus pH for open CO$_2$ system at 25 °C.
Figure 4.2: Effect of temperature on the speciation versus pH for open CO$_2$ system at $P_{\text{CO}_2} = 10$ atm.
Figure 4.3: Equilibrium composition of a solution in presence of CaCO₃(s) (Calcite) at constant $P_{CO_2} = 10^{-3.5}$ atm and 25 ºC.
Figure 4.4: Species in equilibrium with amorphous silica at 25 ºC.
Figure 4.5: Effect of pH on chrysotile (serpentine) dissolution ($P_{\text{CO}_2} = 0$, $T = 25 \, ^\circ\text{C}$) - Dissolution of serpentine without CO$_2$. 

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Figure 4.6: Effect of temperature on chrysotile (serpentine) dissolution ($P_{CO_2} = 0$).
Figure 4.7: Effect of temperature on chrysotile (serpentine) dissolution at $P_{CO_2} = 10$ atm.
Figure 4.8: Effect of the partial pressure of CO₂ on chrysotile (serpentine) dissolution at 75 °C.
Figure 4.9: Effect of ionic strength on chrysotile (serpentine) dissolution ($P_{CO_2} = 10$ atm, $T = 75 \, ^\circ C$, pH = 6): Visual MINTEQ simulation – Dissolution of serpentine with CO$_2$. 
CHAPTER 5

CHEMICALLY ENHANCED DISSOLUTION OF SERPENTINE

The contents in this chapter have been published as an article in Canadian Journal of Chemical Engineering (with R. Jadhav and L.-S. Fan, “CO₂ Mineral Sequestration: Chemically Enhanced Aqueous Carbonation of Serpentine”, CJChE, 81 (3-4), pp. 885-890, 2003).

SUMMARY In this study, extensive literature review was carried out and the mechanisms of the individual reactions involved in mineral sequestration were proposed and experimentally investigated. Specifically, the focus of this study was the enhancement of the dissolution of serpentine into the aqueous phase. With the selection of suitable reagents, aqueous phase carbonation was carried out in a high pressure and temperature gas-liquid-solid fluidized bed reactor. It has been found that the mixture of 1 vol% orthophosphoric acid, 0.9 wt% of oxalic acid and 0.1 wt% EDTA enhanced the dissolution of ground serpentine while preventing the precipitation of Fe(III) on the surface of the Mg-bearing mineral particles. When this acidic solvent was used, the process was limited by the rates of dissolution of CO₂ and dissociation of carbonic acid.
5.1 INTRODUCTION

There are many active research groups investigating the issues relating to carbon mineral sequestration. Most of the researchers in the United States are studying direct aqueous carbonation reactions (i.e., gas-liquid-solid reaction) rather than direct dry mineral carbonation (i.e. gas-solid reaction) for CO₂ sequestration, since dry carbonation has been found to be extremely slow at the desired operating conditions. In this study, the slow reaction kinetic of the direct carbonation has also been experimentally confirmed and the results are shown in Chapter 3.

During the last five years, there has been a great advancement in the field of aqueous mineral carbonation and the DOE Mineral Sequestration Study Group is one of the most advanced groups in this area of study. This study group consists of Albany Research Laboratories (ARC), Los Alamos Laboratory, National Energy Technology Laboratory, Arizona State University, and Science Applications International Co. Table 5.1 summarizes the findings from ARC and DOE Mineral Sequestration Study Group.

In the aqueous mineral sequestration process, the dissolution of the mineral has generally been speculated as the rate-limiting step. When CO₂ is dissolved in water, the solubility of CO₂ will increase with pressure, and therefore, the increase in CO₂ pressure will lower the pH of the solution and consequently enhance the mineral dissolution. This concept was the basis for the carbon mineral sequestration scheme. However, as shown in Table 5.1, it has been observed that the acidity produced by CO₂ dissolution in water is not sufficient to dissolve the mineral. ARC group reported in 2001 that at 185°C and 115 atm, only 34% conversion was achieved after 24 hours.
Therefore, various enhancement schemes were proposed to aid this process. Attempts that have been made to increase the mineral dissolution include the use of chemical additives such as NaHCO$_3$/NaCl and heat treatment, dry or wet attrition grinding (Fauth et al., 2000; O’Connor et al., 2002). As NaHCO$_3$ is dissolved into the aqueous phase, the bicarbonate ion hydrolyzes olivine (Mg-bearing mineral) and the carbonate, hydroxide ions, and free silica are formed by the following reaction (O’Connor et al., 2000).

$$\text{Mg}_2\text{SiO}_4 + 2\text{HCO}_3^- \rightarrow 2\text{MgCO}_3 + \text{SiO}_2 + 2\text{OH}^- \quad (5.1)$$

$$\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^- \quad (5.2)$$

The hydroxide ions then react rapidly with CO$_2$ (aq) to reform the bicarbonate, and the dissolution of CO$_2$ in the aqueous phase is promoted (O’Connor et al., 2000). Thus, the solubility of the mineral increases with increasing NaHCO$_3$ concentration as well as with the solid concentration and the reaction temperature. These finding have been experimentally confirmed and the results are presented in Chapter 3.

In the case of heat treatment, ground serpentine was heated in air or CO$_2$ for 1-2 hours at around 630 °C. By heating ground serpentine at 630 °C for one hour, hydroxyl groups of serpentine can be removed and the serpentine structure can be opened up as shown in Figure 5.1. Thus, the dissolution of serpentine is improved. When chemical additives (NaHCO$_3$ and NaCl) were used as well as heat treatment, the conversion was as high as 83.2 %, but the reaction was carried out over a 6-hour period and the operating conditions were highly severe (185 °C and 115 atm). However, this method is found to be too energy intensive to be practical.
ARC’S more recent results introduce the physical activation using wet or dry attrition grinding. As shown in Figure 5.2, their attrition grinding method enhances the dissolution of olivine and serpentine by reducing the particle size down to approximately 2 µm. After 1 hour of dry attrition, they were able to achieve 45.5% conversion in the solution of NaHCO₃ and NaCl. Again, the operating conditions were severe (185 °C and 150 atm) and the reaction was carried out for 1 hour. They did also achieve 80% of stoichiometric conversion within 30 min at 185 °C and 150 atm via attrition grinding olivine (O'Connor et al., 2002). Unfortunately, the amount of the grinding media required and the concentration of the mineral slurry are expected to be much higher than that of economic feasibility when it is performed at an industrial scale. Since olivine and serpentine are different minerals with distinct characteristics, here only the results on serpentine are presented in Table 5.1. In addition, in the eastern United States there is a greater amount of serpentine than olivine.

In spite of recent research in this area, there is still considerable work to be done in order to address the unanswered questions and discrepancies that remain for the reaction kinetics and mechanisms. Moreover, these pretreatment options are highly energy intensive and may not be suitable and economical for a large-scale CO₂ sequestration. Hence, the search for a more practical activation method is necessary. The goal is to achieve a mineral dissolution at low-energy costs (by using chemical additives/catalysts).

Many studies in the literature suggest that mineral dissolution in the aqueous phase can be increased in the presence of anions, protons, organic ligands, and weak
acids. In this study, solubility studies were carried out to determine the effects of chemical surface activation on the dissolution/leaching of the active species (i.e. Mg) in the aqueous phase. The chemical activation includes adding various catalysts/chemicals such as ascorbic acid, calcium chloride, and potassium dihydrogen phosphate (Wogelius and Walther, 1991; Bonifacio et al., 2001). It has been reported in the literature that the addition of organic ligands improves olivine dissolution rates in acidic and near neutral pH conditions (Wogelius and Walther, 1991).

5.2 EXPERIMENTAL

A surface reaction mechanism was proposed and verified by experiments. First, ground serpentine was dissolved in an acidic medium (1 M HCl). The particles were collected and prepared for the Transmission Electron Microscopy (TEM) analysis to determine the composition change through the cross section of the particle. A focused ion beam (FIB) was used to mill the particle. This was done in a FEI Dual Beam 235 FIB system. It has an ion column to allow micro machining of samples. Ions are charged atoms. They behave somewhat like electrons but have over 100,000 times the mass. This allows a high-energy ion beam to cut and shape materials on a microscopic scale to make, for example, TEM samples. A particle was coated with platinum a few microns thick. It was then milled from two sides to produce a thin wafer a fraction of a micron thick. The wafer was mounted onto a TEM grid and Energy Dispersive Spectroscopy (EDS) was performed to identify the chemical composition change on the cross section of the particle.
For the study of the dissolution of the fine serpentine slurry, nine sets of the proposed weak acids and/or chemical additives were used to dissolve 3 g of ground serpentine in a 200 ml solution at ambient temperature and pressure. The slurry was constantly stirred at 750 rpm during the experiments. Slurry samples were collected periodically and the filtrates were analyzed for Mg in a flame Atomic Absorption Spectrometer (flame-AAS).

Finally, in order to confirm the hindrance of the dissolution process due to limited diffusion, controlled dissolution and carbonation experiments were performed. Two serpentine shards, about 1 cm in diameter, were placed into each flask containing 0.1 M HCl, 0.1 M acetic acid or solvent #7. These shards were relatively nonporous and there were no deep cracks on the surface, since they were used as shipped from the quarries. The solution was constantly stirred to ensure homogeneity of the aqueous phase, while the shards remained stationary at the bottom of the flask to prevent destruction of the surface. The temperature was kept at 90 °C to promote faster dissolution. The color changes of the shard surfaces were observed visually, and SEM photos were taken to examine the changes in the surface structures.

5.3 RESULTS AND DISCUSSION

Serpentine was chosen as the potential reactant for CO₂ mineral sequestration and was procured from D.M. Stoltzfus & Son, Inc due to its massive availability in the eastern United States. Unlike the previous specimen of serpentine, this mineral sample was not asbestos in nature while the chemical and physical properties were the same.
5.3.1 Structure of Serpentine

The micro-scale structure of serpentine was studied in order to understand the surface interaction between serpentine and the aquatic species (e.g. water molecules, dissolved carbon dioxide species, chelating ligands). As shown in Figure 5.3 (a), serpentine being a sheet silicate mineral shows the 1:1 structure due to the alternation of tetrahedral silica-type (lighter gray layer) and octahedral brucite-type layer (dark gray layer). The evidence of the layered structure is also shown in Figure 5.3 (b). The silica-type layer in a sheet silicate mineral is called a “siloxane surface” (Stumm, 1992). “The silica plane is characterized by a distorted hexagonal (i.e. trigonal) symmetry among its constituent oxygen atoms, that is produced when the underlying tetrahedral rotate to fit their apexes to contact points on the octahedral sheet. Further accommodation of the tetrahedral to the octahedral sheet is achieved towards the contact points instead of laying normal to the basal plane of the mineral. As a result of this adjustment, one of the basal oxygen atoms in each tetrahedron is raised about 0.02 nm above the other two and the siloxane surface becomes corrugated (Sposito, 1984).” Thus, the siloxane ditrigonal cavity that acts as a soft Lewis base is formed. In these ditrigonal cavities, water molecules or possibly other neutral dipolar molecules can form complexes with the siloxane surface of the mineral (Stumm, 1992). However, it is still expected that the dissolution at the brucite-type surface be more rapid at low pH (acidic) conditions, whereas the dissolution at the siloxane surface be faster at high pH (basic) conditions. In fact, the dissolution at the edge surface would be the fastest. Since the ionic reaction between the dissolved CO\textsubscript{2} and Mg ions is the key step of the proposed carbon
sequestration process, a low pH approach for the dissolution of the Mg-bearing minerals was chosen for the experimental studies.

