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**THE USE OF CARBONIC ACID IN AN
EX SITU MINERAL CARBONATION PROCESS**

A Dissertation in
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by

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ABSTRACT

The reaction of common magnesium and calcium silicate minerals with carbon dioxide can provide benign and long-term carbon storage. The prevalence of antigorite, its ability to buffer against acidic conditions from the dissociation of carbonic acid, and the resultant extraction of magnesium show promise as an underlying strategy for the production of magnesium carbonates without the consumption of additional reagents. This process circumvents several challenges that are associated with the use of strongly acidic media, but is limited by the rate and extent of dissolution. A parametric study on the effects of CO₂ partial pressure, particle size, reactor temperature, and solids concentration has been conducted to evaluate the extraction of magnesium.

The presence of accessible and large-scale deposits of magnesium silicates owes to the recalcitrant nature of these minerals. As the dissolution of silicate minerals is critical to an ex situ mineral carbonation process, the quantification and characterization of this reaction is important. In this study, the evolution of the solution pH and release of magnesium from different particle size fractions of antigorite in the presence of carbonic acid provide insight into the potential for a large-scale, direct ex situ mineral carbonation process. Carbonic acid is shown to be capable of disrupting magnesium-oxygen bonds at reactive sites that were generated during the grinding process. However, the proportion and reactivity of these sites may be incapable of sustaining a dissolution rate that is commensurate with the scale of CO₂ production for a coal-fired power plant without further technological advances. In addition to the challenges associated with magnesium silicate dissolution, the carbonation of magnesium ions once in solution is not trivial.

The potential for the precipitation of magnesium carbonates was evaluated for a series of experiments that varied the partial pressure of CO₂, particle size, reactor temperature, and solids

concentration. This range of experimental conditions results in only modest improvements in the activity of magnesium in solution. However, these conditions lead to a range of bicarbonate activities that spans three orders of magnitude. Geochemical modeling indicates a high degree of supersaturation with respect to magnesite, although no precipitates have been observed. Kinetic limitations within the Mg-H₂O-CO₂ system favor the formation of the metastable magnesium carbonates hydromagnesite, Mg₅(CO₃)₄(OH)₂·4H₂O, and nesquehonite, MgCO₃·3H₂O, under these reaction conditions. The saturation indexes for these phases indicate that the solutions in this study are likely undersaturated with respect to hydromagnesite and nesquehonite. The precipitation of magnesium carbonates can be facilitated by mitigating the strong Mg²⁺-H₂O interactions. An initial investigation into the effects of methanol and monoethylene glycol indicates that the solubility of hydromagnesite and magnesite could be reduced without the consumption of additional reagents.

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CHAPTER 1. INTRODUCTION

In 2007, the Intergovernmental Panel on Climate Change stated, "[m]ost of the observed increase in globally averaged temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations." As global CO₂ emissions from the consumption of energy are expected to increase at a rate of 1% per year through 2035 (U.S. EIA, 2011), further global warming could be anticipated (IPCC, 2007). The scale of this problem (discussed further in Chapter 3) cannot be overstated. Changing course would almost certainly require a multi-pronged approach that could include a reduction in energy demand, improved energy efficiencies (with respect to production and consumption), increased use of carbon-free or low-carbon fuels, and the use of Carbon Capture and Storage technologies (CCS). CCS represents a potential mitigation strategy; however, obstacles such as storage capacity and uncertainty in the fate of the sequestered CO₂ exists. Ex situ mineral carbonation, as a CO₂-mitigation strategy, was first proposed by Seifritz in 1990 which provides long-term storage of CO₂ in the form of benign mineral carbonates. Since then, our understanding of this CO₂ sequestration technology has grown and evolved. A host of processes has been explored, from direct carbonation routes such as aqueous and solid-gas reactions to indirect routes that include the use of acidic media (e.g., sulfuric acid), ammonium salts, and molten salts (Huijgen and Comans, 2003). This range of processing options reflects not only a multitude of potential pathways, but more importantly, the challenges inherent in each one. Challenges such as low conversion rates or the need for elevated reaction conditions and intensive pretreatment stages in addition to the costs associated with mining and transportation have limited the development of this technology. The environmental costs associated with this technology would have to be weighed against the benefits of CO₂ avoidance.

With the considerable volume of mineral carbonation research that has been conducted, it can be easy to lose track of one of the principal challenges: the formidable scale of a potential ex situ mineral carbonation process. For example, the sequestration of CO₂ generated from a large coal-fired power plant, in the form of mineral carbonates, would require on the order of one ton of magnesium silicate minerals to be digested every second. Although sufficient quantities of these minerals exist in accessible deposits (Goff and Lackner, 1998), the deposits are intrinsically stable. Mineral carbonation research has focused heavily on accelerating the extraction of metals from these minerals. However, the overall process rapidly tends towards untenable with even minor augmentation of reaction conditions. This constraint has provided the framework for this research.

Previous research by this author (Alexander et al., 2007) evaluated the extraction of magnesium from antigorite, Mg₃Si₂O₅(OH)₄, with sulfuric acid. Subsequent research was then conducted on the carbonation of those magnesium-rich solutions. However, the challenges associated with the carbonation reaction were immediately evident. Significant volumes of concentrated sodium hydroxide were consumed in shifting from highly acidic (pH of -0.4) to basic solution conditions. The basic magnesium-rich solutions were then placed in a stirred reactor and pressurized with CO₂, but the presence of carbon dioxide continually acted to reduce the pH of solution. Consequently, the carbonate and bicarbonate ion activities were too low to precipitate magnesium carbonates. Following research that had been conducted by the U.S. Department of Energy, National Energy Technology Laboratory (NETL) in Albany, Oregon, the use of sodium bicarbonate and sodium carbonate was evaluated in synthetic carbonation reactions. The researchers at NETL hypothesized that these reagents acted as CO₂ carriers and were regenerated throughout the course of the carbonation reaction. The addition of these reagents readily resulted in the formation of magnesium carbonates. Although not demonstrated conclusively, the evidence unfortunately suggested that these reagents were

consumed rather than catalytic. The potential exists for a complex mineral carbonation route and important research continues to advance novel processes that may enable the use of a strongly acidic medium. However, the feasibility of these routes becomes progressively less likely with each additional processing stage.

During the course of investigating process options for forming magnesium carbonates from acidic solutions, results from a preliminary experiment to evaluate the buffering capacity of antigorite in carbonic acid showed promising results. The presence of antigorite in solution was shown to provide a significant measure of buffering capacity against carbonic acid. Weighing the challenges associated with more complex routes, a relatively simple *ex situ* mineral carbonation process relying on carbonic acid was investigated.

The dissolution of silicate minerals by carbonic acid has been studied extensively as it represents a natural weathering process. In addition, several research programs have investigated this direct approach to *ex situ* mineral carbonation (Giammar et al., 2005; O'Connor et al., 2005). However, the focus of these programs has typically involved extensive mineral pretreatment stages and high reactor temperatures and pressures. These conditions impart costs that remain a significant impediment (IPCC, 2005) and comparatively little research has been published on the potential use of more mild reaction conditions.

The use of carbonic acid to extract metals and form mineral carbonates may provide for an *ex situ* mineral carbonation process without the consumption of additional reagents. An initial investigation was conducted to evaluate the extraction of magnesium and buffering capacity of antigorite, with respect to reaction time, particle size, CO₂ partial pressure, reactor temperature, and solids concentration. It was demonstrated that carbonic acid at ambient temperature and pressure was capable of extracting a modest amount of magnesium from antigorite and of providing a degree of buffering capacity. As the rate of extraction is critical to a large-scale *ex situ* mineral carbonation process, a study was conducted to assess the mechanisms and rate of

magnesium extraction. In addition to dissolution, the hydration of magnesium ions poses a significant challenge to the carbonation reaction. The series of experiments conducted in the parametric study was investigated to assess the conditions for carbonation of magnesium ions derived from the carbonic acid leaching of antigorite.

Based on the limitations that are associated with more cost-intensive approaches and limited research into the use of carbonic acid, this research provides a preliminary investigation into the feasibility of a simplistic mineral carbonation approach. Accordingly, a range of experiments was designed to evaluate (i) the effect of various experimental parameters that may affect dissolution (Chapter 2), (ii) the potential for a carbonic acid approach based on the rate of dissolution (Chapter 3), and (iii) the potential for a carbonic acid approach based on the carbonation conditions (Chapter 4). This research is a scoping level study to understand the relative effects of several key parameters and provide a preliminary assessment of the potential for a simplistic ex situ mineral carbonation process. Replicates of the experiments in this study have not been conducted; however, the experimental errors and uncertainties associated with the presented data are not expected to impact the conclusions of this research. The consistency between the experiments carried out in the parametric study and the magnitude of the inconsistency in the dissolution rate observed in the kinetic study with the rate of CO₂ production are adequate for decision-making purposes.

The parametric study consisted of thirty-six individual experiments that evaluated incremental changes in several parameters. The release of magnesium into solution and the pH values showed a high degree of consistency between the experiments. Accordingly, the experimental error is likely to be small relative to the trends in the data. These experiments indicated that although antigorite is susceptible to certain parameters, the rate of dissolution in the presence of carbonic acid is inconsistent with the rate of CO₂ generated from coal-fired power plants. The rate of dissolution for all of the dissolution experiments conducted in this

study is several orders of magnitude less than what would be required for an industrial-scale process. This, in combination with the challenges associated with the formation of magnesium carbonates, dictates that significant improvement in both the dissolution and carbonation reaction would need to be achieved prior to large-scale implementation of this process.

This thesis comprises a series of three papers for publication. In order by chapter, these papers are:

Chapter 2. Alexander, G., Maroto-Valer, M., and Schobert, H. Parametric study of carbonic acid leaching of antigorite for mineral carbonation.

Chapter 3. Alexander, G., Maroto-Valer, M., and Schobert, H. Kinetics of magnesium extraction from antigorite via carbonic acid leaching.

Chapter 4. Alexander, G., Schobert, H., and Maroto-Valer, M. Conditions for the carbonation of magnesium ions derived from the leaching of antigorite with carbonic acid.

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CHAPTER 2. PARAMETRIC STUDY OF CARBONIC ACID LEACHING OF ANTIGORITE FOR MINERAL CARBONATION

2.1 Abstract

Reacting common magnesium and calcium silicate minerals with carbon dioxide can provide benign and long-term carbon storage. The prevalence of antigorite, its ability to buffer against acidic conditions from the dissociation of carbonic acid, and the resultant extraction of magnesium show promise as an underlying strategy for the production of magnesium carbonates without the consumption of additional reagents. Improvements in magnesium extraction can be achieved through an increase in CO₂ partial pressure from 1 atm to 50 atm (17%), reduction in particle size from 38 x 150 μm to less than 38 μm (12%), increase in reactor temperature from 25°C to 100°C (31%), and a decrease in solids concentration from 100 g/L to 5 g/L (50%). In addition, the conditions for the carbonation reaction were significantly improved by increasing the solids concentration, as the activity of bicarbonate ions in solution increased by a factor of 40. Although carbonic acid only extracted up to 13% of the magnesium from the antigorite samples, the use of carbonic acid under mild reaction conditions could facilitate a range of processing options to increase extraction.

2.2 Introduction

Research in carbon capture and storage continues to advance, but the uncertainty in the interactions between storage technologies and natural systems presents challenges. Furthermore, feedback loops that exist between these scientific uncertainties, actual or perceived, and public sentiment provide additional challenges in moving forward. Geological sequestration of CO₂ is the most mature storage technology and offers a relatively simple and cost-effective means for CO₂ storage (IPCC, 2005). However, large-scale implementation is hindered by a limited understanding of the fate of the injected CO₂. In contrast, ex situ mineral carbonation provides long-term storage of CO₂ in the form of benign mineral carbonates.