5.3.2 Mechanism of Congruent Dissolution of Serpentine

According to the literature, chrysotile (i.e. serpentine) can dissolve congruently as indicated in the following reaction equation:

\[ \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \rightarrow 3\text{Mg}^{2+} + 2\text{Si(OH)}_4 + \text{H}_2\text{O.} \]  \hspace{1cm} (5.3)

Congruent solution occurs when a mineral is totally dissolved in the ground water. Incongruent solution occurs when the mineral and water react but leave a new solid along with parts of the old mineral in solution. However, during the early stage of the dissolution of serpentine the mineral dissolves in a noncongruent pattern as a result of an initial exchange of surface Mg\(^{2+}\) ions with H\(^+\) on the brucite-type surface. Figure 5.4 shows the distribution of the surface species on chrysotile at various pH conditions. Under acidic conditions where we perform the serpentine dissolution, >Mg-OH and >Mg-OH\(_2^+\) are predominant surface species.

Based on the serpentine structure and dominating surface species, the surface dissolution mechanism has been proposed as illustrated in Figure 5.5. First, H\(^+\) ions are adsorbed on the mineral surface with either >Mg-OH and >Mg-OH\(_2^+\). This process would be reversible and relatively fast. Next, the detachment of the Mg center occurs and this is the rate limiting step. In a fast subsequent step Si is released from the same surface site as salicylic acid. By repeating these steps serpentine gets dissolved into the aqueous phase. However, in nature, H\(^+\) ions are not readily available. Thus, the
dissolution of serpentine takes a long time geologically. Therefore, throughout this study, it was proposed to use high pressure CO$_2$ to create low pH acidic conditions promoting the mineral dissolution.

Figure 5.6 shows a Geochemical model of the proposed process. First, high-pressure carbon dioxide is dissolved in water. Since CO$_2$ is an acid gas, this will lower the pH of the aqueous phase. As the liquid phase becomes acidic, the magnesium component in the mineral particles is dissolved via a surface reaction. The leached out Mg ions then react with carbonate ions in the liquid phase and magnesium carbonate is precipitate. It is also expected that there could be undesirable side reactions that could terminate the dissolution of the Mg-bearing minerals. The fate of silica and trace metals in the minerals is to be determined.

It is possible that the acidic condition produced by the high pressure CO$_2$ alone is not enough to dissolve olivine and serpentine. Thus, the addition of the chelating agents is proposed as another enhancement method for the dissolution of the Mg-bearing minerals. As shown in Figure 5.7, a ligand with negative functional groups can form a stable complex with Mg on the serpentine surface and weakens the Mg-O bonds. As a result, the dissolution of the mineral is promoted. The key factor is to find a chelating agent that forms a stable complex with Mg but not as effective as CO$_3^{2-}$, so that the ligand can readily give out Mg$^{2+}$ during the carbonation stage.

This proposed surface reaction mechanism described above was first verified by TEM analysis. Figures 5.8 (a) and (b) show the cross sectional view of the dissolved serpentine particle. For this specimen, the EDS analysis was conducted along the line
shown in Figure 5.8 (b). It was found that there was the chemical composition near the surface was mainly SiO\(_2\), whereas there was increased content of undissolved serpentine at the inner portion of the particle. In other words, as proposed earlier Mg ion was leached out from the particles into the aqueous phase while the silica phase was remained within the mineral matrix. These findings were further investigated in the following sections.

5.3.3 Dissolution of Fine Serpentine Slurry

The dissolution of the mineral is a multi-step surface chemical reaction process, and the reaction was reported to be pseudo-first order overall for less than 30 % conversion with respect to the magnesia in serpentine ore (Fouda et al., 1996). Serpentine consists of layers of octahedral Mg(OH)\(_2\) situated between the layers of sheet silicate tetrahedrons. Therefore, Si dissolution or physical removal is also essential in order to expose the underlying Mg-rich layers. In the aqueous solutions, negatively charged organic ligands react with exposed Mg on the mineral surface and form organo-metallic surface complexes. Figure 5.9 shows examples of the structures of the ligands used in this work. These complexes polarize and the weakening of Mg-O or Mg-OH bonds results. As Mg-ligand complexes disengage the surface, the underlying layers are exposed to further interaction with the solvent (Swaddle, 1997). The complex ions are soluble in the aqueous phase, and, therefore, the solubility of an insoluble salt is increased as a complex forms. Specifically, polydentate ligands are used to dissolve deposits of metal oxides, hydroxides, sulfides, and carbonates
(Swaddle, 1997). For example, the parent acid $H_4(EDTA)$ is dissolved in water which results in a negatively charged EDTA with the successive pKa values of 2.0, 2.7, 6.2, and 10.3 at room temperature (Swaddle, 1997). The negatively charged EDTA ions displace solubility equilibria to the formation of complex ions by reducing free metal ion concentration to very low levels (Swaddle, 1997). As $CO_2$ is introduced into the aqueous phase containing Mg-ligand complexes, magnesium carbonate will be formed. Since these chelating effects occur near neutral pH, there is no need to use costly acids to lower the solution’s pH.

Various complexing agents were selected and nine different sets of solvents were prepared. There were no detailed data available for the dissolution of serpentine, but there were some results available for olivine dissolution. First, sodium acetate and EDTA were chosen since they have been tested for their effectiveness in dissolving olivine (Grandstaff, 1978; Davie and Durrani, 1978). EDTA, which is a polydentate ligand, is known to have very high binding constants with most metals. Ascorbic acid and potassium acid phthalate (KHP) are buffering agents that are chemically similar to various organic molecules present in the natural environment, and they have also been used to dissolve olivine (Furrer and Stumm, 1986). In addition, phosphate ions were reported to take a part in the ligand exchange buffering mechanism during the dissolution of serpentine in the presence of Cl$^-$ ions (Bonifacio et al., 2001). In this work, potassium hydrogen phosphate (KH$_2$PO$_4$) was used as the source of the phosphate ions. Solvent #7 was prepared by simulating the recipe of the etchant for olivine crystals used by Davie and Durrani (1978). However, in this case the
concentration of each of the components were modified and NaOH was not added to adjust pH, since the lower pH is favorable for mineral dissolution. Solvents #2-5 and solvent #8 contained weak acid, 0.1 M acetic acid, in order to eliminate the delay in lowering pH by dissolving CO₂. Since strong acids such as HCl have been commonly used to extract Mg from serpentine, the dissolution rate of 0.1 M HCl solution was first examined as the reference case. Figure 5.10 lists the detailed compositions of the solvents.

As Figure 5.10 shows, higher initial solubility was observed in all cases. This might be due to the disordering of crystal surfaces during grinding. The total amounts of Mg leached out into the aqueous phase were up to 15 % after 20 min and 20 % after 2 hours. Acetic acid (0.1 M) was not as effective as hydrochloric acid, or orthophosphoric acid and oxalic acid at removing Mg from the mineral surface structure. The addition of sodium acetate (solvent #3), ascorbic acid (solvent #4), and KHP (solvent #5) to acetic acid solution did not significantly affect the dissolution rate of serpentine. It was found that solvent containing phosphate ions and CaCl₂ (solvent #6) digested mineral as much as 0.1 M acetic acid. These dissolution rates were much higher than that in the case without any chemical additives, but the dissolution rate in 0.1 M HCl (solvent #1) was still approximately 1.3 to 2 times greater than in these solvents (solvents #2-6).

When solvent #7 was used, the amount of Mg that was dissolved was about 1.5 times higher than that with 0.1 M HCl. Again, it was a very fast process and more than 80 % of total dissolved Mg was leached out within the first 10 minutes. Considering
that the dissolution was performed at ambient temperature and pressure, these results are very promising. Then, solvents #8 and 9 were tested to confirm the effectiveness of EDTA\(^4\). In the acetic acid solution, the role of EDTA was not significant in aiding the dissolution rate. EDTA is also a weak acid, but when EDTA alone was added to the distilled water, the dissolution rate was found to be the lowest. Once Fe and Mg ions were extracted from the mineral and formed complex ions with the chelating agent (i.e. EDTA and oxalate ion), further dissolution of serpentine was promoted.

Although in all solvent cases the dissolution rate is considered to be surface reaction controlled, early leveling off of the Mg concentration in the filtrates shown in Figure 5.10 suggests a diffusion limitation on the dissolution at the later part of the process. In fact, from preliminary experiments, it was suspected that the remaining skeleton of SiO\(_2\) or precipitation of iron oxide on the surface of serpentine particles hinders the further dissolution of Mg and other components. Both speculations assume that MgCO\(_3\) does not precipitate on the surface of the mineral particles. Figure 5.11 illustrates the change in surface characteristics of ground serpentine after dissolution with solvent #7. Figure 5.11 (a) shows the disordered crystal surfaces after 10 minutes of grinding in a mixer/mill. It is clear from Figure 5.11 (b) that the surface of serpentine particle becomes more complex during dissolution in acidic condition. This could be due to either a remaining skeleton of silica or precipitated silica. Jonckbloedt (1998) has reported a layer of precipitated silica during dissolution of olivine with acids at elevated temperatures. He suggested that the reaction slurry must be mixed vigorously to prevent the precipitation of silica on the dissolving olivine particles.
In fact, the initial color of the slurry was dark gray, and, in all cases, the color of the slurry became lighter as the dissolution proceeded. The final colors of the filtrates of solvents #7 and 8 were yellow/green due to free iron ions in the solution, while, that of solvents #2, 3 and 5 were red/brown which corresponds to the color of iron precipitates. The colors of the filtrates of solvents #1, 4, 6, and 9 were clear. In other words, when no effective chelating agents exist in the solution, the leached out iron ions will form precipitates and change the color of the slurry to red/brown. Subsequently, the precipitated layer of iron-bearing phase impedes the further surface dissolution reaction of serpentine. However, if strong chelating agents such as EDTA and oxalate ion were added to the solution, ferrous ions would form complex ions with these organic ligands, which are soluble in water. This complexation process would reduce the activity of the ferrous ion in the solution and thus also reduce the precipitation of an iron-bearing phase on the serpentine surface (Mast and Drever 1987).

5.3.4 Dissolution of Serpentine Shards

As expected, after two hours of the dissolution process, the color of the serpentine shards in acetic acid solution changed to reddish brown, indicating the precipitation of iron ions. On the other hand, the surface of the shards in both HCl solution and solvent #7 turned white due to higher silica content on the surface. These results are comparable with the observation made during dissolution experiments performed using serpentine slurries. CO₂ was then bubbled through these flasks containing shards in order to proceed with carbonation at 90 °C. After two hours of
carbonation, a white surface layer that is the same color as MgCO₃ was observed on the surface of the shards in HCl solution and solvent #7. No significant evidence of carbonation was observed in the acetic acid case. This was expected because the dissolution rate of serpentine was slower in acetic acid. The shards were then fractured to show the cross-sectional view.

Figure 5.12 shows the surface characteristics of serpentine at the various stages of the process. As shown in Figure 5.12 (b), the inner surface, which is the unreacted portion of serpentine shard, is quite smooth and shows nonporous characteristics. Figure 5.12 (c) was taken near the surface of the shard, and at the same magnification, etch-pits, cracks and precipitated silica are visually discernible due to dissolution. These SEM photos illustrate how the specific surface area of the serpentine was increased due to the etching out of cleavage surfaces and the creation of higher relief (Grandstaff, 1978). This was not because of the formation of authigenic phases that have high specific surface areas as others have claimed. Figure 5.12 (d) shows a growth of MgCO₃ crystal on the very surface of the serpentine shard. This precipitated carbonate resembles the crystal formed during the carbonation of Mg(OH)₂ solution.

The dissolution rate would be further improved if the reaction temperature were increased, although the increased temperature would slow down the dissolution rate of CO₂. Figure 5.13 shows the experimental results for the dissolution of serpentine with NaHCO₃ at the various temperatures. The dissolution of serpentine increased up to seven times as the temperature was raised by 30°C.
5.4 CONCLUSIONS

In this chapter, an extensive literature review was carried out, and the mechanism of the serpentine dissolution was proposed based on the serpentine structure and the surface species on the serpentine particles in the aqueous phase. This mechanistic study is significant, since this was the first attempt to identify the detailed steps on the serpentine dissolution. With this much needed basic understanding, the project is now expected to move forward faster in the coming quarters.

According to the experimental results, the chemically enhanced aqueous carbonation of serpentine showed promising results. From the investigation of serpentine dissolution in various solvents, it was found that a mixture of 1 vol % orthophosphoric acid, 0.9 wt % of oxalic acid and 0.1 wt % EDTA greatly enhanced the Mg leaching process of ground serpentine while preventing the precipitation of Fe(III) on the surface of the mineral particles. When this acidic solvent was used for the aqueous mineral carbonation, the overall process was limited by the rates of dissolution of CO₂ and dissociation of carbonic acid, rather than the dissolution rate of the mineral. The solid products were examined using a TGA, XRD and SEM in order to quantify the degree of carbonation and identify the reaction mechanisms.
<table>
<thead>
<tr>
<th>Group</th>
<th>Particle size</th>
<th>Chemical additives</th>
<th>T [°C]</th>
<th>P [atm]</th>
<th>Rxn time [hr]</th>
<th>Conversion [%]</th>
<th>Pretreatment</th>
</tr>
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<tbody>
<tr>
<td>ARC</td>
<td>&lt; 37 µm</td>
<td>None</td>
<td>185</td>
<td>115</td>
<td>24</td>
<td>34</td>
<td>None</td>
</tr>
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<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>&lt; 37 µm</td>
<td>0.5 M NaHCO₃, 1 M NaCl</td>
<td>185</td>
<td>115</td>
<td>6</td>
<td>6.8</td>
<td>None</td>
</tr>
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<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>DOE Mineral Seq. Study Group</td>
<td>&lt; 37 µm</td>
<td>0.5 M NaHCO₃, 1 M NaCl</td>
<td>185</td>
<td>115</td>
<td>6</td>
<td>40.6</td>
<td>Heat treatment in air for 2 hrs at 600-650 ºC</td>
</tr>
<tr>
<td></td>
<td>&lt; 37 µm</td>
<td>0.5 M NaHCO₃, 1 M NaCl</td>
<td>185</td>
<td>115</td>
<td>6</td>
<td>83.2</td>
<td>Heat treatment in CO₂ for 2 hrs at 600-650 ºC</td>
</tr>
<tr>
<td></td>
<td>&lt; 75 µm</td>
<td>0.64 M NaHCO₃, 1 M NaCl</td>
<td>185</td>
<td>150</td>
<td>1</td>
<td>9</td>
<td>None</td>
</tr>
<tr>
<td>ARC</td>
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<td>0.64 M NaHCO₃, 1 M NaCl</td>
<td>185</td>
<td>150</td>
<td>1</td>
<td>43.5</td>
<td>Heat treatment in air for 1 hour at 630 ºC</td>
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<td></td>
<td>&lt; 75 µm</td>
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<td>185</td>
<td>150</td>
<td>1</td>
<td>45.5</td>
<td>Dry attrition grinding for 1 hr</td>
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</tbody>
</table>

Table 5.1: Comparison of results on carbon mineral sequestration studies performed by leading groups in USA using serpentine.
Figure 5.1: Structure change before and after the heat treatment of serpentine.
Figure 5.2: Wet / dry attrition grinding utilized by ARC group.
(a) Layered structure of serpentine

(b) SEM photo of serpentine particle

Figure 5.3: Serpentine structure.
Figure 5.4: Distribution of surface species on chrysotile (Bales and Morgan, 1985).
Figure 5.5: Our proposed mechanism of congruent dissolution of serpentine at the edge surface.
1. Dissolution of CO$_2$
2. Dissolution of mineral *
3. Carbonation/Precipitation
4. Termination of reaction
5. Precipitation of silica phases
6. Precipitation of phases of iron and other minor/trace elements

Figure 5.6: Geochemical model of CO$_2$ mineral sequestration via aqueous carbonation.
Figure 5.7: Process of enhancement of serpentine dissolution using chelating agent.
Figure 5.8: TEM photos of dissolved serpentine particle.
Figure 5.9: Structure of various complexing agents.
Figure 5.10: Dissolution of serpentine: Time versus Mg concentrations in filtrates for various compositions of solvents at ambient temperature and pressure (15 mg/mL initial solid concentration).
Figure 5.11: SEM of surfaces of serpentine particle before and after dissolution in solvent #7 at 20°C: (a) After 10 min grinding and (b) After 2 hours of dissolution.
Figure 5.12: SEM of cross-sectional view of serpentine shard dissolved and carbonated in solvent #7: (a) Overall view of cross-sectional area; (b) Inner surface; (c) Dissolved outer surface; (d) MgCO₃ crystal.
Figure 5.13: Effect of temperature on the dissolution of serpentine (initial solid concentration = 25 mg/mL, total dissolution time = 20 min, concentration of NaHCO$_3$ = 0.4 M).
CHAPTER 6

PHYSICAL ACTIVATION OF SERPENTINE


SUMMARY The effect of the physical activation on the dissolution of serpentine was investigated to improve the overall conversion of the CO₂ mineral sequestration process. Various methods of the surface agitation such as ultrasound, acoustic, microwave and internal grinding were examined for their effectiveness in removing the diffusion limiting SiO₂ layer in order to promote further dissolution of the inner Mg layer of serpentine. It was found that the fluidization of the serpentine slurry with glass beads was most effective in refreshing the surface of the serpentine particles during the dissolution process. Unlike the external attrition grinding, this method is much less energy intensive. It was also found that the mechanical agitation via the internal grinding alone did not enhance the dissolution of serpentine, while the
combination of the internal grinding and Mg-leaching solvent resulted in rapid serpentine dissolution.

6.1 INTRODUCTION

In the aqueous mineral sequestration process, the dissolution of the mineral was generally considered to be the rate-limiting step. Since it was observed that the acidity produced by carbon dioxide dissolved in water was not sufficient to dissolve the mineral (O’Connor et al., 2002), various physical and chemical enhancement schemes were proposed to aid in this process. The study presented in Chapter 5 showed that a mixture of weak acids and chemical additives enhanced the dissolution of ground serpentine at low-energy costs while preventing the precipitation of Fe(III) on the surface of the Mg-bearing mineral particles (Park et al., 2003). A problem faced during the development of the chemically enhanced process of serpentine dissolution was the generation of diffusion limiting silica and/or magnesium carbonate layers. Thus, the present work mainly focused on a continued effort of enhancing serpentine dissolution in order to develop an advanced energy efficient CO₂ mineral sequestration process. Particularly, physical activation using the internal grinding unit was preferred because when a fluidized bed reactor is used, this method could provide physical agitation without significant energy requirements. The bombardments between the larger and harder (may not be particularly denser) grinding media and fine serpentine particles in the slurry would chip away the layer of SiO₂ that inhibits further dissolution. Compared to the external attrition grinding system used by ARC group, this method requires a
smaller ratio of the grinding media to unit mass of serpentine. In addition, a lower concentration of the mineral slurry can be used since the main purpose of the internal grinding system is not to reduce the actual particle size but rather refresh the surface of the mineral particles during the dissolution step. Thus, the energy consumption of the proposed physical activation system is expected to be much lower than that of the external attrition grinding system.

6.2 EXPERIMENTAL

Serpentine mined from Pennsylvania was again used throughout the experiments, and it contains approximately 27, 20, and 4.3 wt % of Mg, Si, and Fe, respectively. Serpentine was first ground and sieved to less than 75 µm (average particle size of 37 µm). In this work, fine serpentine powder was used for the purpose of studying the reaction kinetics, but when a suitable grinding medium is selected, a larger average particle size could be used. Depending on the effectiveness of the internal grinding system and the economics of the overall process, the initial particle size of the serpentine will be optimized. Surface and pore properties of serpentine samples were determined using a low temperature N$_2$ adsorption BET apparatus (NOVA 2200). The specific surface area and the total pore volume of serpentine were 4.6 m$^2$/g and 0.013 mL/g, respectively. The measured density of serpentine was about 2.55 g/mL. Most physical activation experiments were carried out in a 5 cm diameter fluidized bed reactor, which was constructed of Plexiglas, while a glass batch reactor was used for the serpentine dissolution step at high temperature.
6.2.1 Removal of SiO$_2$ Layers from Surface of Serpentine Particles

From our earlier work, it was found that removing the diffusion limiting SiO$_2$ layer to expose the inner Mg layer is important to promote the further dissolution of the mineral (Park et al., 2003). Several methods were proposed including internal grinding, ultrasound, acoustic, and microwave. First, the ground serpentine was dissolved in 1 M HCl for five hours at 70 ºC and ambient pressure. Approximately 40 % of Mg was leached out from the serpentine slurry. Since the purpose of this dissolution step was to prepare the solid samples with a high concentration of SiO$_2$ on the surface, the dissolution process was not carried out to the full conversion at this point. The solids were then collected via vacuum filtration and washed with distilled water three times before air-drying. As desired, these solids had thick layers of the SiO$_2$ skeleton that remained on the surface. Six sets of the slurries were prepared using these SiO$_2$-rich solids with dissolved surfaces. The slurry concentration was 2.5 g / 80 mL, which is ideal for particle size analysis using the SediGraph5100.

Table 6.1 describes each method in detail. When using microwave, the slurry temperature exceeded its boiling temperature during its operation; thus, the results were not compared with other methods, because the temperature increase may have promoted the dissolution of serpentine. Although the digestion of the mineral is desired for the overall process, the effect of temperature had to be minimized in order to determine the isolated effects of various surface-renewing methods. All other methods were tested under ambient temperature and pressure. In addition, there were no chemical additives (i.e. acids) added to the system. The four other cases were compared for their
effectiveness in removing the SiO$_2$ layer. Figure 6.1 illustrates how the internal (*in-situ*) grinding system was applied. This proposed *in-situ* physical activation method is much less energy intensive compared to the wet / dry attrition grinding that has been utilized by the group at the Albany Research Center. Their attrition grinding method enhances the dissolution of olivine and serpentine by reducing the particle size down to approximately 2 µm, while the proposed physical activation is mainly used to refresh the surface of the mineral particles during dissolution.