Mineral carbonation is the formation of stable calcium, magnesium, and iron carbonates from the reaction between metals in common minerals and CO₂. Advancements have led to the circumvention of the low carbonation conversion associated with solid-gas reactions (Larachi et al., 2010; Zevenhoven et al., 2002). By reacting magnesium silicates in aqueous solution with dissolved CO₂, carbonation efficiency has increased from just a few percent to over 90% in 1 hour (O'Connor et al., 2005; Zevenhoven et al., 2002). O'Connor et al. (2005) conducted an extensive mineral carbonation investigation that evaluated a series of different minerals, particle sizes, and reactor temperatures and pressures. The optimum reaction conditions included temperatures and pressures that ranged from 155°C to 185°C and 115 atm to 150 atm for olivine and serpentine, respectively. Subsequent research focused on improving upon the rate-limiting step of magnesium removal from silicate minerals (e.g., olivine and serpentine) and reducing the carbonation conditions. The use of strong acids facilitated magnesium extraction and reduced the required reactor temperature and pressure. Maroto-Valer et al. (2005) demonstrated that the reaction conditions could be reduced to ambient temperature and lower pressure (45 atm) with the use of sulfuric acid to accelerate leaching (Maroto-Valer et al., 2005). In addition, researchers have utilized concurrent, or in situ, grinding to more than double the extraction rate

of magnesium in combination with a suite of acids (Park and Fan, 2004) or a single strong acid, such as sulfuric acid (Van Essendelft and Schobert, 2009). However, the use of these acids imparts additional process challenges and costs.

The dissolution of magnesium silicates and carbonation of magnesium ions occur at opposing pH levels. The addition of basic reagents to raise the solution pH after acidic extraction can accomplish the pH swing, but currently the regeneration of these reagents is a key obstacle (Teir et al., 2007). Research into novel approaches is ongoing with advances being made (e.g., the use of ammonium salts [Wang and Maroto-Valer, 2011]), but the feasibility of these approaches is yet to be demonstrated. The extraction of metals from silicate minerals is a significant challenge and the primary focus of the mineral carbonation research has been on accelerating the dissolution of silicate minerals. However, the optimization of the dissolution reaction tends to be at the cost of the carbonation reaction. Due to the contrast in conditions favoring dissolution and precipitation, optimization of the overall mineral carbonation process is likely to be unique from the optimization of either reaction.

The use of carbonic acid to extract metals and form carbonates, owing to the concomitant buffering of solution, may provide for an ex situ mineral carbonation process without the consumption of additional reagents. If magnesium silicates are susceptible to extraction via carbonic acid leaching, a relatively simple and balanced mineral carbonation approach may exist that would provide additional process options. This parametric study has been undertaken to further understand the extraction of magnesium and buffering capacity of a serpentine polymorph, antigorite ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), with respect to reaction time, particle size, CO_2 partial pressure, reactor temperature, and solids concentration toward the development of a direct ex situ mineral carbonation process.

2.3 Experimental

Antigorite from the Cedar Hills quarry in southeastern Pennsylvania was provided by the U.S. Department of Energy, National Energy Technology Laboratory (NETL) in Albany, Oregon for dissolution and carbonation studies. Prior to experimentation, X-ray diffraction (XRD) was conducted with a Philips Analytical 1050 XRD to characterize the mineral sample, as shown in Figure 2.1. XRD patterns show antigorite as the primary phase in the serpentine sample and lizardite and chrysotile as secondary phases.

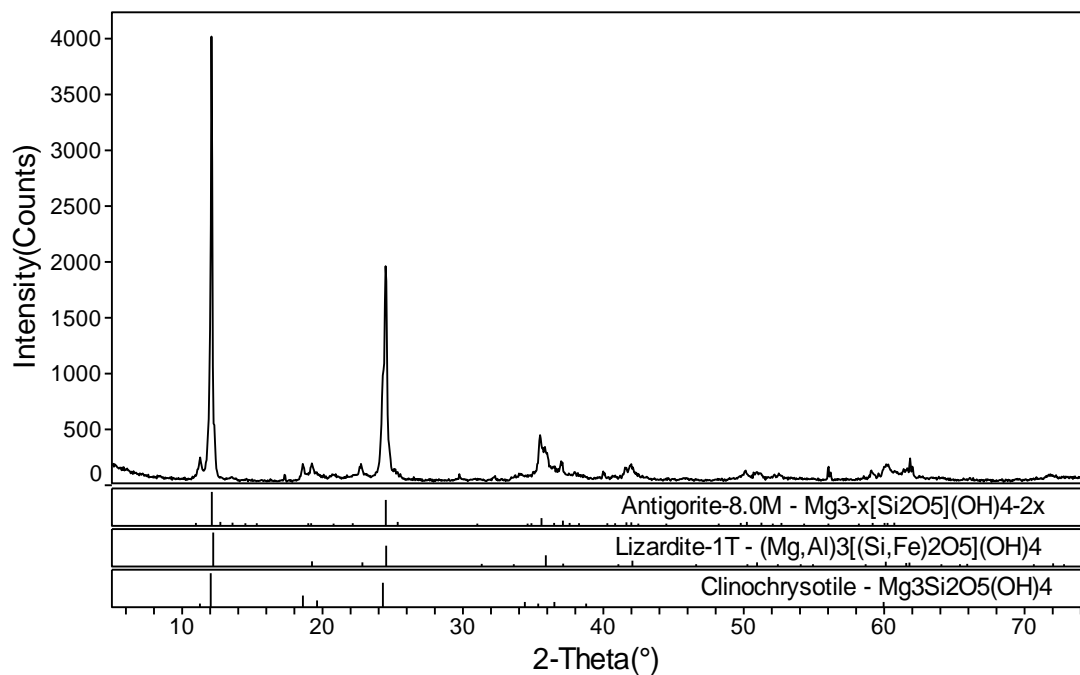


Figure 2.1. XRD graph of serpentine

The as-received antigorite sample from NETL was sized at 80% passing 4 mm. Before being used in our laboratory, it was ground in a cup-and-puck mill for 30 seconds in 150 g batches. This ground sample was dry sieved, followed by wet sieving, and then a final dry sieving stage into three particle size fractions, $-38\ \mu\text{m}$, $38\ \text{x}\ 150\ \mu\text{m}$, $150\ \text{x}\ 300\ \mu\text{m}$. The

chemical composition of the three particle size fractions was analyzed by inductively coupled plasma–atomic emission spectroscopy (ICP-AES), prior to experimentation and is shown in Table 2.1. The antigorite samples were also characterized by a Malvern Mastersizer utilizing a laser-light scattering technique with particle size distributions shown below in Figure 2.2.

Table 2.1. Initial chemical composition of antigorite samples

Species	-38 μm	38 x 150 μm	150 x 300 μm
Al ₂ O ₃ (%)	0.39	0.50	0.41
CaO (%)	3.79	2.86	0.13
Fe ₂ O ₃ (%)	10.8	12.1	8.24
MgO (%)	33.8	36.3	39.1
MnO (%)	0.09	0.10	0.10
Na ₂ O (%)	0.05	0.05	0.05
SiO ₂ (%)	30.9	33.5	35.6
TiO ₂ (%)	0.03	0.26	0.02
LOI*	20.0	14.42	16.34

*LOI is the loss on ignition due to water content

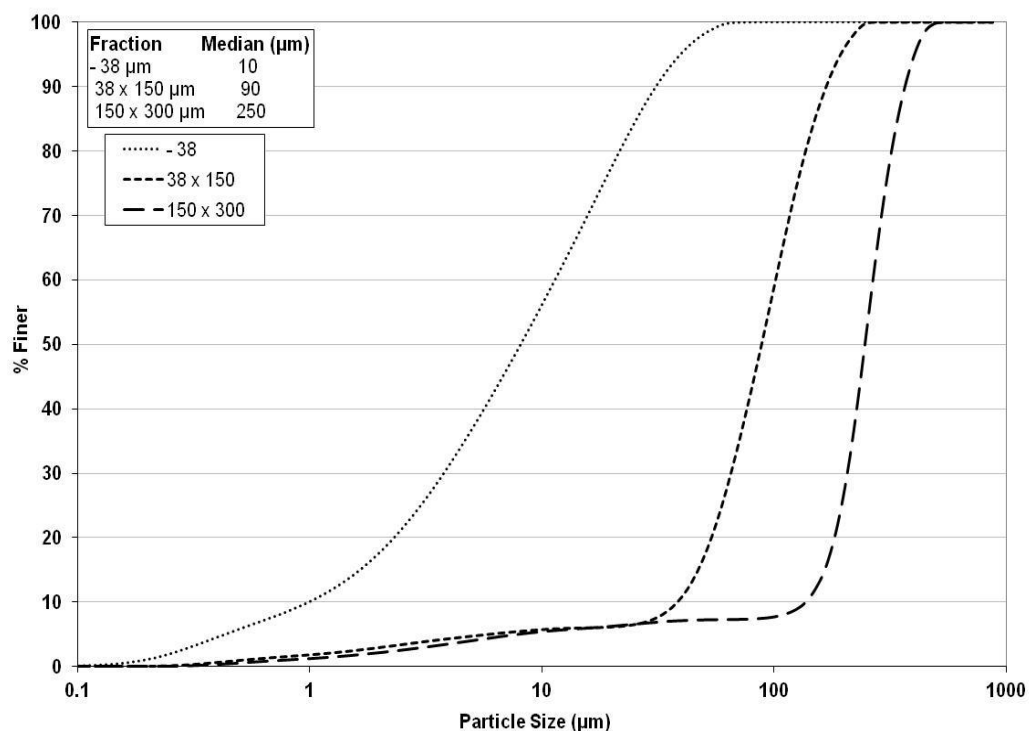


Figure 2.2. Particle size distributions for the antigorite particle size fractions and median particle size

Experiments were carried out with ultrapure Millipore water (18.2 MΩ·cm) in a 300 mL Parr continuously stirred tank reactor (Model 4651). Prior to initiating reactor conditions, the reactor was charged with N₂(g) to 6.8 atm and purged (three times) to reduce atmospheric contamination. Table 2.2 shows the matrix of leaching experiments with baseline conditions (*) that were held constant at 50°C, 25 g/L of water, and 30 atm for the reactor temperature, solids concentration, and pressure, respectively, while the remaining conditions were varied.

Table 2.2. Reaction variables in the parametric study of carbonic acid leaching of antigorite

Particle Size	Temperature	Solids Concentration	CO ₂ Pressure
-38 μm	25°C	5 g/L	0 atm
38 x 150 μm	50°C (*)	25 g/L (*)	1 atm
150 x 300 μm	100°C	50 g/L	10 atm
		100 g/L	30 atm (*)
		200 g/L	50 atm

(*) denotes experimental baseline condition

The pH measurements were obtained with an Orion 720APlus pH meter immediately upon opening the reactor vessel. Ion concentrations were determined at the end of the extraction experiments with ICP-AES in a 10% HNO₃ solution with sample acidification occurring after the filtration stage.

2.4 Results and Discussion

The overall mineral carbonation process depends on reaction conditions that promote the extraction of magnesium from antigorite and facilitate the carbonation of magnesium ions. The dissolution of CO₂ (g) and consequent reduction in pH (Equations 1 through 4) promote the extraction of metals from silicates (Equation 5). The pH is a primary variable, not only for extraction, but also with respect to the conditions for the carbonation reaction. The consumption of protons by antigorite may provide conditions suitable for the formation of magnesium carbonates (Equation 6), which will be discussed further in Chapter 4.