6.2.2 Effect of Internal (*in situ*) Grinding Unit on Serpentine Dissolution

From various proposed methods of physical activation, an internal (*in-situ*) attrition grinding system was chosen to investigate its effect on serpentine dissolution with and without adding any chemical additives. 20 vol % of both glass beads (2 mm diameter) and zirconia balls (5 mm diameter) were used as the grinding media. Air was used as the fluidizing gas to study the effect of internal grinding on serpentine dissolution independently from the mineral dissolution and the carbonation caused by dissolved carbon dioxide.

6.3 RESULTS AND DISCUSSION

6.3.1 Removal of SiO$_2$ Layers from Surface of Serpentine Particles

Serpentine is a sheet silicate mineral with a 1:1 structure due to the alternation of tetrahedral silica-type and octahedral brucite-type layer. It is expected that the
dissolution at the brucite-type surface be more rapid at low pH conditions. In fact, the
dissolution at the edge surface would be the fastest. Natural minerals are not
homogeneous in their compositions, and thus, Fe may occasionally replace Mg in the
serpentine structure. As a result, serpentine as a mineral usually contains a small
amount of Fe (~ 4.3 wt %). The dissolution mechanism of the FeO containing layer is
expected to be similar to that of the MgO layer. Due to this difference in the initial
dissolution rates of the silica-type and brucite-type layer, it was expected that any
undissolved siloxane layer would act as the diffusion limiting layer that inhibits the
dissolution of the inner Mg layers. This was confirmed in the earlier work presented in
Chapter 5 (Park et al., 2003). From the equilibrium calculation undertaken in Chapter
4, it was also found that the dissolved Si-oxide layer of serpentine would form SiO_2(s)
and H_4SiO_4(aq) during the mineral carbonation process.

Various methods were tested for their effectiveness in removing the diffusion
limiting layer on the particle surface during serpentine dissolution. In the case of
internal grinding with 20 vol % of 2 mm glass beads, the densities of the serpentine
particles and the glass beads were very similar so that both the serpentine particles and
the glass beads were easily fluidized even at a low gas flow rate. By increasing the gas
velocity (up to 20 cm/s), the bombardment action between the glass beads, which
refreshed the surface of the serpentine particles, was increased.

When a much denser material, zirconia balls, was used, a lower gas velocity (U_g
= 7 cm/s) was applied. Even at a high gas velocity (U_g > 20 cm/s), the zirconia balls
were not fluidized. Instead, they were acting as a fixed layer on top of the gas
distributor, and the gap between the zirconia balls was filled with high velocity gas rather than the slurry, which eliminated the physical interaction between the grinding media and the mineral particles. Thus, a lower gas velocity was used to maintain the slurry circulation around the fixed zirconia ball layer during fluidization. At a gas velocity of 7 cm/s, the slurry at the bottom of the column was agitated by the air bubbles rising through the network of the zirconia balls.

After processing five sets of slurries with the proposed physical activation methods, the samples were analyzed for their particle size distributions (PSD), and the results are shown in Fig. 6.2. The PSD of the unprocessed original SiO₂-rich serpentine particles followed the normal distribution quite closely. The average particle size was 29 µm. This value was smaller than the initial average particle size of 37 µm due to dissolution. When various methods of removing the SiO₂ layer were employed, the overall PSD shifted to the smaller particle size, and there was an increase in the amount of particles smaller than 5 µm. The generation of extremely fine particles was expected due to broken pieces of surface SiO₂ in the slurry. Particularly, the fluidization with 2 mm glass beads was found to be very successful at removing the diffusion limiting SiO₂ layer. In this case, the average particle size was decreased down to 17 µm. The ultrasonic method also showed promising results in removing the SiO₂ layer, but the extra energy consumption was a concern.

To confirm the physical removal of the SiO₂ layer using 2 mm glass beads, SEM photos were obtained after collecting solid samples. Figure 6.3 (a) shows the very porous and complex surface of a large serpentine particle after dissolution in 1 M HCl.
solution. This surface morphology can be compared to those shown in Figures 6.3 (b) and (c). The surface of the large particle shown in Figure 6.3 (b) is similar to that before dissolution. Clearly, the removal of the SiO₂ layer was successful and the inner layer of serpentine was exposed for further dissolution. Only a small amount of the SiO₂ skeleton remained on the mineral surface. Figure 6.3 (c) shows clusters of the broken pieces of SiO₂, which were much smaller in size and showed a similar morphology as the surface shown in Figure 6.3 (a). Based on Moh’s hardness scale, serpentine (hardness ~3) is softer than glass (hardness ~5.5), and therefore, the smaller particles in Figure 6.3 (c) not only contained broken SiO₂, but also small pieces of serpentine.

6.3.2 Effect of Internal (in situ) Grinding Unit on Serpentine Dissolution

The effect of an internal (in-situ) attrition grinding system was further studied. This system was proposed to provide physical activation without significant additional energy requirements. Glass beads and zirconia balls (both 20 vol %) were used as the grinding media in order to minimize the potential impurities, and they were about 2 mm and 5 mm in diameter, respectively. A denser bed was formed by these grinding media at the bottom of the reactor, and this region acted as the internal attrition grinder. During the experiments, air was used to fluidize the slurry instead of CO₂ gas to ensure that there was no carbonation occurring during the dissolution process.

As shown in Figure 6.4, the physical activation by internal grinding alone did not significantly enhance the dissolution of serpentine. Since the concentration of the
grinding media (20 vol %) was much lower than that of an external attrition grinder (up to 50 vol %), less interaction was occurring between grinding media. Thus, this method of grinding was not as effective as external attrition grinding used by the group at the Albany Research Center (final average particle size $\sim 2 \, \mu \text{m}$) (Penner et al., 2003). However, since the main goal of the internal grinding was not particle size reduction, the internal grinding method would be sufficient to refresh only the surface of the particles with less energy requirements. As shown in Figure 6.5, the presence of grinding media in the slurry during the dissolution aided the access of leaching acid to the inner portion of the serpentine particles and resulted in a higher overall conversion. Therefore, the key to the fast serpentine dissolution process will be to find a suitable combination of solvents and internal grinding. Compared to the energy requirement of an external attrition grinder, this internal (in-situ) grinding unit would be much more energy efficient and easy to incorporate into the overall CO$_2$ mineral sequestration scheme.

6.4 CONCLUSIONS

The effect of the physical activation on the dissolution of serpentine was investigated in order to better-design mineral sequestration processes that can convert separated and captured CO$_2$ to products appropriate for long-term, environmentally benign, and unmonitored storage. Various physical agitation methods were used to remove the SiO$_2$ layer on the surface of the serpentine particles that created a diffusion problem for further dissolution of the inner Mg layer. It was found that although the
physical activation caused by the interaction with the grinding media alone did not significantly dissolve serpentine, the use of the grinding media in the acidic solvent resulted in a radical improvement in the serpentine dissolution rate.
Table 6.1: Various methods of removing of SiO$_2$ layer.
Figure 6.1: Application of internal grinding system.
Figure 6.2: Particle size distribution for various internal grinding methods.
Figure 6.3: SEM photos of particles before and after fluidization with 2 mm glass beads for 15 min.
Figure 6.4: Effect of internal grinding on serpentine dissolution without any chemical additives under neutral pH condition.
Figure 6.5: Effect of internal grinding on serpentine dissolution with chemical additives under acidic condition.
CHAPTER 7

pH SWING PROCESS


SUMMARY A pH swing scheme was developed to improve the overall conversion of the CO₂ mineral sequestration process. As discussed in Chapter 5 and based on the carbonation results given in this chapter, it was found that when the solution is acidic, the overall rate was limited by the rate of carbonation, which was limited by dissolution of CO₂ and dissociation of carbonic acids into bicarbonate or carbonate ions. Since bicarbonate and carbonate ions are favored more at higher pHs, using the proposed pH swing scheme, the overall conversion of the mineral carbonation radically improved. By controlling the pH of the system, three solid products were
generated from the mineral carbonation process: SiO$_2$-rich solids, iron oxide and MgCO$_3$·3H$_2$O. Since the iron oxide and magnesium carbonate produced were highly pure, these value-added products could eventually reduce the overall cost of the carbon sequestration process.

7.1 INTRODUCTION

In the aqueous mineral sequestration process, the dissolution of the mineral has generally been speculated as the rate-limiting step. In this work, the dissolution of serpentine has been successfully enhanced using a mixture of weak acids and chelating agent while preventing the precipitation of Fe(III) on the surface of the Mg-bearing mineral particles. The next step was to evaluate the rate of aqueous carbonation of leached Mg ions.

U.S. patent 3,338,667 (Pundsack, 1967) describes a process using an acid developed for the purpose of extracting silica and iron oxides from serpentine in which magnesium carbonate is one of the products and the acid is regenerated via heat decomposition. In this process, serpentine is dissolved in the acidic ammonium salt, NH$_4$SO$_4$, as shown in the following chemical reaction.

\[
\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{NH}_4\text{HSO}_4 \rightarrow 3\text{MgSO}_4 + 3(\text{NH}_4)_2\text{SO}_4 + 2\text{SiO}_2(s) + 5\text{H}_2\text{O} \quad \text{(7.1)}
\]

The pH of the solution is brought up to 8.5 with ammonium hydroxide (NH$_4$OH) to precipitate ferric and/or ferrous ions of the solution in the forms of Fe$_2$O$_3$ and FeO. The potential economical benefit of these by-products should be investigated. As the pH is
further increased while gaseous carbon dioxide is pumped into the solution, magnesium carbonate will precipitate out.

\[
\text{MgSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{CO}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{MgCO}_3 + 2(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O} \quad (7.2)
\]

Finally, ammonium sulfate can be converted back into ammonium bisulfate by means of heat decomposition:

\[
(\text{NH}_4)_2\text{SO}_4 + \text{heat}_{330^\circ\text{C}} \rightarrow \text{NH}_4\text{HSO}_4(\text{s}) + \text{NH}_3(\text{g}) \quad (7.3)
\]

This is a good example of the desirable processes for the CO\textsubscript{2} mineral sequestration, although the energy requirement is still significant.

Therefore, for this study, another route of aqueous carbonation was developed by incorporating the results from Chapters 5 and 6. In addition, the fate of other dissolved species such as ferrous ions was controlled in order to produce valuable by-products.

### 7.2 EXPERIMENTAL

Aqueous carbonation studies were performed in a high pressure, high temperature three-phase fluidized bed reactor shown in Figure 3.11 using both pure Mg(OH)\textsubscript{2} and serpentine without chelating agents. The maximum operating pressure and temperature of this system are 210 atm and 250 °C, respectively. The reactor is 4.0” diameter and 54” height, and three pairs of quartz windows were installed on the front and rear sides of the column for visualization purposes. A T-type thermocouple was inserted directly into the reactor to monitor the reaction temperature, and a backpressure regulator was used at the downstream of the reactor to control the internal
pressure. The high pressure CO$_2$ gas was then introduced into the reactor from the bottom through a distributor, and the vigorous movement of CO$_2$ bubbles provided a mixing to the slurry.