2.4.1 Effect of reaction time

This study included a preliminary evaluation of reaction time that showed a high initial rate of magnesium extraction in the presence of carbonic acid. Three separate experiments were conducted at 6, 24, and 72 hours while the remainder of the reaction conditions (50°C, -38 μm, 25 g/L, and 10 atm) were held constant. Table 2.3 provides a compilation of the experimental results, including magnesium extraction with respect to time. As anticipated, these experiments showed a high initial release rate of magnesium with the dissolution rate decaying over the course of the experiments. Different processes are to likely control magnesium release over the course of complete mineral dissolution. The initial rate of extraction is likely to be controlled by the removal of highly reactive edge sites created during the grinding process. As the reactive edge sites become depleted, the dissolution rate tends to be controlled by the rate of edge retreat. Ultimately, the long-term dissolution rate may be controlled by the formation of a diffusive barrier created by the preferential extraction of magnesium relative to silica. In addition, solution feedback mechanisms can inhibit the extraction of magnesium. These experiments approached the solubility limit for SiO₂(am) (~50-60 ppm) which may have affected antigorite dissolution for several of the experiments. Although the solubility of crystalline silica, or quartz, is less than that of amorphous silica, the formation of amorphous silica is likely favored due to a lower interfacial energy relative to the crystalline phase (Steeffel

and Van Cappellen, 1990). Table 2.3 shows that a significant degree of $\text{SiO}_2(\text{am})$ supersaturation was not achieved for any of the experiments, which could have otherwise resulted in the precipitation of $\text{SiO}_2(\text{am})$ and a reduction in magnesium extraction. Magnesium, on the other hand, was supersaturated with respect to magnesium carbonates, which could have also limited the dissolution reaction. Although a degree of supersaturation was achieved, the presence of magnesium carbonates was not observed in any of the experiments. The challenges associated with the precipitation of magnesium and an initial investigation into improving the carbonation reaction will be discussed in Chapter 4.

As only an incremental improvement in magnesium extraction occurred with time, the remainder of the parametric study was conducted at 24 hr. A more detailed investigation into reaction time and particle size will be discussed in Chapter 3.

Table 2.3. Carbonic acid leaching experiments and results

	-38 μm			38 x 150 μm			150 x 300 μm			
	pH	Mg, ppm	Si, ppm	pH	Mg, ppm	Si, ppm	pH	Mg, ppm	Si, ppm	
<i>25 g/L 50°C 10 atm</i>										
Time (hr)	6	6.15	657	--						
	24	6.18	661	--						
	72	6.32	758	--						
<i>24 hr 50°C 30 atm</i>										
Solids Conc. (g/L)	5	5.78	167	17	5.15	152	16	5.14	147	18
	25	6.04	694	43	6.04	632	39	6.02	617	45
	50	6.21	1274	52	6.37	1165	54	6.30	1155	54
	100	6.60	2248	59	6.44	1978	51	6.35	1994	48
	200	6.92	5158	57	6.87	4616	61	6.69	4533	54
<i>24 hr 25 g/L 30 atm</i>										
Temp. (°C)	25	6.20	545	14	5.98	484	11	6.06	495	11
	50	6.04	694	43	6.04	632	39	6.02	617	45
	100	6.06	737	71	5.90	647	61	5.90	615	56
<i>24 hr 25 g/L 50°C</i>										
Press. (atm)	0	9.00	80	0	9.20	13	0	8.96	6	0
	1	5.99	624	14	5.90	530	9	5.96	541	9
	10	6.18	661	--	6.02	585	31	5.79	591	33
	30	6.04	694	43	6.04	632	39	6.02	617	45
	50	6.17	724	48	5.85	660	42	5.95	606	47

2.4.2 Effect of particle size reduction

Particle size reduction facilitates dissolution by creating lattice vacancies (e.g., edge sites and kink sites) and imparting structural defects into the crystalline matrix (i.e., amorphization). Several research programs have demonstrated that an intensive grinding stage can significantly increase the reactivity of magnesium silicates (Gerdemann et al., 2007; Haug et al, 2010; Zhang et al., 2007). Zhang et al. (2007) showed that by completely disrupting the crystalline structure via dry grinding, magnesium extraction from serpentine can be increased from virtually 0% to greater than 90%, under otherwise equivalent reaction conditions. However, the energy consumption for high-intensity grinding is prohibitively expensive for a carbon sequestration scheme (Gerdemann et al., 2007; Haug et al., 2010). (Note: Gerdemann et al.[1997] described high-intensity grinding as 150 kW·h/ton.) The use of concurrent, or in situ, grinding may provide an option to improve extraction without the same energy penalty associated with attrition grinding (Park and Fan, 2004; Van Essendelft and Schobert, 2009).

As particle size is a primary variable for extraction, the remaining reaction conditions were varied for each of the particle size fractions in this study. The particle size fractions were selected based on approximately equivalent yields for each fraction. Figures 2.3, 2.4, 2.6, and 2.7 demonstrate the influence of particle size on leaching. Only a 2% improvement in magnesium extraction is observed between the 38 x 150 μm and 150 x 300 μm particle size fractions over the course of all the experimental conditions. Magnesium extraction averaged 12% higher for the particles less than 38 μm relative to the 38 x 150 μm particle size fraction. This result likely stems from the $-38 \mu\text{m}$ particles having no lower limit on particle size. Figure 2.2 illustrates that the $-38 \mu\text{m}$ particles consist of a large percentage of fines, or particles less than approximately 10 μm , which have a disproportionate number of highly reactive edge sites. Accordingly, there may exist a range where particle size reduction provides limited improvement in extraction.

2.4.3 Effect of CO₂ partial pressure

Experiments were conducted to evaluate the effects of CO₂ partial pressure for each particle size fraction while maintaining the baseline conditions (50°C, 25 g/L, and 24 hr), with the experimental results shown in Figure 2.3. A leaching test with a partial pressure of CO₂ of 0 atm (reactor purged 3 times at 6.8 atm with gaseous N₂) indicates that the wet-sieving process during sample preparation likely removed the most soluble fraction from the surface of the antigorite particles. The presence of 1 atm of CO₂(g) results in the removal of approximately 500-600 ppm of magnesium within 24 hr. Magnesium removal continues to increase monotonically, although modestly, with increasing CO₂ partial pressure in experiments also being conducted at 10 atm, 30 atm, and 50 atm. This result is consistent with research that indicated a weak direct effect of CO₂ partial pressure on the dissolution of silicates (Giammar et al., 2005; Golubev et al., 2005). Although it was not significant for these experiments, there is the potential for an indirect effect associated with a reduction in the solution pH.

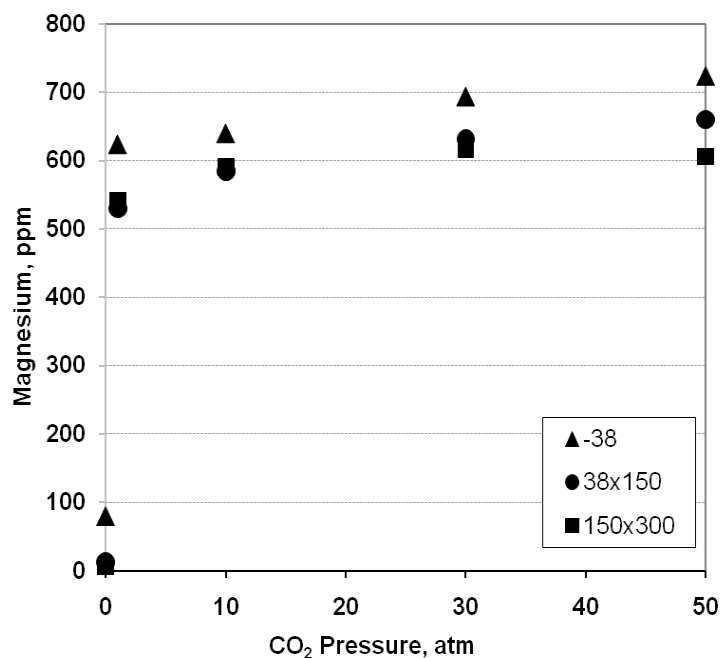


Figure 2.3. The effect of CO₂ partial pressure on the extraction of magnesium from antigorite

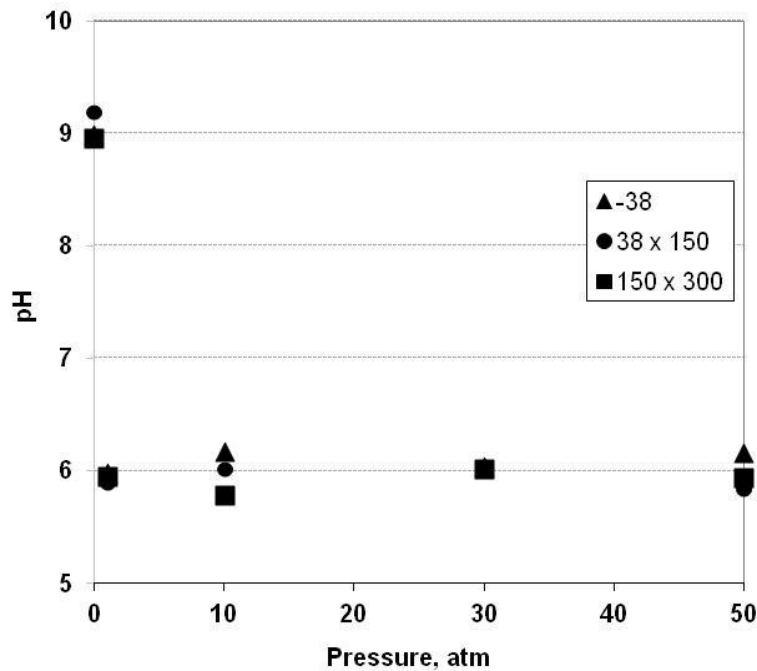


Figure 2.4. The effect of CO₂ partial pressure on the pH of solution

Through the course of these experiments, the pH remained relatively constant except for the difference between the experiments conducted at CO₂ partial pressures of 0 and 1 atm and as the solids concentration is varied (discussed in Section 2.4.5). An increase in CO₂ partial pressure from 0 atm to 1 atm resulted in the decrease in pH shown in Figure 2.4. CO₂ partial pressures greater than 1 atm did not significantly increase the acidity and consequently, the extraction of magnesium with increasing CO₂ partial pressure is modest. Although greater partial pressures of CO₂ do not provide significant returns with respect to extraction, the ability of antigorite to buffer the solution provides an opportunity to improve upon the conditions for the carbonation reaction, which will be discussed further in Chapter 4.

2.4.4 Effect of temperature

Alexander et al. (2007) were able to show a 70% increase in magnesium extraction from antigorite with the use of sulfuric acid as the reactor temperature increased from 25°C to 50°C. However, there was only a 31% increase in magnesium extraction from 25°C to 100°C for the three tested particle size fractions with carbonic acid, as shown in Figure 2.5. The increase in reaction rates accompanied with elevated reactor temperatures is likely offset by the reduction in CO₂ solubility, and therefore acidity, as shown in Figure 2.6.