Based on the findings in the dissolution studies, aqueous carbonation of serpentine was investigated using ground serpentine and the prepared solvent. The overall reaction for serpentine can be given as:

\[
\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 3\text{MgCO}_3 + 2\text{Si(OH)}_4 \text{ or } 3\text{MgCO}_3 + 2\text{SiO}_2 + 4\text{H}_2\text{O} \quad (7.4)
\]

First, at 70 °C ground serpentine (< 75 µm) was dissolved in acidic solvents ((a) a mixture of 1 vol% orthophosphoric acid, 0.9 wt% of oxalic acid and 0.1 wt% EDTA that was earlier used by the authors (Park et al., 2003), (b) 1.4 M ammonium bisulfate), while being fluidized with internal grinding media (20 vol % of 2 mm glass beads at the superficial gas velocity of 20 cm/s). At this stage, the reactor was not pressurized since the rate of surface dissolution was not a function of the operating pressure when acids and internal grinding system were used to leach out Mg.

After the dissolution stage, the slurry was filtered and the undissolved solids were collected as Product 1, which should be high in SiO$_2$ content. Next, the Mg- and Fe-rich solution was cooled to ambient temperature and the pH of the solution was increased to pH ~ 8.6 by adding NH$_4$OH where iron oxide was expected to precipitate. It was important to increase the pH slowly to minimize the gelation. Product 2 was separated out from the Mg-rich solution. Finally, pure CO$_2$ was bubbled through the ambient temperature Mg-rich solution for 10 min. Once the solution was saturated with
dissolved CO₂, the pH of the solution was further increased to ~ 9.5 by adding additional NH₄OH. After 5 minutes, the slurry was collected and filtered. The white precipitates (Product 3) were dried in a low temperature oven. All three solid products were analyzed using an X-ray Diffractometer (XRD) and Thermal Gravimetric Analyzer (TGA).

7.3 RESULTS AND DISCUSSION

7.3.1 Aqueous Carbonation of Mg(OH)₂ and Serpentine

First, a 10 wt% slurry of Mg(OH)₂, which has a higher solubility in water than serpentine, was prepared. Using the reactor shown in Figure 3.11, carbonation reaction was carried out by bubbling CO₂ through this solution. It was found that at 15 atm the conversions were 32 % and 90 % for 160 ºC and 20 ºC, respectively. The conversion at the lower operating temperature was higher, as both CO₂ and Mg(OH)₂ are more soluble at a lower temperature. Through the viewing windows of the reactor it was observed that Mg(OH)₂ was completely dissolved and the total reaction time was approximately 1 hour, which is still not sufficiently fast for an economical application. As expected, the rate of carbonation/precipitation was relatively fast in this case. The solid product was characterized using TGA and XRD. The results of the TGA analysis are presented in Figure 7.1.

The first weight lose shown in Figure 7.1 was probably due to the evaporation of moisture. The second weight lose which started at around 270 ºC corresponds for the
calcination reaction. There was approximately 44.4% weight loss of the product. If we assume that the solid product was only magnesium carbonation, this result indicates very high stoichiometric conversion of magnesium hydroxide. But the possibilities of undesired products and of the weight loss due to losing water from magnesium hydroxide have to be checked. Therefore, XRD was also performed to confirm the composition of the reaction product and it was found that when Mg(OH)₂ was used, MgCO₃·3H₂O was the final form of the product. Generally, magnesium carbonates associate with 1, 3 or 5 molecules of water during crystallization (Durrant and Durrant, 1970). Figure 7.2 shows the change in crystalline structures when Mg(OH)₂ was converted to MgCO₃ through the aqueous carbonation process.

Lackner et al. (1997) described the direct (gas-solid) carbonation of Mg(OH)₂ extracted from Mg-bearing rock was found to be a environmentally safe method of CO₂ disposal. There was another literature investigating the carbonation of Mg(OH)₂ as a method of CO₂ sequestration. McKelvy et al. (2001) reported their optimization study of the reaction rates for direct Mg(OH)₂ carbonation at CO₂ reaction pressures that just exceed the minimum pressure needed to stabilize MgCO₃ formation. The authors claimed that dramatically enhanced carbonation reactivity can be achieved via rehydroxylation-carbonation for low-temperature dehydroxylated Mg(OH)₂, even at ambient temperature (McKelvy et al., 2001). This paper provided a mechanistic understanding of CO₂ mineral sequestration processes and confirmed that Mg(OH)₂ is another potential candidate for the CO₂ sequestration reactant. Similar to the carbonation of olivine and serpentine, the thermodynamically stable waste product of
the carbonation of magnesium hydroxide eliminates both the danger of a sudden accidental release and a slow re-introduction of the CO₂ into the atmosphere that could result in a climate problem. Therefore, basalt, a mineral containing large amount of magnesium hydroxide, is suggested as an alternative source of magnesium.

Next, based on the findings in the dissolution studies discussed in Chapter 5, the carbonation studies were carried out using ground serpentine (< 75 µm) and solvent #7 at 7 MPa and 80 °C. The superficial gas velocity (99.999 % of CO₂) was maintained at 5 cm/s. The slurry was mixed by the vigorous movement of CO₂ gas bubbles. After 30 minutes of reaction time, the slurry was collected and filtered. The extent of carbonation was determined by calcining the final product at 500 °C using a TGA since the weight change during calcination corresponds to the amount of CO₂ captured by carbonation. Note that TGA experiments could be complicated by dehydroxylation reactions of MgCO₃·xH₂O (x = 1, 3 or 5). The solid product was found to contain approximately 25 % carbonated material from the TGA analysis. It was noticed that the filtrate of the slurry was still green in color, indicating high concentration of free Fe(II) in the solution.

When it was tested for Mg ion concentration, it was found that large amounts of Mg ions (~ 22 % of total Mg content) were not carbonated and remained in the aqueous phase. In other words, when the solvent was acidic, the overall reaction rate was limited by the rate of carbonation, which was limited by dissolution of CO₂ and dissociation of carbonic acids. A lower reaction temperature would increase the dissolution of CO₂ and thus could increase the overall conversion.
From these results, it was found that when the solution was acidic, the overall rate was limited by the rate of carbonation, which was limited by dissolution of CO$_2$ and dissociation of carbonic acids into bicarbonate or carbonate ions. Since bicarbonate and carbonate ions are favored more at higher pHs, a pH swing was proposed to achieve a higher overall conversion for the CO$_2$ aqueous mineral sequestration process. To prove this conclusion, simple calculations were carried out using the amount of CO$_2$ dissolved in the aqueous phase given in the literature.

According to Figure 7.3, the amount of CO$_2$ that dissolves in 100 g of water is about 3 g at 80 °C and 70 atm (operating conditions used for the aqueous carbonation studies). This translates into 0.68 M of CO$_2$ in the aqueous phase. Since the final Mg$^{2+}$ concentration measured during the dissolution studies in solvent #7 was 700 µg/mL, the rate of CO$_2$ dissolution seems to exceed the required amount of CO$_2$ to react with Mg$^{2+}$ (1:1 ratio). However, the rate of dissociation of carbonic acids was found to be extremely slow. Figure 7.4 shows the speciation in an open CO$_2$ system as a function of pH. Since the reactor was operated in the continuous mode for CO$_2$ gas, while the slurry was in batch, the open system was used to estimate CO$_3^{2-}$ concentration in the slurry. At pH = 2, the estimated [CO$_3^{2-}$] was 2.53x10$^{-6}$ M. This value was obtained considering the pressure and temperature effects on the dissolution of CO$_2$. Therefore, it was confirmed that actual [CO$_3^{2-}$] was much smaller than [Mg$^{2+}$]. Thus, it is important to raise the pH of the solution to increase the degree of aqueous carbonation. As indicated in Figure 7.4 with the dotted line, the optimum pH for the aqueous
carbonation is around 10. Therefore, a pH swing was proposed to achieve a higher conversion for the CO₂ mineral carbonation process.

### 7.3.2 Development of pH swing process

From our earlier work, it was found that when the aqueous phase was fairly acidic, the overall conversion was limited by the extent of carbonic acids dissociation into bicarbonate or carbonate ions (Park et al., 2003). From a thermodynamic equilibrium calculation, it was confirmed that even at high partial pressures of CO₂, actual concentration of CO₃²⁻ was much smaller than the concentration of Mg²⁺. Consequently, the overall conversion of the aqueous carbonation of serpentine was limited at low pH conditions. Thus, it was important to raise the pH of the solution to increase the degree of aqueous carbonation. The optimum pH for the aqueous carbonation is around 10, while the dissolution of serpentine is preferred at low pH conditions.

Based on these findings, a pH swing was proposed to achieve a higher overall conversion for the CO₂ aqueous mineral sequestration process and its overall process is illustrated in Figure 7.5. First, at 70 °C the ground serpentine was dissolved in the prepared solvents ((a) a mixture of 1 vol % orthophosphoric acid, 0.9 wt % of oxalic acid and 0.1 wt % EDTA that was earlier used by the authors (Park et al., 2003) and (b) 1.4 M ammonium bisulfate) with aid of an internal grinding system (20 vol % of 2 mm glass beads at U_g = 20 cm/s). The reactor was operated at ambient pressure, which would allow for a lower capital cost for the future dissolution unit. After 1 hour of the
dissolution process, the first solid product was separated via vacuum filtration. SiO₂ should be the only solid component left in the reactor if the dissolution was fully completed, but according to the flame-AAS analysis on the liquid samples, the amounts of Mg leached out within 1 hour were approximately 65 % in solvent (a) and 42 % in solvent (b).

As shown in Figure 7.5, the color of the dried solid sample (Product 1), which resembled white SiO₂ powder, was much whiter than the ground serpentine. Some unreacted serpentine was also detected in the first solid product. Although pure SiO₂ will have a higher economical value, it would be rather energy intensive to separate pure SiO₂ as the first solid product from serpentine. Low quality SiO₂ might be able to be reused as the seed material for the carbonation process. Unlike in U.S. Patent 3,338,667 (Pundsack, 1967), the dissolution took much less time due to the successful application of both chemical and physical activation of serpentine.

Next, the second product, iron oxide, was precipitated from the cooled Mg- and Fe-rich solution by raising the pH of the solution to pH ~ 8.6 with NH₄OH. Product 2 was quite pure since the precipitation was carried out in a controlled pH condition. NH₄OH was added dropwise to ensure isolated precipitation of iron oxide without formation of Mg(OH)₂. Based on the XRD findings, the iron oxide powder (Product 2) was found to be amorphous.