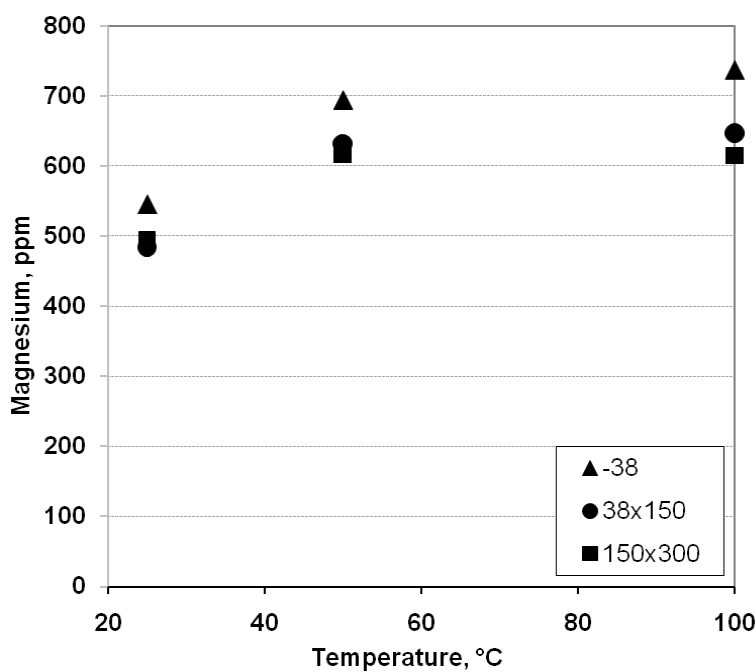


Figure 2.5. Effect of temperature on the extraction of magnesium from antigorite using carbonic acid

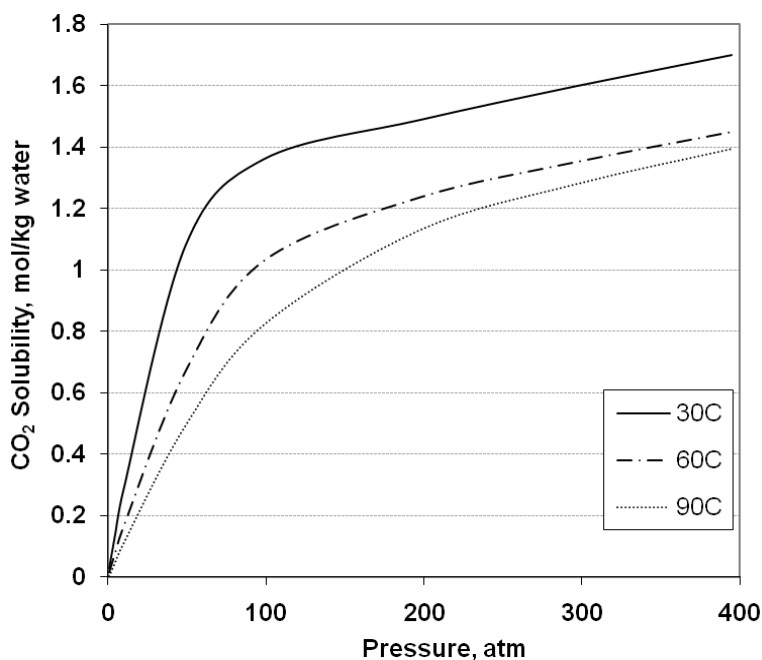


Figure 2.6. Solubility of CO₂ (g) with pressure at 30°C, 60°C, 90°C (adapted from Duan and Sun, 2003)

2.4.5 Effect of solids concentration

Figure 2.7 illustrates a monotonic decrease in the fraction of the total magnesium removed from the samples with each incremental increase in solids concentration from 5 g/L to 100 g/L. The average increase in magnesium extraction from the 100 g/L to 5 g/L samples was 50%. A lower solids concentration provides a greater reaction affinity for dissolution by reducing solution feedback mechanisms such as the precipitation of silica and magnesium carbonates that may inhibit the extraction of magnesium. However, from 100 to 200 g/L the fractional release of magnesium increases. This counter-intuitive result may be due to the mass loading of antigorite in the Parr reactor passing a threshold where autogenous grinding is contributing to the release of magnesium.

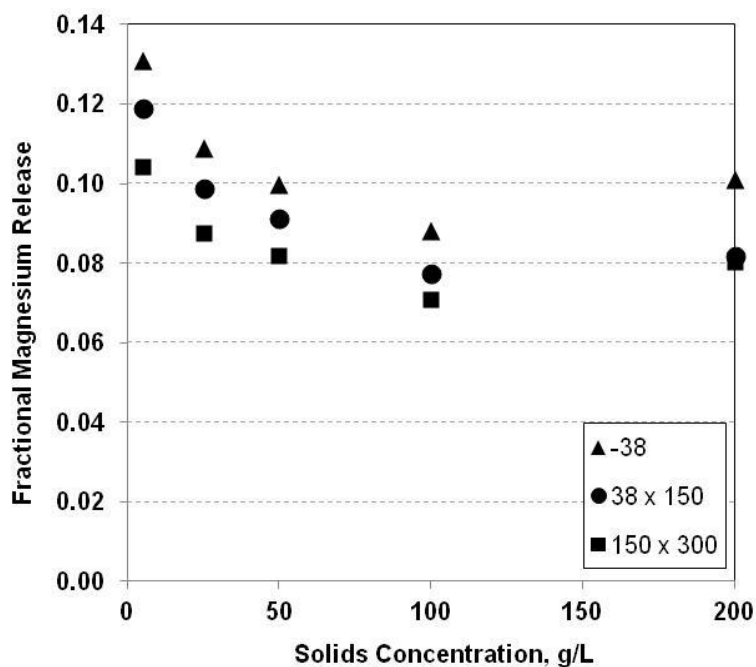


Figure 2.7. Fractional release of magnesium from antigorite at different solids concentrations

A trade-off exists with the solids concentration, as a decreasing solids concentration resulted in a magnesium extraction of approximately 13%, the overall carbonation conditions improved significantly when increasing the solids concentration. An increase in the solids loading of antigorite reduces the effect of CO_2 partial pressure on pH due to the buffering capacity of antigorite, as shown in Figure 2.8. Although a pH increase from 5.78 to 6.92 appears modest for the $-38 \mu\text{m}$ sample between the experiments with a solids concentration of 5 g/L and 200 g/L, respectively, it results in a factor of 40 increase in the activity of bicarbonate ions. The significance of this effect is discussed further in Chapter 4.

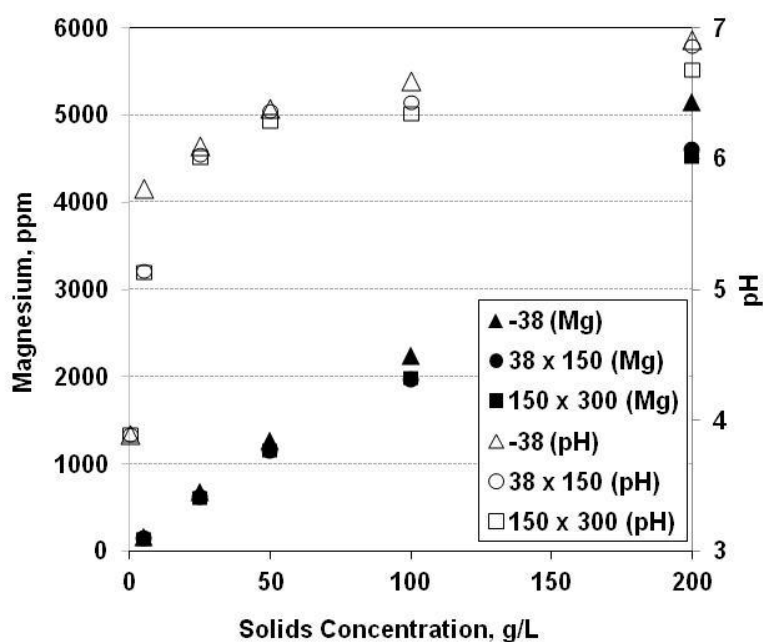


Figure 2.8. Effect of solids concentration on the extraction of magnesium from antigorite and solution pH

2.5 Conclusions

Serpentine has the potential to be a magnesium precursor in an ex situ mineral carbonation process as deposits are prevalent and readily accessible. In this parametric study, antigorite, which is a polymorph of serpentine, has been shown to be susceptible to leaching via carbonic acid. The extraction of magnesium from antigorite in these experiments had a high initial rate, followed by a steady rate decay due to the exhaustion of highly reactive surface sites and/or solution feedback mechanisms. The influence of particle size reduction appeared to be dominated by the effect of highly reactive edge sites. Only a 2% improvement in magnesium extraction was observed for the experiments conducted with the 38 x 150 μm fraction relative to the 150 x 300 μm samples. Leaching was improved 12% by decreasing the particle size from 38 x 150 μm to -38 μm , which was likely due to a relatively large proportion of fine particles. The competing effects of higher reaction rates and reduced $\text{CO}_2(\text{g})$ solubility with temperature

were likely to have limited the effect of reactor temperature on magnesium extraction. A 31% improvement was observed for the experiments with an increase in reactor temperature from 25°C to 100°C. As the CO₂ partial pressure for the different experiments was increased from 1 atm to 50 atm, the extraction gradually increased by 17%. The effect of solids concentration on magnesium release from antigorite was comparatively large, which indicates that solution feedback mechanisms can be important for these systems. A 50% improvement was observed for the experiments conducted with 5 g/L relative to 100 g/L, however, extraction improved from 100 g/L to 200 g/L. This counterintuitive result was likely due to the effects of autogenous grinding.

In addition, antigorite has been shown to be capable of buffering the solution to a pH of 6.92 at a solids concentration of 200 g/L, which corresponded to an increase in the bicarbonate ion activity by a factor of 40 relative to a solution with 5 g/L. Although the maximum extraction of magnesium from antigorite was only 13% in these experiments, the mild reaction conditions that were used would facilitate a range of processing options. Future work that elaborates on a potential processing scheme that would rely on ambient temperature and pressure is discussed in Chapter 5.

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CHAPTER 3. KINETICS OF MAGNESIUM EXTRACTION FROM ANTIGORITE VIA CARBONIC ACID LEACHING

3.1 Introductory Comment

The previous chapter evaluated the effects of CO₂ partial pressure, particle size, reactor temperature, and solids concentration on the extraction of magnesium. In addition to the extent of magnesium extraction, the dissolution rate is also critical to a large-scale ex situ mineral carbonation process. Chapter 3 evaluates the rate and mechanism of magnesium extraction from antigorite via carbonic acid leaching at early time periods.

3.2 Abstract

The range of steady-state dissolution rates for silicate minerals in the laboratory spans approximately eight orders of magnitude (10^{-6} to 10^{-14} mol/m²/s). As the formation of carbonate minerals should be at a rate commensurate with the levels of CO₂ generation ($\sim 10^4$ mol CO₂/s for a large coal-fired power plant), the dissolution rate of silicate minerals is of primary importance, as this is typically the rate-limiting step. In this study, the evolution of the solution pH and release of magnesium from different particle size fractions of antigorite, Mg₃Si₂O₅(OH)₄, via carbonic acid at early time periods provide insight into the potential for a direct ex situ mineral carbonation process. Carbonic acid was shown to be capable of providing an initial dissolution rate of 10^{-6} mol/m²/s, which decreased to slightly less than 10^{-8} mol/m²/s in 24 hr for particles ranging in diameter from ~ 38 μ m to 600 μ m. In addition to the rate of magnesium release, these carbonic acid leaching experiments resulted in the extraction of 7.4% to 11.4% of the initial magnesium content within 24 hr.

3.3 Introduction

Over the past two decades, researchers have explored different ex situ mineral carbonation approaches for the sequestration of carbon dioxide. These have included direct or indirect approaches in gaseous or aqueous media (Sipilä et al., 2008). There is not a clear path towards implementation as each approach has its own limitations. Of the ex situ mineral carbonation approaches, the aqueous mineral carbonation routes have received the most attention and afford a range of potential pathways. The rate-limiting step of these processes is typically the extraction of metals such as calcium and magnesium. Several options have been explored that improve upon this step including: (i) heat pretreatment (O'Connor et al., 2005; Gerdemann et al., 2007), (ii) the use of an acidic medium (Kosuge et al., 1995; Lackner et al., 1995; Maroto-Valer et al., 2005; Park and Fan, 2004; Van Essendelft and Schobert, 2009), and (iii) extensive grinding (Zhang et al., 1997). O'Connor et al. (2005) demonstrated that a heat pretreatment stage could increase the reactivity of antigorite, however the energy penalty rendered the process not viable. Research at The Pennsylvania State University showed that almost complete removal of magnesium from antigorite can be achieved on the order of hours with the use of sulfuric acid and concurrent grinding (Van Essendelft and Schobert, 2009). However, a significant challenge to the acidic dissolution route is the avoidance of costly acid regeneration and the supply of a base to provide conditions suitable for carbonation (Teir et al., 2009). In an effort to avoid this consumption of reagents, researchers at the University of Nottingham are currently working on an ammonium salt process that is effective at removing magnesium from antigorite (Wang and Maroto-Valer, 2011). Lastly, an intensive grinding stage has also been shown to significantly increase the rate of removal of magnesium from siliceous minerals (Gerdemann et al., 2007; Zhang et al., 1997). Gerdemann et al. (2007) stated that the associated energy penalty for high-energy attrition of minerals with a low reactivity effectively eliminates them from consideration in an ex situ mineral carbonation process. However, the extent of

grinding that is required for a silicate mineral with respect to an ex situ mineral carbonation process has not been investigated.

The extent of mineral comminution that is required for an ex situ mineral carbonation process is dependent on the solubility of the specific silicate mineral. The steady-state rate of dissolution for silicate minerals can vary by seven to eight orders of magnitude, as illustrated in Figure 3.1, depending on the degree of silica polymerization and the specific cation(s) that are required for charge balance. The silicates that are accessible and commensurate in scale with anthropogenic CO₂ emissions, are inherently of low reactivity, as the more reactive (i.e., more soluble) silicate minerals have been preferentially eroded. The selection of a silicate precursor mineral for an ex situ mineral carbonation process should be cognizant of the relative weathering rates of the different silicates, in combination with mineral abundance, proximity to CO₂ source, and solubility of the corresponding mineral carbonate (e.g., calcium carbonate has a lower solubility relative to iron and magnesium carbonates).

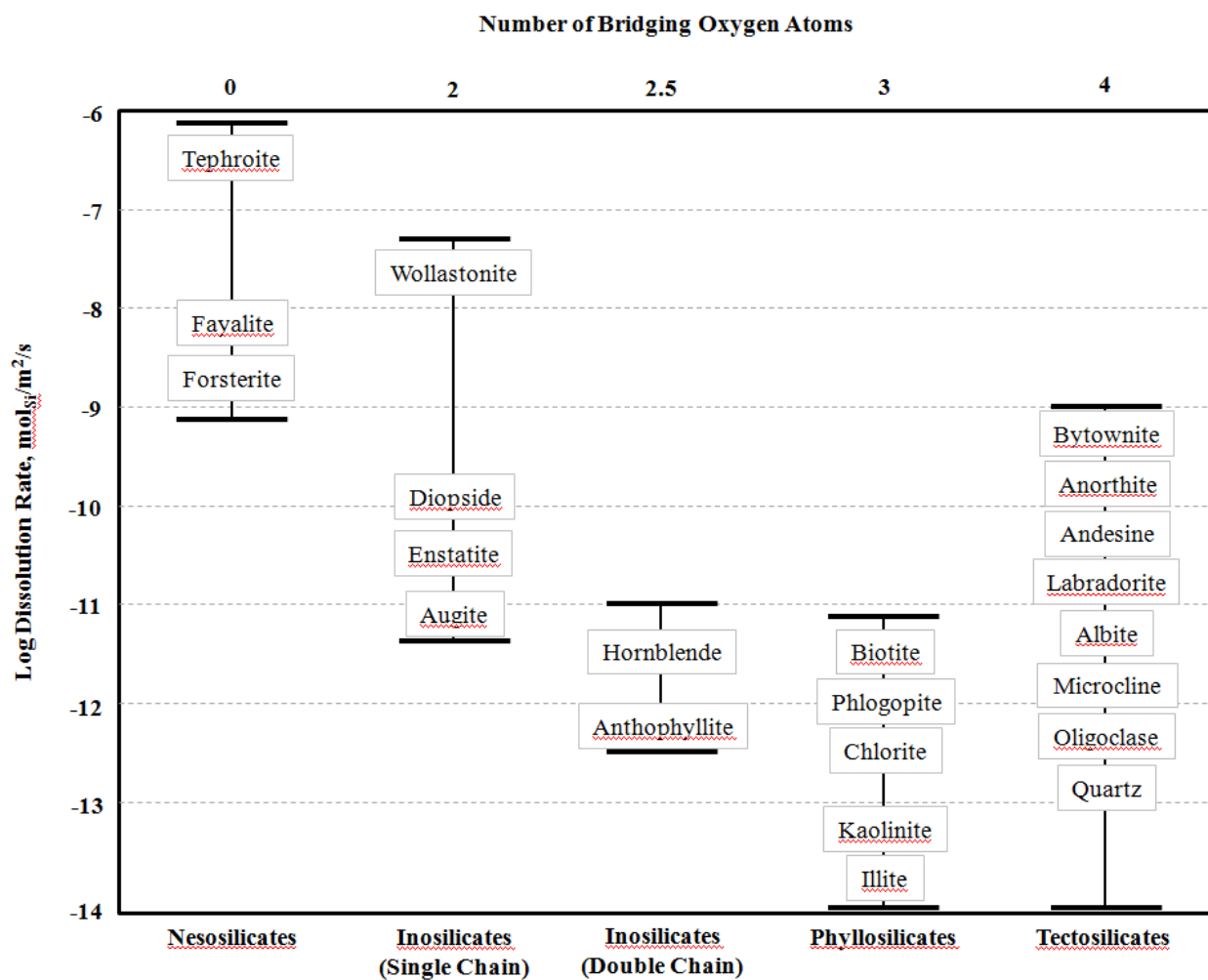


Figure 3.1. Steady-state dissolution rates of various silicate minerals according to the degree of polymerization (adapted from Criscenti et al., 2006 and Wolff-Boenisch et al., 2006)

As CO₂ generation is on the order of 10⁴ mol/s for a large coal-fired power plant, even the steady-state rate of dissolution for the more soluble silicate minerals can be seen as inadequate. If the rate of extraction of calcium or magnesium were 10⁻⁶ mol/m²/s, it would require significant capital expenditures and operating costs to provide a processing capacity that could supply metals at a rate consistent with CO₂ production. However, depending on the quantity and susceptibility of reactive sites that are generated during grinding, the steady-state dissolution rates may be irrelevant. Grinding imparts reactive surface sites that result in

elevated initial rates of dissolution. Depending on the proportion of these reactive sites, the use of CO₂ under mild reaction conditions may be capable of extracting magnesium at a rate that is sufficient for a large-scale ex situ mineral carbonation process. This research focuses on the dissolution of an abundant, but relatively non-reactive magnesium silicate, antigorite, under ambient reaction conditions. Characterization of the dissolution rate and mechanisms that control the extraction of magnesium from antigorite via carbonic acid at early reaction periods provides insight into the potential for silicates with low reactivity to act as precursor minerals in an ex situ mineral carbonation process.

3.4 Experimental

Antigorite from the Cedar Hills quarry in southeastern Pennsylvania was provided by the U.S. Department of Energy, National Energy Technology Laboratory at Albany, Oregon (NETL), with 80% of the material being less than 4 mm. An X-ray diffraction (XRD) analysis was conducted on the provided antigorite sample with results described in Chapter 2. The sample was ground further in a cup-and-puck mill in batches of 150 g for 30 seconds and wet-sieved into four particle size fractions: <38 μm, 38 x 150 μm, 150 x 300 μm, and 300 x 600 μm. The chemical composition of the four particle size fractions was analyzed by inductively coupled plasma–atomic emission spectroscopy (ICP-AES), before and after experimentation, as shown in Table 3.1 and Table 3.2, respectively. The particle size distribution was characterized by a Malvern Mastersizer (Figures 3.2) and the specific surface area before and after experimentation was characterized by the BET method for N₂ (g) adsorption (Table 3.3).

In this study, the Geochemist's Workbench® software, which is available from Aqueous Solutions LLC in Champaign, IL, was used to evaluate the potential for carbonation of the magnesium ions derived from the leaching experiments. The activities of the aqueous species

were calculated with the SpecE8 program with the thermo.dat database which utilizes an extended form of the Debye-Hückel equation (Bethke, 2006).

Table 3.1. Initial chemical composition of antigorite samples

Species	-38 μm	38 x 150 μm	150 x 300 μm	300 x 600 μm
Al ₂ O ₃ (%)	0.39	0.50	0.41	0.34
CaO (%)	3.79	2.86	0.13	0.16
Fe ₂ O ₃ (%)	10.8	12.1	8.24	6.95
MgO (%)	33.8	36.3	39.1	39.1
MnO (%)	0.09	0.10	0.10	0.10
Na ₂ O (%)	0.05	0.05	0.05	0.06
SiO ₂ (%)	30.9	33.5	35.6	36.0
TiO ₂ (%)	0.03	0.26	0.02	0.01
LOI*	20.0	14.42	16.34	17.28

*LOI is the loss on ignition due to water content

Table 3.2. Final chemical composition of antigorite samples

Species	-38 μm	38 x 150 μm	150 x 300 μm	300 x 600 μm
Al ₂ O ₃ (%)	0.28	0.49	0.29	0.25
CaO (%)	3.47	2.17	0.12	0.16
Fe ₂ O ₃ (%)	11.3	13.2	8.62	7.23
MgO (%)	34.2	34.5	38.5	38.6
MnO (%)	0.07	0.08	0.08	0.08
Na ₂ O (%)	<0.05	<0.05	<0.05	<0.05
SiO ₂ (%)	34.2	34.6	37.5	38.0
TiO ₂ (%)	0.03	0.47	0.05	0.02
LOI*	16.45	14.49	14.84	15.66

*LOI is the loss on ignition due to water content

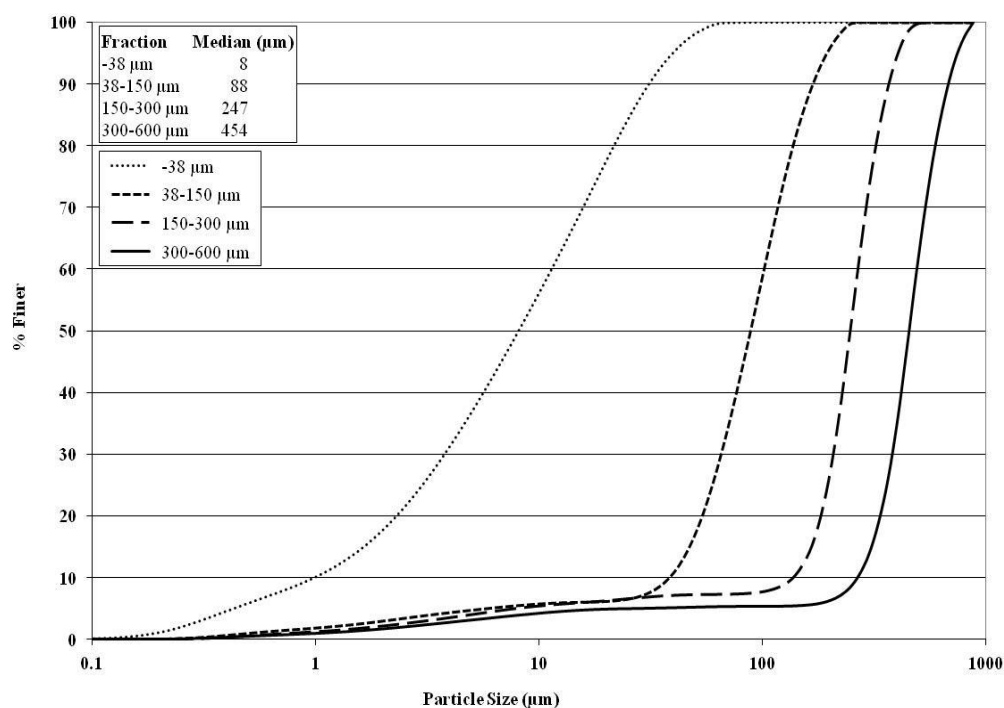


Figure 3.2. Particle size distributions of antigorite particle size fractions

Table 3.3. Surface area of the antigorite samples before and after dissolution tests