Finally, while bubbling pure CO₂, Mg²⁺ was carbonated and MgCO₃ (Product 3) was precipitated at ambient temperature. Due to the higher partial pressure of CO₂ in the system and low operating temperature, the dissolution of gaseous CO₂ into the
aqueous phase was rapid. As the pH of the solution was increased to ~ 9.5 with additional NH₄OH, the dissociation of carbonic acids quickly took place and carbonation occurred spontaneously. From XRD analysis, it was found that the final product was relatively pure MgCO₃·3H₂O (Product 3). The SEM photos in Figure 7.6 illustrate the morphologies of the three solids products. The crystal structure shown in Figure 7.6 (c) is very similar to the one shown in Figure 7.2 since both carbonation processes produced MgCO₃·3H₂O as the final product. The surface structure of the particle in Figure 7.6 (a) was somewhat similar to that of serpentine although the Si-rich particle was more porous. This might be due to the components of the undissolved serpentine. The second solid product, iron oxide, was very fine in nature and Figure 7.6 (b) shows the agglomerated lumps of the iron oxide particle, which were generated during the drying process.

Although pure CO₂ at 1 atm was used during this study due to the physical limitation of the pH probe, in the future a much higher pressure of CO₂, which is captured from power plants and transported to the sequestration site, could be used to carbonate the Mg-rich solution. The higher partial pressure of CO₂ will result in a larger amount of dissolved CO₂. Both precipitation of iron oxide and magnesium carbonate were almost instantaneous once the desired pH condition was reached. Thus, the overall conversion to MgCO₃ was ~ 65 % for solvent (a) and ~ 42 % for solvent (b) and the dissolution process was again the rate-limiting step. Considering that these results were obtained at a much lower temperature and pressure (70 ºC and 1 atm) than the operating conditions used by others (i.e., 185 ºC and 150 atm (O’Connor et al.,
it is expected that the operating cost for this proposed process will be much lower. In addition, the overall capital cost is also lower for this process, since only the carbonation unit may require a high pressure reactor.

Using TGA, it was confirmed that the final product, MgCO$_3$·3H$_2$O, is thermally stable up to 320 ºC. This makes the proposed process a permanent solution to carbon sequestration. Innovative heat integration between the dissolution unit and the precipitation units and recycling of the chemicals will be essential for the further reduction of the operating cost.

### 7.3.3 SO$_2$ Scrubbing Effect of Mg-rich Solution

The current flue gas desulfurization technologies include lime and limestone scrubbing, modified limestone scrubbing (double alkali systems), etc. In our group, OSCAR process is in its demonstration stage for using PCC to remove SO$_2$ in hot flue gas. Until now, most carbon sequestration technologies based on the assumption that captured and pressurized (~ 110 atm) pure CO$_2$ will be transferred to the sequestration sites. Recently, questions were raised whether CO$_2$ can be sequestered directly from flue gas. This is another possible scenario for the carbon sequestration technologies, although lower CO$_2$ partial pressure will result in slower dissolution of CO$_2$ into aqueous phase. However, since SO$_2$, which is another pollutant of interest, is also an acid gas and dissolves rapidly into water, there could be an added benefit of operating the system with flue gas. Therefore, literature review and preliminary experiments were performed to investigate the SO$_2$ removal capability of Mg-rich solution.
SO$_2$(g) dissolves in a similar manner as CO$_2$(g). Both are acid gases, but SO$_2$(aq) turns into H$_2$SO$_3$ rather quickly and H$_2$SO$_3$ dissociates into HSO$_3^-$ and SO$_3^{2-}$ faster than the dissociation of carbonic acid. Like in case of CO$_2$ dissolution, the dissolution of SO$_2$ increases with an increase in partial pressure of SO$_2$ and decreases with a rise in temperature. The dissociation of H$_2$SO$_3$ shows the same trend as the dissociation of carbonic acid. SO$_2$(aq) is dominant at pH below 1.89, while HSO$_3^-$ and SO$_3^{2-}$ are dominant at pH between 1.89 and 7.21, and pH higher than 7.21, respectively. Figure 7.7 was generated using the following equations and the equilibrium constants for each of the reactions assuming the open system with pure SO$_2$.

\[
\text{SO}_2(g) \rightarrow \text{SO}_2(aq) \quad : \text{calculated based on Henry’s constant} \quad (7.5)
\]

\[
\text{SO}_2(aq) \rightarrow \text{H}_2\text{SO}_3 \quad : K << 1 \times 10^{-9} \quad (7.6)
\]

\[
\text{H}_2\text{SO}_3 \rightarrow \text{H}^+ + \text{HSO}_3^- \quad : K = 1.32 \times 10^{-2} \quad (7.7)
\]

\[
\text{HSO}_3^- \rightarrow \text{H}^+ + \text{SO}_3^{2-} \quad : K = 6.20 \times 10^{-8} \quad (7.8)
\]

The solubility of SO$_2$ is much higher than CO$_2$ in water. Once SO$_2$ is dissolved in water, the following reactions occur (Auer et al., 1997).

\[
\text{Mg}^{2+} + \text{SO}_3^{2-} \rightarrow \text{MgSO}_3 \quad (7.9)
\]

\[
\text{MgSO}_3 + \text{H}_2\text{SO}_3 \rightarrow \text{Mg}^{2+} + 2\text{HSO}_3^- \quad (7.10)
\]

Using an open system bubbler connected to the fume hood, 6000 ppm SO$_2$ was bubbled through the Mg-rich solution. There was no visually observed precipitation but pH of the solution decreased as SO$_2$ dissolved. Further experiments are required to determine what is the final product and how much SO$_2$ in the flue gas can be scrubbed using this method. According to the literature, Ca- and Mg-rich solution can remove
more than 90 % of SO₂ with lower power consumption and no scaling (Auer et al., 1997). The amount of SO₂ in the flue gas is ~1/50 of CO₂, thus, it is expected that SO₂ will not interfere with CO₂ sequestration significantly. This has to be confirmed in future experiments. If successful, this method can be used for multipollutant control.

One of the possible final products of SO₂ scrubbing is magnesium sulfite, MgSO₃. Unlike MgSO₄, it is reported to be insoluble in water. Magnesium sulfite is generally manufactured by treating magnesium sulfate with sodium sulfate.

\[
\text{MgSO}_4 + \text{Na}_2\text{SO}_3 \rightarrow \text{MgSO}_3 + \text{Na}_2\text{SO}_4
\]  

(7.11)

Magnesium sulfite is used in medicine and paper pulp (Vishal Chemical Industries, 2003). MgSO₃ is white crystalline powder or colorless crystals, which do not dissolve well in water (1:150) (CHEMWATCH MSDS, 2003). Unfortunately, MgSO₃ oxidizes to sulfate when exposure to air. Therefore, the oxidation rate should be identified in order to determine the long-term stability of the final product. A secondary treatment might be required unless the final product is stable.

### 7.4 CONCLUSIONS

A pH swing process was developed to achieve a higher overall conversion, since the bicarbonate and carbonate ions are predominant at higher pHs. Using the proposed pH swing process, CO₂ was successfully sequestered via aqueous mineral carbonation. By carefully controlling the pH, three solid products were generated: SiO₂-rich powder, iron oxide and MgCO₃·3H₂O. In addition, a technical feasibility of the multi-pollutant control process using the Mg-rich solution that was prepared during the pH swing
process was evaluated. According to the experimental results, both acid gases, SO$_2$ and
CO$_2$, can be sequestered simultaneously using this technique. Most likely, SO$_2$ was
absorbed as HSO$_3^-$.

The integration of this pH swing process into the coal burning
power plants will further reduce the capital and the operating costs of the overall air
pollution control system compared to the existing control systems.
Figure 7.1: TGA plot for calcination reaction of carbonated product of Mg(OH)$_2$ under N$_2$ flow.
Figure 7.2: SEM photos of pure Mg(OH)$_2$ (left) and reaction product MgCO$_3$·3H$_2$O (right).
Figure 7.3: Solubility of CO$_2$ in water at various temperatures and pressures

(Pierantozzi, 1991).
Figure 7.4: Speciation versus pH for open CO₂ system.
Grind Serpentine

Serpentine + Acid + chelating agent at higher T

pH 2 → SiO$_2$

Mg- and Fe-rich solution at room T

pH 8.6 → Precipitated iron oxide

Mg-rich solution at room T

pH 9.5 → Precipitated MgCO$_3$

Figure 7.5: Summary of pH swing process.
Figure 7.6: SEM photos of three solid byproducts of pH swing process: (a) Si-rich solids with two different magnifications, (b) precipitated iron oxide, and (c) precipitated magnesium carbonate.
Figure 7.7: Speciation versus pH for open SO$_2$ system.
CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

In this study, the reaction mechanisms and kinetics of carbon dioxide interaction with serpentine were investigated in order to better-design mineral sequestration processes that can convert separated and captured CO₂ to products appropriate for long-term, environmentally benign, and unmonitored storage. The impacts of this study are expected to be on the technology development for mineral sequestration of CO₂, which would benefit various industries including energy, chemical and petrochemical industries that generate CO₂. Preliminary screening of mineral samples for their application in the CO₂ mineral sequestration scheme identified both olivine and serpentine to be the viable candidates. Particularly, the procured Mg-rich serpentine samples contained approximately 27.1 wt% of magnesium. The amount of Mg-bearing mineral deposits is estimated to far exceed worldwide coal reserves.

During the last decade, many researchers have been working towards the improvement of dissolution of Mg-bearing minerals, which has been considered to be the rate-limiting step. According to the experimental results, the chemically enhanced
aqueous carbonation of serpentine showed promising results. From the investigation of serpentine dissolution in various solvents, it was found that a mixture of 1 vol % orthophosphoric acid, 0.9 wt % of oxalic acid and 0.1 wt % EDTA greatly enhanced the Mg leaching process of ground serpentine while preventing the precipitation of Fe(III) on the surface of the mineral particles. In fact, when this acidic solvent was used for the aqueous mineral carbonation, the overall process was limited by the rates of dissolution of CO₂ and dissociation of carbonic acid, rather than the dissolution rate of the mineral. The solid products were examined using a TGA, XRD and SEM in order to quantify the degree of carbonation and identify the reaction mechanisms.

Next, the effect of the physical activation on the dissolution of serpentine was investigated, and a pH swing scheme was developed. Various physical agitation methods were used to remove the SiO₂ layer on the surface of the serpentine particles, which created a diffusion problem for further dissolution of the inner Mg layer. Although the physical activation caused by the interaction with the grinding media alone did not significantly dissolve serpentine, the use of the grinding media in the acidic solvent resulted in a radical improvement in the serpentine dissolution rate. A pH swing process was then proposed to achieve a higher overall conversion. Since the bicarbonate and carbonate ions are predominant at higher pHs, by carefully controlling the pH, three solid products were generated from the mineral carbonation process: SiO₂-rich solids, iron oxide and magnesium carbonate. The Mg-rich solution prepared during the pH swing process was also effective in removing SO₂ from flue gas. A patent describing this pH swing process was filed at the United States Patent Office in 2003.
The commercial application of the proposed aqueous mineral carbonation process can be envisioned as following: Mineral sequestration would form one part of the overall carbon sequestration strategy. A concentrated and pressurized CO$_2$ stream will be available to be pumped to a sequestration site, which will be close to the mineral mine to minimize sorbent transportation costs. The CO$_2$ stream will be contacted with an aqueous slurry of minerals in a reactor maintained at high temperature and pressure. A process of recycling chemicals through each reaction cycle will be employed to reduce the operating cost. Alternatively, if the reaction rates are high enough, the pressurized CO$_2$ stream may also be injected directly into the mine to react with Mg-rich minerals.