Surface Area, m ² /g	-38 μm	38 x 150 μm	150 x 300 μm	300 x 600 μm
Initial	2.9	2.5	2.3	2.3
Final	14.9	10.7	10.7	10.4

The antigorite dissolution experiments were carried out at room temperature for 24 hr in parallel 200 mL continuously stirred tank reactors (CSTR) at 300 rpm, shown in Figure 3.3. The slurries consisted of 2.5 g of antigorite and 100 mL of distilled water and 30 mL/min of bone-dry CO₂ percolated through the system. The extraction of solutions alternated between the duplicate experiments to minimize the change in solids concentration throughout the experiments. Approximately 0.5 mL of solution was periodically extracted from the CSTRs, filtered with 0.45 μm membrane, and acidified with 7 mL of a 2% HNO₃ solution. The change in solids concentration from 25 g/L of water initially to approximately 26 g/L was assumed to be relatively insignificant and not taken into further account. The filtrates and solid samples

were analyzed by ICP-AES. The pHs of solutions were taken from each CSTR and subsequently averaged.

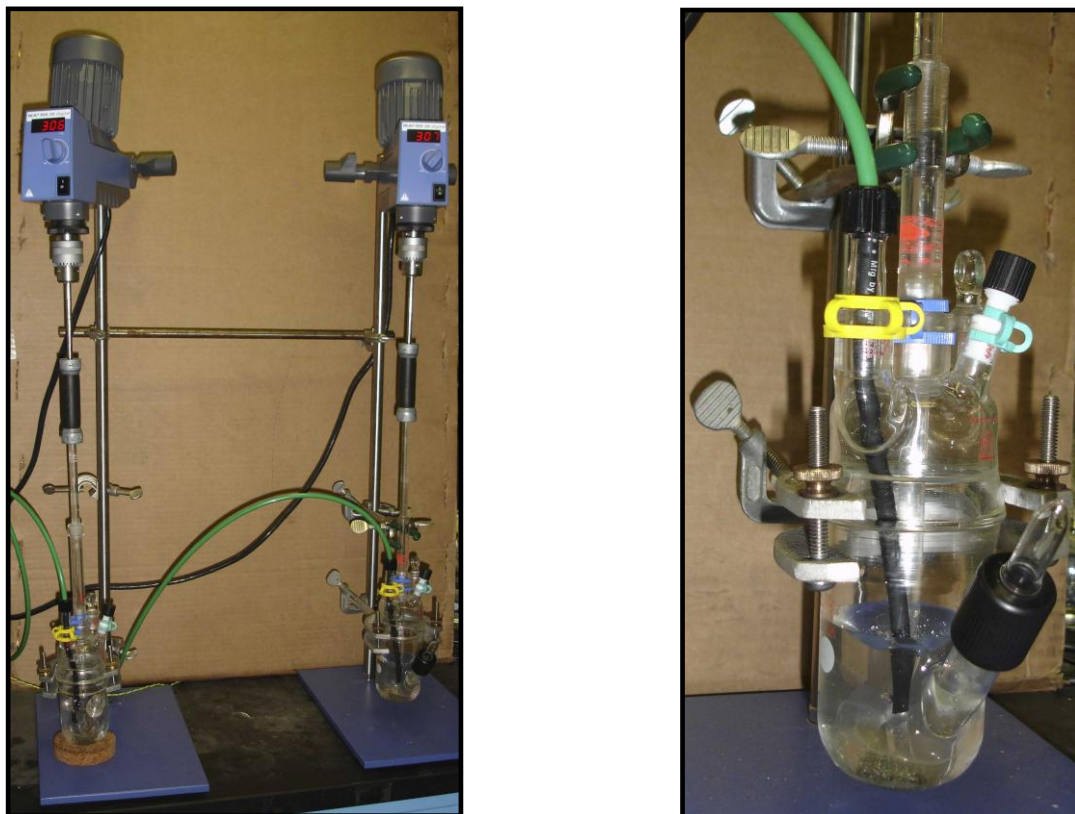


Figure 3.3. 200mL continuously stirred tank reactors for the antigorite dissolution experiments

3.5 Results and Discussion

3.5.1 pH-dependence of dissolution reaction mechanisms

The dissolution of silicates is generally regarded as being controlled by inner-sphere surface complexes (Brady and Walther, 1989; Schott et al., 2009), as research has shown that dissolution rates are directly proportional to the concentration of ionized surface sites (Carroll et al., 2002). The prevalence of these precursor sites (depicted in Figure 3.4) is a function of pH, mineralogy, and surface morphology. Equivalent concentrations of the charged $>XO^-$ and $>XOH_2^+$ sites exist at the mineral-specific isoelectric point (pH_{IEP}), where X represents either silicon or a metal (e.g., Na, Ca, Fe, Mg, Al). As the alkalinity increases above the pH_{IEP} , the concentration of $>XO^-$ sites increases at the expense of $>XOH_2^+$ sites, with the opposite trend occurring as the pH of solution decreases below the pH_{IEP} . The concentration of neutral $>SiOH$ sites is relatively insensitive to pH.

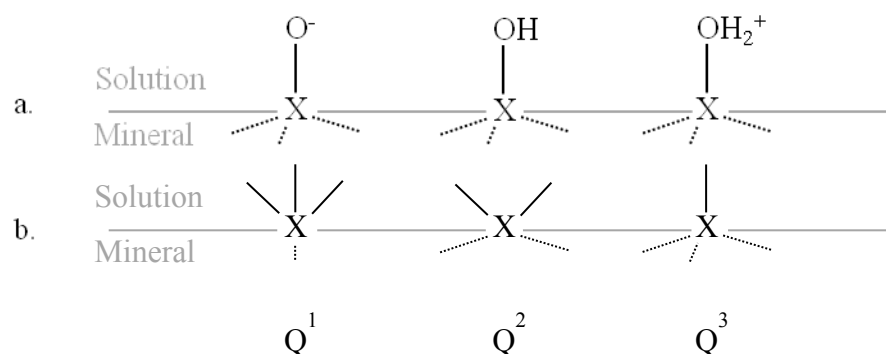


Figure 3.4. a. Negative, neutral, and positive surface complexes at the mineral-solution interface with X representing silicon or a metal (adapted from Brady and Walter, 1989; Schott et al., 2009) and b. number of nearest neighbors (adapted from Washton et al., 2008).

As the acidity of solution increases, Me-O bonds are preferentially hydrolyzed relative to Si-O bonds, and according to Brady and Walther (1989), this is the rate-controlling step. Strong acids such as sulfuric and hydrochloric acid readily hydrolyze Me-O bonds in silicate minerals

and potentially Si-O bonds, as well. However, the use of strong acids may be cost-prohibitive to an ex situ mineral carbonation process. As basic conditions are required for the formation of magnesium carbonates, the addition of a basic reagent or an acid-regeneration process would be required to provide suitable conditions. Depending on the stability of the specific silicate mineral particles, carbonic acid may be capable of disrupting the magnesium-oxygen bonds, thereby circumventing the need for additional reagents or processing.

Phyllosilicates, such as antigorite, are characterized by the sharing of three basal oxygen atoms of the silica tetrahedra, resulting in a sheet-like structure of silica interspersed with octahedral layers (Figure 3.5). In antigorite, the sheets are bonded to brucite, $\text{Mg}(\text{OH})_2$, octahedra in a corrugated fashion to compensate for the mismatch in size. The result is a chemically and structurally resistant basal plane with strong preferential dissolution at the edge sites. These Q1 and Q2 sites, which are illustrated in Figure 3.4, contain broken bonds and therefore charged inner-sphere complexes (Bickmore et al., 2001).

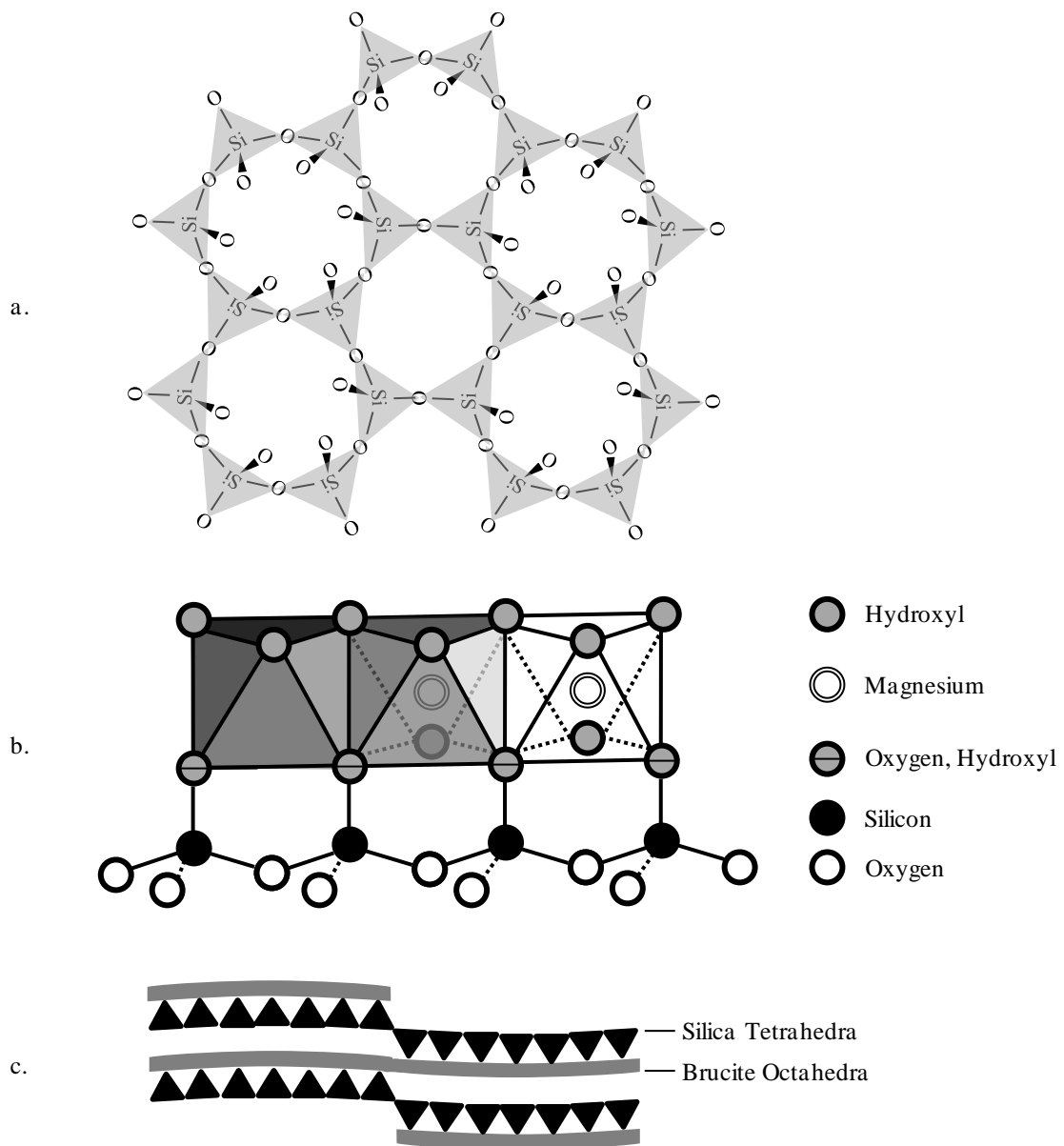


Figure 3.5. a. Sheet-like structure of silica tetrahedra in phyllosilicates, b. molecular structure of silica tetrahedra and brucite octahedra, and c. corrugated structure of antigorite

The pH response and magnesium and silicon release from four different antigorite particle size fractions reacting with carbonic acid for 24 hr are shown in Figure 3.6 and Figure 3.7. As expected, the pH and magnesium release are highly correlated and reflect rapid and substantive changes in surface chemistry. The change in pH (i.e., consumption of protons from solution),

illustrated in Figure 3.6, corresponds to the hydrolysis of the antigorite surface. A rapid proton-metal exchange occurs with the reactive surface sites. However, as magnesium release progresses from Q1 to Q2 to Q3 sites, more and more protons are required for each additional release of magnesium. Depending on the stage of dissolution, the dissolution reaction may be controlled by the growth of a silica-rich layer, the exhaustion of reactive surface sites, and/or a decreasing reaction affinity.