There are various carbon sequestration schemes that are being developed, and it is not likely only one method will be selected as the universal carbon sequestration technique. In many cases, carbon sequestration will be associated with the large point source of CO$_2$, such as coal-fired power plants, and a suitable process will be selected based on the location and resources available for each case. Since geological sequestration is the lowest cost application, it has been selected to be demonstrated in large scales. It is inevitable that more permanent methods, such as the proposed carbon mineral sequestration, are necessary to ensure the long-term stability of stored carbon dioxide and prevent its accidental release. Carbon mineral sequestration is the only method of its kind that does not require long-term maintenance after disposal. The final product (magnesium carbonate) is thermodynamically stable, and as a result, there is of little likelihood of accidental release. If large amounts of carbon dioxide is released, the results can be quite devastating. In 1986, 1700 people died in Cameron,
Africa, by suffocation because a large amount of CO₂ was released as Lake Nyos overturned. Therefore, there should be continued effort in the development of the proposed carbon mineral sequestration.

The results obtained in this study would also open up new frontier areas of research in carbon management as applied to the geological sequestration. In geological sequestration, the high pressure CO₂ is directly injected into aquifers or geological formations where CO₂ interacts with brine and/or minerals. The advances gained in this study will be of help to the understanding of the reactions associated with the geological sequestration.

### 8.2 RECOMMENDATIONS FOR FUTURE WORK

The thermodynamic limit of the mineral carbonation process for solvents of various compositions can be obtained from the MINTEQ simulations. However, the kinetics for each solvent case should be evaluated before the final selection is made for the solvent recipe. Particularly, the selection of the suitable chelating agents is very important for the overall conversion of the proposed carbon sequestration process. Generally, chelating agents do enhance the dissolution of minerals; however, due to the increased solubility, the precipitation step of the overall process is inhibited. Thus, it is essential to find the chelating agents that are not only effective at improving the mineral dissolution but also do not interfere with the precipitation process. Although EDTA and oxalic acid were very effective at aiding the dissolution of serpentine, the cost of these
chemicals was relatively high, and as a result, a search for less expensive chelating agents is desired.

Table 8.1 lists various ligands in the order of their affinities for Mg$^{2+}$. The subsequent rows in Table 8.1 list the affinities of these ligands for Fe$^{2+}$ and Fe$^{3+}$ ions. The log of equilibrium constants given in Table 8.1 corresponds to a general complexation of the type

\[ m \, M + l \, L + h \, H = M_mL_lH_h \]  

(8.1)

where \( M \) = metal, \( L \) = ligand, \( H \) = proton.

Stability constant, \( \beta_{mlh} = \frac{(M_mL_lH_h)}{(M)^m(L)^l(H)^h} \)  

(8.2)

Generally, trivalent metals (e.g. Fe$^{3+}$) are more reactive than divalent ones (e.g. Mg$^{2+}$ and Fe$^{2+}$), but their activities are also affected by the solubility of their corresponding oxides and hydroxides (Morel, 1983). For example, many complexing agents have a relatively high affinity for Fe$^{3+}$. However, the ferric hydroxides, including the solid Fe(OH)$_3$, are very stable, and as a result, the free ferric ion activity is kept very low, and consequently, the extent of Fe complexation is limited (Morel, 1983).

Nevertheless, the list given in Table 8.1 should be used as a criterion for the selection of the complexing agent. Note that as mentioned earlier, the stability constants of these ligands should be lower than that of the carbonate ion, particularly for Mg ion. Otherwise, magnesium carbonate would not form/precipitate readily, which then limits the overall minerals conversion. In other words, Ethylene-diamine, Acetate,
Glycolate, $\text{S}_2\text{O}_3^{2-}$, $\text{F}^-$, $\text{SO}_4^{2-}$, $\text{OH}^-$, Picolinate, Glycine, Glutamate, and Malonate are perceived to be potential candidates for carbonate formation.

Also, in order to prevent the precipitation of iron compounds on the mineral surface during mineral dissolution, the ligands with high affinities on ferric ions are preferred. As discussed earlier, the precipitated iron phases inhibit the further dissolution of minerals by creating the diffusion limiting layer on the surface of serpentine particles. Other factors in choosing suitable complexing agents are the cost of the chemicals and ease of recovery. Future studies should be conducted based on these criteria to improve the overall conversion and the economic feasibility of the proposed carbon sequestration process.
<table>
<thead>
<tr>
<th>Ligands</th>
<th>Mg\textsuperscript{2+}</th>
<th>Fe\textsuperscript{2+}</th>
<th>Fe\textsuperscript{3+}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ethylene-diamine(0.4), Acetate(1.3), Glycolate(1.3), S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}(1.8), F-(1.8), SO\textsubscript{4}\textsuperscript{2-}(2.36), OH-(2.56), Picolinate(2.6), Glycine(2.7), Glutamate(2.8), Malonate(2.9), CO\textsubscript{3}\textsuperscript{2-}(3.4), Citrate(4.7), PO\textsubscript{4}\textsuperscript{3-}(4.8), SiO\textsubscript{3}\textsuperscript{2-}(5.3), NTA(6.5), EDTA(10.6), HCO\textsubscript{3}-(11.49), CDTA(12.8),…</td>
<td>Ethylene-diamine(4.3), Acetate(1.4), Glycolate(1.9), S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}(-), F-(1.4), SO\textsubscript{4}\textsuperscript{2-}(2.2), OH-(4.5), Picolinate(5.3), Glycine(4.3), Glutamate(4.6), Malonate(-),…</td>
<td>Ethylene-diamine(-), Acetate(4.0), Glycolate(3.7), S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}(3.3), F-(6.0), SO\textsubscript{4}\textsuperscript{2-}(4.0), OH-(11.8), Picolinate\textsubscript{2}(13.9), Glycine(10.8), Glutamate(13.8), Malonate(9.3),…</td>
</tr>
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Table 8.1: Stability constants for formation of complexes from metals and ligands.
APPENDIX A

LIFE CYCLE ANALYSIS

A.1 INTRODUCTION

In order to completely evaluate the proposed system for the CO\textsubscript{2} sequestration, a life-cycle assessment (LCA) should be performed using an appropriate system boundary. In 1993, Japanese researchers shifted their study to the development of a methodology for a life-cycle assessment of power-generation systems including evaluation of externalities, in addition to traditional technical and economical feasibilities (Akai et al., 1996). Although it is difficult to perform a LCA without full understanding of the CO\textsubscript{2} mitigation technology, it is a necessary tool to evaluate the overall performance of the proposed process during its development.

Capturing CO\textsubscript{2} from the flue gas of the coal-fired power plant and sequestering it can reduce the Global Warming Potential (GWP) of the electricity production, however the overall penalty is an increase in fossil energy consumption, which would result in further CO\textsubscript{2} emission. The additional energy will be used to maintain a designated plant capacity, to capture and pressurize CO\textsubscript{2}, to transport and execute the sequestration process. Therefore, it will be important to carry out the Net Energy
Analysis (NEA) and the Emission Inventory Analysis (EIA) that cover the entire carbon mitigation “life cycle” of capture, separation, transportation, and sequestration (Audus and Freund, 1997; Spath, 2001).

A.2 RESULTS AND DISCUSSION

Based on the proposed carbon mineral sequestration process, Figure A.1 was prepared by setting a system boundary. Since some of the components within the system boundary are still unknown, it was necessary to create some assumptions in order to simplify the problem. Here is the list of assumptions used during the life cycle analysis.

Assumptions:

• The proposed process is successfully developed and adopted for practical use.

• Pure CO₂ is transported to the sequestration site via pipeline (CO₂ separation and transportation are not included in this analysis).

• GWP due to transportation and grinding of serpentine are relatively small compared to other CO₂ inputs, thus neglect those.

• Serpentine mined from Pennsylvania is utilized for the process, with the sequestration plant located next to the mine site.

• Since we are proposing to sell all the solid products, neglect the post processing for now.
Next, a set of the reactor conditions were chosen based on the experimental results discussed throughout this dissertation.

Given reactor conditions:

- Composition of serpentine (Mg = 27 wt %, Si = 20 wt%, and Fe = 5 wt %)
- Overall reaction:  
  \[ \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 3\text{MgCO}_3 + 2\text{Si(OH)}_4 \text{ or } 3\text{MgCO}_3 + 2\text{SiO}_2 + 4\text{H}_2\text{O} \]
- Operating conditions: 30 min residence time, \( T = 70 \, ^\circ\text{C} \), \( P_{\text{CO}_2} = 2000 \, \text{psi} \) (13.8 MPa), gas velocity = 0.2 m/s
- Assume volume of reactor to be 1 m\(^3\)
- 30 wt % solids in slurry = 1 M initial concentration of serpentine (solid holdup = 0.09, gas holdup = 0.40, liquid holdup = 0.51 for the slurry bubble column reactor)
- Chemicals required: 0.01 M orthophosphoric acid, 0.003 M EDTA, 0.01 M NH\(_4\)OH
- 85 % reaction efficiency for the mineral carbonation process.

Using the given phase holdups, the pressure drop for the slurry bubble column reactor can be estimated.

\[
\Delta P / \Delta z = \left( \varepsilon_g \rho_g + \varepsilon_l \rho_l + \varepsilon_s \rho_s \right) g 
= (0.4 \times 0.213 \, \text{g/mL} + 0.51 \times 1 \, \text{g/mL} + 0.09 \times 2.55 \, \text{g/mL}) \times 9.81 \, \text{m/s}^2
= 0.00953 \, \text{kg/m}^2\text{s}^2
\]
Energy used during 30 min operation of the fluidized bed reactor is estimated based on the pressure drop across the bed using the following equation.

\[
\frac{\Delta P}{\Delta z} U_g t V_{\text{reactor}} = (0.00953 \text{ kg/m}^2\text{s}^2)(0.2 \text{ m/s})(1800 \text{ s})(1 \text{ m}^3) = 3.4 \text{ J} \quad (A.2)
\]

The next component in the energy requirement of the proposed pH swing process is heating. Energy is used to maintain the dissolution unit at 70 °C during 30 min operation. The heat capacity of the slurry is assumed to be the same as water. Therefore,

\[
Q = C_p m \Delta T = (4.18 \text{ J/g °C})(1.38\times10^6 \text{ g})(70-25 \text{ °C}) = 2.6E8 \text{ J} \quad (A.3)
\]

Thus, the energy required for heating is much greater than the energy required for operating a fluidized bed reactor. The total energy required for the mineral carbonation processing is calculated to be 2.6E8 J.

In Figure A.1, the inputs and the outputs of CO₂ are highlighted with colored boxes and darker lined boxes, respectively. Next, a simple material balance was carried out to determine the amount of each compound in this process and the results are summarized in Table A.1. Note that the reaction conversion was assumed to be 85 % to give a rather conservative prediction for the life cycle analysis and unreacted serpentine and CO₂ are recycled throughout the system. The amount of CO₂ sequestered by the mineral carbonation process is 151.9 kg for the given reactor condition.