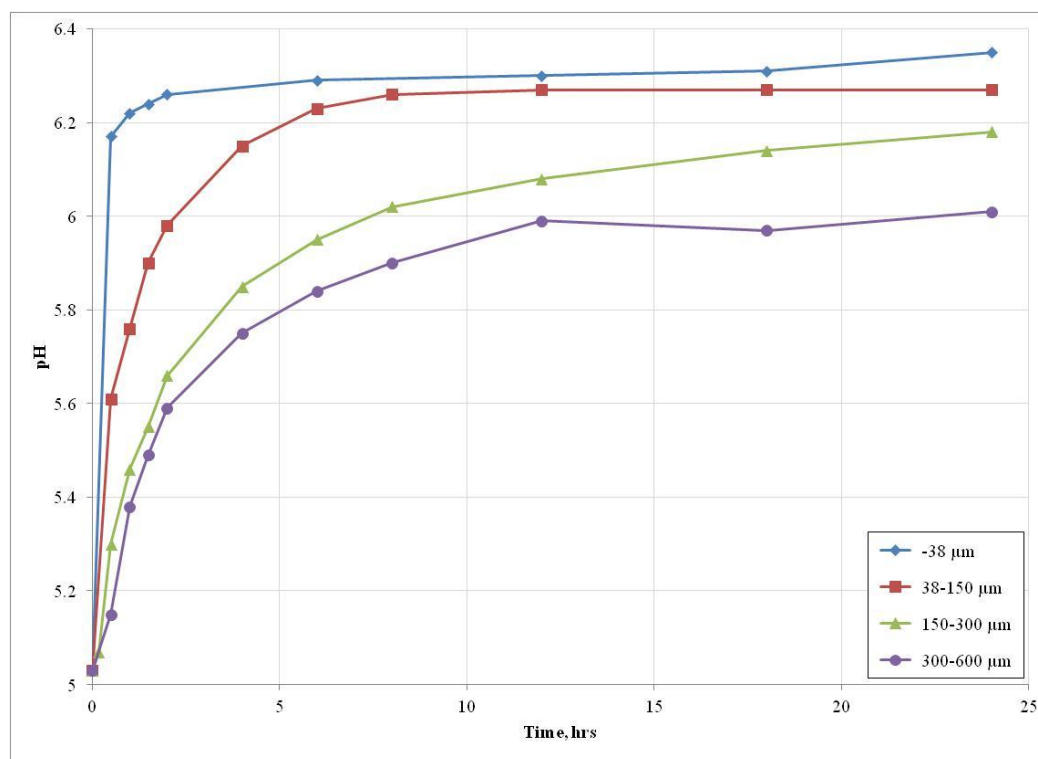


Figure 3.6. Evolution of pH for the antigorite particle size fractions

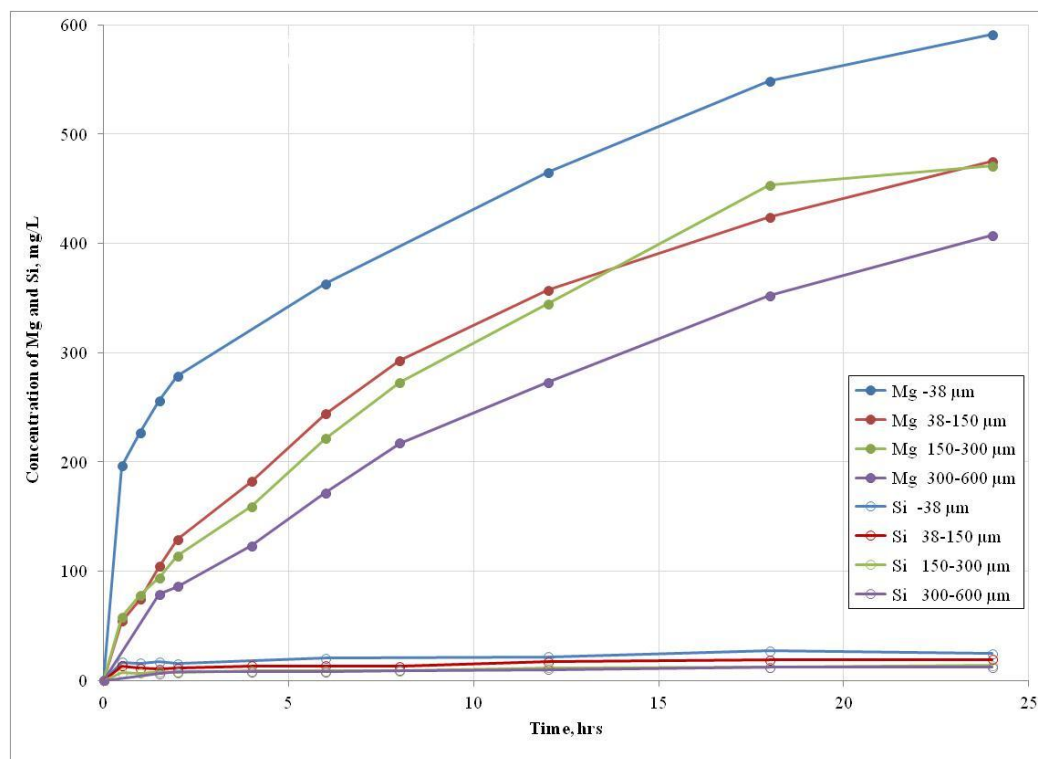


Figure 3.7. Magnesium and silicon release for the antigorite particle size fractions

3.5.2 Potential formation of a silica-rich layer

The preferential release of metals from a silicate mineral or the dissolution of silanol groups followed by the precipitation of amorphous silica can result in the formation of a silica-rich layer [Steeffel and Van Cappellen, 1990]. Acidic conditions have the potential to exacerbate the formation of a silica-rich layer, as research has demonstrated the polymerization of silanol groups (Carroll et al., 2002). Consequently, the release of metals may diminish with time due to the thickening of this diffusive barrier. The release of magnesium from antigorite could then be facilitated by the minimization or removal of this layer. Jonckbloedt (1998) and Park and Fan (2004) observed silica precipitation on the surfaces of olivine and serpentine, respectively, during dissolution with strong acids. In an effort to remove the silica, researchers have implemented autogenous or semi-autogenous grinding schemes, which have significantly

improved dissolution (Jonckbloedt et al., 1998; Park and Fan, 2004; Van Essendelft and Schobert, 2009).

The decay in magnesium extraction in these experiments is not expected to be due to precipitation of a diffusion barrier, as the solutions were calculated to be undersaturated with respect to amorphous silica. Although concurrent grinding may improve upon the release of magnesium by increasing the number of reactive sites, it would not be expected to improve upon release due to the removal of a silica-rich layer acting as a diffusive barrier.

3.5.3 Effect of particle size reduction

Comminution increases the dissolution rate by increasing the number of reactive sites, which stem from the creation of lattice vacancies (e.g., kink sites and edge sites) and lattice defects (i.e., amorphization). The disruption of the crystal lattice at the mineral surface creates a charge imbalance that water molecules act to minimize, leading to the formation of positively-charged surface groups for a mineral in solution below its pH_{IEP} (Oelkers et al., 2009; Washton et al., 2008). The release of magnesium from the relatively stable antigorite mineral for different particle size fractions provides insight into the effects of comminution. Figure 3.6 and Figure 3.7 illustrate that (i) the four particle size fractions differed in response to carbonic acid at the onset of the experiments, (ii) the parabolic magnesium release approached linearity with reaction time, and (iii) a marked similarity in rate of magnesium release existed between all of the fractions after the initial few hours of dissolution.

The divergence in magnesium release between the different particle size fractions observed within the initial hour of experimentation is consistent with the dissolution of fine particles present in the samples. Schott et al. (1981) and Helgeson et al. (1984) discussed that the nonlinear or parabolic kinetics observed in early dissolution stages is not due to the formation of a diffusive barrier, but instead derives from the high reactivity of fine particles as an artifact of

grinding. As shown in Figures 3.2, the three largest size fractions have a similar percentage of particles less than approximately 30 μm whereas the -38 μm fraction is unique. The -38 μm sample does not contain a minimum particle size and accordingly, the proportion of particles less than 10 μm in this sample is significantly greater than for the other fractions. Once the most reactive sites are depleted in the first hour of experimentation, the different particle size fractions gradually approach a linear release rate and demonstrate similar reactivities. (Note: although the -38 μm sample contains a relatively large proportion of finer particles, the surface areas shown in Table 3.3 are similar for the different particle size fractions.)

The parallel magnesium release curves indicate that, for these four particle size fractions, the number of reactive sites is largely independent of particle size once the most reactive sites are depleted. If a disparity were present, the magnesium release for the different size fractions would continue to diverge throughout the course of these experiments. This observation is consistent with research conducted by Holdren and Speyer (1985), who observed a comparable number of reactive sites for five different particle size fractions of feldspar ranging from -38 μm to +600 μm . The implication of this result is that particle size reduction may not improve the rate-limiting step of dissolution for antigorite in carbonic acid unless there is either a significant proportion of fine particles generated or a large degree of amorphization imparted to the crystal structure during grinding.

3.5.4 Dissolution rate

The initial dissolution rate (on a magnesium basis) approached 10^{-6} mol/m²/s due to the susceptibility of reactive sites to carbonic acid. With the depletion of these sites, the dissolution rate decayed to slightly less than 10^{-8} mol/m²/s for all of the particle size fractions over the course of the 24 hr experiment (Figure 3.8). In addition, carbonic acid was unable to extract the bulk of the magnesium from these samples, as the number of reactive sites is small relative to

the average particle size. The extraction percentages of magnesium and silicon from antigorite, based on analyses of the solid samples and solutions, are shown in Table 3.4. As expected, the use of carbonic acid led to the preferential extraction of magnesium, which ranged from 7.4% to 11.4% and 5.7% and 9.3% based on the solids and solutions, respectively. Although research on the dissolution of antigorite under similar experimental conditions is limited, research conducted by Lin and Clemency (1981) provides insight into a relatively long-term dissolution rate. (Note that the calculated dissolution rate is based on an assumed surface area that was determined by linear interpolation between the initial and final surface areas, according to reaction time. The dissolution rate is normalized against total surface area, however the dependence is directly related to the reactive surface area and not the total surface area. See Holdren and Speyer [1985] for additional discussion on reactive versus total surface area.)