Next, using the tool available at www.eiolca.net, GWP of each CO₂ input and output is obtained. For now, these values are based on 1 million dollars (Table A.2). Due to the simplicity of the program found at www.eiolca.net, various chemicals are not
distinguishable during the life cycle analysis. For example, the CO₂ emission and
global warming potential for EDTA and orthophosphoric acid were the same according
to their database. The results for all the minerals were also the same. Now, these values are corrected based on the material balance given in Table A.1. Table A.3 shows the dollar amounts of each input and output compound of the proposed process based on the material balance. The prices of minerals and mineral products are obtained from publications by the United States Geological Survey. The bulk prices of the chemical are roughly estimated based on the quote given by various chemical companies. The price of the electricity of 7.93 cents per kWh was used for the calculation of the energy requirement. For the given reactor condition, $3.37 was spent to sequester 152 kg of CO₂. This value is translated to approximately $60 per ton of CO₂ sequestered, which is even lower than the best result obtained by the group at the Albany Research Center. Moreover, with the sale of the three solid products, this cost can be further reduced. In fact, for the given reactor condition, the cost was estimated to be $3.37 whereas the total projected economic value of the three solid products was $76.97. In other words, if all the solid byproducts are sold, the proposed pH swing process could result in a profit. This is a very promising result.

Going back to the life cycle analysis, the following question has to be answered. Is the proposed carbon mineral sequestration process a “net consumer of CO₂?” The answer to this question is essential for the justification of the proposed carbon sequestration process. Table A.4 shows each component that was used to calculate the net change in the CO₂ flow throughout the system boundary. The second entry in the
last row in Table A.4 is \(-0.02182\). The negative sign of this value indicates that the proposed carbon sequestration approach is a “net consumer of CO\(_2\)” Total of 21.8 kg of net CO\(_2\) was sequestered by the proposed carbon mineral sequestration process under the given reactor conditions and specified assumptions. This value is smaller than 151.9 kg, which was calculated from the material balance. This is due to CO\(_2\) outputs that occurred during the operation. From Table A.4, it is also shown that the major contributors of the CO\(_2\) output are the procurement of serpentine and the energy requirement for the process. Since most of the energy requirement comes from heating the reactor, a lower reaction temperature is desired for the better performance of the process. In addition, the net change in GWP is negative largely due to the CO\(_2\) input by selling precipitated MgCO\(_3\). For example, MgCO\(_3\) could be sold as paper fillers, which will replace the market of the precipitated calcium carbonate and reduce its production. Thus, it will be important to identify and ensure the use of these valuable byproducts in order to carry out the proposed carbon sequestration process as a net consumer of CO\(_2\).
### Table A.1: Material balance for the proposed process.

<table>
<thead>
<tr>
<th></th>
<th>MW [g/mol]</th>
<th>IN [M]</th>
<th>OUT [M]</th>
<th>IN [kg]</th>
<th>OUT [kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>serpentine</td>
<td>336.2</td>
<td>1.35</td>
<td>0.20</td>
<td>455.0</td>
<td>68.2</td>
</tr>
<tr>
<td>CO2</td>
<td>44.0</td>
<td>4.06</td>
<td>0.61</td>
<td>178.7</td>
<td>26.8</td>
</tr>
<tr>
<td>MgCO3</td>
<td>84.3</td>
<td>3.45</td>
<td></td>
<td>290.9</td>
<td></td>
</tr>
<tr>
<td>SiO2</td>
<td>60.1</td>
<td>2.30</td>
<td></td>
<td>138.2</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>55.8</td>
<td>0.34</td>
<td></td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>Fe2O3</td>
<td>159.7</td>
<td></td>
<td>0.17</td>
<td></td>
<td>26.8</td>
</tr>
<tr>
<td>H3PO4</td>
<td>98.0</td>
<td>0.01</td>
<td></td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>EDTA</td>
<td>336.2</td>
<td>0.003</td>
<td>0.003</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>NH4OH</td>
<td>35.0</td>
<td>0.01</td>
<td></td>
<td>0.4</td>
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</tr>
</tbody>
</table>
Basis = 1 million dollars

<table>
<thead>
<tr>
<th>CO2 OUTPUT</th>
<th>GWP MTCO2E</th>
<th>CO2 MTCO2E</th>
<th>CH4 MTCO2E</th>
<th>N2O MTCO2E</th>
<th>CFCs MTCO2E</th>
</tr>
</thead>
<tbody>
<tr>
<td>serpentine</td>
<td>2797.781</td>
<td>2493.263</td>
<td>48.49521</td>
<td>254.1349</td>
<td>1.887832</td>
</tr>
<tr>
<td>Orthophosphoric acid</td>
<td>2512.433</td>
<td>2221.844</td>
<td>26.55557</td>
<td>176.7797</td>
<td>87.2539</td>
</tr>
<tr>
<td>EDTA</td>
<td>2512.433</td>
<td>2221.844</td>
<td>26.55557</td>
<td>176.7797</td>
<td>87.2539</td>
</tr>
<tr>
<td>NH4OH</td>
<td>2512.433</td>
<td>2221.844</td>
<td>26.55557</td>
<td>176.7797</td>
<td>87.2539</td>
</tr>
<tr>
<td>Energy required for processing (electricity)</td>
<td>14201.45</td>
<td>12439.74</td>
<td>308.9151</td>
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<td>Coal (amount of CO2 to be sequestered)</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CO2 INPUT</th>
<th>GWP MTCO2E</th>
<th>CO2 MTCO2E</th>
<th>CH4 MTCO2E</th>
<th>N2O MTCO2E</th>
<th>CFCs MTCO2E</th>
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</thead>
<tbody>
<tr>
<td>amount of CO2 sequestered during processing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>amount of CO2 avoided by selling SiO2</td>
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<td>2493.263</td>
<td>48.49521</td>
<td>254.1349</td>
<td>1.887832</td>
</tr>
<tr>
<td>amount of CO2 avoided by selling Fe2O3</td>
<td>2797.781</td>
<td>2493.263</td>
<td>48.49521</td>
<td>254.1349</td>
<td>1.887832</td>
</tr>
<tr>
<td>amount of CO2 avoided by selling MgCO3</td>
<td>2797.781</td>
<td>2493.263</td>
<td>48.49521</td>
<td>254.1349</td>
<td>1.887832</td>
</tr>
</tbody>
</table>

Table A.2: Raw LCA data based on 1 million dollars of each input and output components.
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</thead>
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<td>serpentine</td>
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<td>455.0</td>
<td>68.2</td>
<td>3.00</td>
<td>1.36</td>
<td>0.20</td>
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<td>CO2</td>
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<td>4.06</td>
<td>0.61</td>
<td>178.7</td>
<td>26.8</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgCO3</td>
<td>84.3</td>
<td>3.45</td>
<td></td>
<td>290.9</td>
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<td>249.20</td>
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<td>SiO2</td>
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<td>138.2</td>
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<td>21.36</td>
<td>2.95</td>
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<tr>
<td>Fe</td>
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<td>0.34</td>
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<td>18.8</td>
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<td>60.00</td>
<td>1.13</td>
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<tr>
<td>Fe2O3</td>
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</tr>
<tr>
<td>H3PO4</td>
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<td>0.01</td>
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<td></td>
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<td>0.003</td>
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<td>1.0</td>
<td>608.55</td>
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<td>0.61</td>
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<tr>
<td>NH4OH</td>
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<td>0.01</td>
<td></td>
<td>0.4</td>
<td></td>
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<tr>
<td>sum</td>
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<td>76.97</td>
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</table>

Table A.3: Cost of each component in the proposed process.
<table>
<thead>
<tr>
<th>CO2 OUTPUT</th>
<th>GWP MTCO2E</th>
<th>CO2 MTCO2E</th>
<th>CH4 MTCO2E</th>
<th>N2O MTCO2E</th>
<th>CFCs MTCO2E</th>
</tr>
</thead>
<tbody>
<tr>
<td>serpentine</td>
<td>0.076375</td>
<td>0.068062</td>
<td>0.001324</td>
<td>0.006937</td>
<td>5.15E-05</td>
</tr>
<tr>
<td>Orthophosphoric acid</td>
<td>0.00047</td>
<td>0.000415</td>
<td>4.97E-06</td>
<td>3.31E-05</td>
<td>1.63E-05</td>
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<tr>
<td>EDTA</td>
<td>0.001542</td>
<td>0.001364</td>
<td>1.63E-05</td>
<td>0.000109</td>
<td>5.36E-05</td>
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<tr>
<td>NH4OH</td>
<td>0.000198</td>
<td>0.000176</td>
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<td>1.4E-05</td>
<td>6.89E-06</td>
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<tr>
<td>Energy required for processing (electricity)</td>
<td>0.081335</td>
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<td>0.001769</td>
<td>0.008317</td>
<td>3.03E-06</td>
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<tr>
<td>Coal (amt of CO2 to be sequestered - inlet value)</td>
<td>0.178668</td>
<td>0.178668</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>total</td>
<td>0.338588</td>
<td>0.31993</td>
<td>0.003116</td>
<td>0.01541</td>
<td>0.000131</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>CO2 INPUT</th>
<th>GWP MTCO2E</th>
<th>CO2 MTCO2E</th>
<th>CH4 MTCO2E</th>
<th>N2O MTCO2E</th>
<th>CFCs MTCO2E</th>
</tr>
</thead>
<tbody>
<tr>
<td>amount of CO2 sequestered during processing</td>
<td>0.151868</td>
<td>0.151868</td>
<td></td>
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<tr>
<td>amount of CO2 avoided by selling SiO2</td>
<td>0.00826</td>
<td>0.007361</td>
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<td>0.001742</td>
<td>3.39E-05</td>
<td>0.000178</td>
<td>1.32E-06</td>
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<tr>
<td>amount of CO2 avoided by selling MgCO3</td>
<td>0.202853</td>
<td>0.180774</td>
<td>0.003516</td>
<td>0.018426</td>
<td>0.000137</td>
</tr>
<tr>
<td>total</td>
<td>0.364936</td>
<td>0.341745</td>
<td>0.003693</td>
<td>0.019354</td>
<td>0.000144</td>
</tr>
</tbody>
</table>

CO2 output from the electricity generation by combusting coal and the amount of CO2 sequestered are based on the material balance results.

Net change in GWP = CO2 OUTPUT - CO2 INPUT

<table>
<thead>
<tr>
<th>GWP MTCO2E</th>
<th>CO2 MTCO2E</th>
<th>CH4 MTCO2E</th>
<th>N2O MTCO2E</th>
<th>CFCs MTCO2E</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.026348</td>
<td>-0.02182</td>
<td>-0.00058</td>
<td>-0.00394</td>
<td>-1.2E-05</td>
</tr>
</tbody>
</table>

Table A.4: LCA results of the proposed pH swing process based on the material balance.
Figure A.1: Flowsheet of CO$_2$ mineral sequestration LCA system
LIST OF REFERENCES


Gale, J., “Geological Storage of CO₂: What do we know, where are the gaps and what more needs to be done?” Energy, 29, 1329-1338, 2004.


Pettit, D., Sales Engineer, Unimin Corp., Personal communication, January 2002.