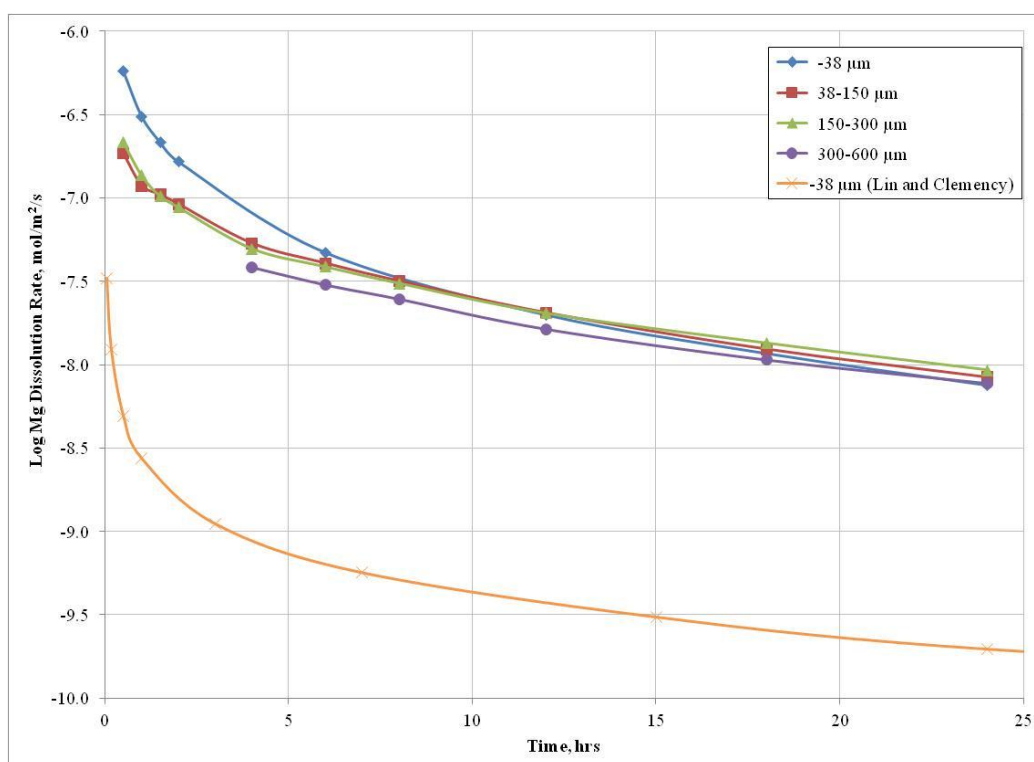


Figure 3.8. The magnesium dissolution rate through 24 hr for each particle size fraction and data adapted from research conducted by Lin and Clemency (1981).

Table 3.4. Antigorite dissolution for the -38 μm , 38 x 150 μm , 150 x 300 μm , and 300 x 600 μm particle size fractions based on solid and solution analyses.

Particle Size, μm	Solids			Solutions	
	% Mass Extracted	% Mg Extracted	% Si Extracted	% Mg Extracted	% Si Extracted
-38	8.4	11.4	3.0	9.3	1.0
38 x 150	5.8	10.2	2.6	7.4	0.8
150 x 300	5.2	8.3	1.9	6.7	0.7
300 x 600	4.3	7.4	0.9	5.7	0.8

Lin and Clemency (1981), conducted an experiment on the dissolution of antigorite over approximately 1200 hr with otherwise similar experimental conditions (e.g., a solids concentration of 25 g/L, percolation of CO_2 through solution, room temperature, and the sample was less than 38 μm). The dissolution rate in their experiment decreased rapidly to 10^{-10} mol/m²/s by 48 hr before gradually decaying to approximately 10^{-11} mol/m²/s by 1200 hr (Figure 3.8 and Figure 3.9) with approximately 5% of the magnesium having been extracted. The authors noted that the solution was oversaturated with respect to amorphous silica and magnesite, MgCO_3 . These saturation levels may have resulted in a decreased dissolution rate due to the formation of a silica-rich diffusion barrier or to a decrease in the reaction affinity. As the free energy of the system approaches equilibrium, the reaction rate would be expected to decrease (Ebert, 2010).

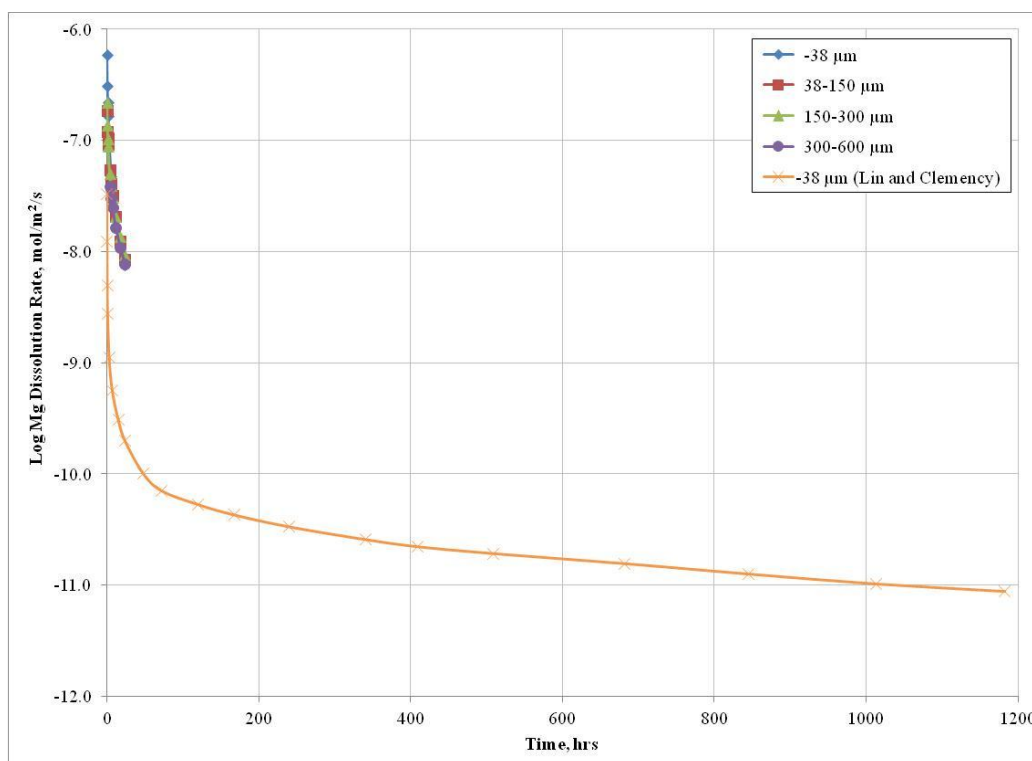


Figure 3.9. The magnesium dissolution rate through 1200 hr from research conducted by Lin and Clemency (1981).

A marked disparity is evident between these two research programs as the experimental results differ significantly with respect to the dissolution rate and extraction percentage. The experiments conducted in this study were unsaturated with respect to amorphous silica. It is not clear why the experiments conducted by Lin and Clemency reached saturation with respect to amorphous silica within 30 min, while saturation was not observed within 24 hr of experimentation in this study. The differences in these results may be indicative of the significance of variability in mineralogy and/or sample preparation.

This study and the research conducted by Lin and Clemency (1981) demonstrate that the use of carbonic acid, under the conditions that have been evaluated, is insufficient for a large-scale ex situ mineral carbonation process. Although grinding created reactive sites on the surface of the antigorite particles, carbonic acid was unable to extract magnesium at a rate

commensurate with CO₂ production. With the scale of CO₂ emissions from coal-fired power plants, dissolution rates would need to be in excess of 10⁻⁶ mol/m²/s to provide a suitable quantity of metals without impracticable capital expenditures and operating costs. Further development of a carbonic acid approach would require additional advances in the rate of magnesium release. Due to the limited improvement in the rate of magnesium release with particle size reduction, it appears unlikely that grinding would be capable of achieving the requisite dissolution rates in a carbonic acid solution short of a high-intensity grinding scheme. Chapter 5 discusses future work that may provide additional improvement in magnesium extraction. In addition to the importance of the dissolution rate and extent of extraction is the formation of magnesium carbonates. Based on thermodynamic calculations using Geochemist's Workbench, the experiments conducted by Lin and Clemency (1981) as well the experiment conducted with the -38 μm sample in this study were saturated with respect to magnesite. However, the presence of magnesium carbonates was not observed in either study. Chapter 4 evaluates the conditions required for the formation of magnesium carbonates.

3.6 Conclusions

A carbonic-acid-only ex situ mineral carbonation process would provide a benign and long-term CO₂ sequestration option and avoid several of the challenges associated with alternative mineral carbonation schemes. Acid-promoted hydrolysis of silicate minerals releases metals into solution and results in the consumption of protons by the silicate mineral, facilitating the carbonation reaction. However, the silicate minerals that are available in quantities commensurate with anthropogenic CO₂ emissions are inherently recalcitrant. Accordingly, varying degrees of pretreatment stages, particle comminution, and/or the use of acidic medium to accelerate leaching are required to provide adequate mineral dissolution rates.

Particle comminution results in the disruption of the crystal lattice, which leads to a high proportion of charge-imbalanced surface sites and consequently, a relatively high reactivity that requires only a minimal degree of protonation for metal extraction. Controlling dissolution at time periods immediately after grinding is simply the number of highly reactive sites (i.e., edge sites with the fewest neighbors or sites with the most significant crystalline disruption). This research has shown that for a common magnesium silicate, antigorite, the creation of reactive sites from grinding leads to initial dissolution rates of almost 10^{-6} mol/m²/s, which decrease rapidly to slightly less than 10^{-8} mol/m²/s for all of the particle size fractions by 24 hr. The exploitation of these reactive sites resulted in the extraction of magnesium ranging from 7.4% to 11.4% for the four particle size fractions. The dissolution rates observed in this study are inconsistent with the rate of CO₂ production from coal-fired power plants. However, the simplicity of a carbonic acid approach may provide important opportunities for process improvement.

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CHAPTER 4. CONDITIONS FOR THE CARBONATION OF MAGNESIUM IONS DERIVED FROM THE LEACHING OF ANTIGORITE WITH CARBONIC ACID

4.1 Introductory Comment

The previous chapter evaluated the potential for a direct ex situ mineral carbonation process with antigorite based on the rate of magnesium extraction. It was concluded that the dissolution of antigorite, which is a prevalent, but relatively recalcitrant magnesium silicate, would need to be increased prior to large-scale implementation. Although the extraction of metals is clearly a critical step in any ex situ mineral carbonation process, the challenges associated with the carbonation reaction should not be neglected. This chapter investigates the challenges associated with the hydration of magnesium ions in aqueous solution and potential mitigation options.

4.2 Abstract

The potential for the precipitation of magnesium carbonates is evaluated in a series of experiments that varies the particle size (-38, 38 x 150, 150 x 300 μm), CO_2 partial pressure (1, 10, 30, 50 atm), reactor temperature (25, 50, 100°C), and solids concentration (5, 25, 100, 200 g/L of water). This range of experimental conditions results in only modest improvements in the activity of magnesium ions in solution, $\alpha_{\text{Mg}^{2+}}$; however, these conditions lead to a range of $\alpha_{\text{HCO}_3^-}$ that spans three orders of magnitude. Geochemical modeling indicates a high degree of supersaturation with respect to magnesite, although no precipitates have been observed. Kinetic limitations within the Mg-H₂O-CO₂ system favor the formation of the metastable magnesium carbonates hydromagnesite and nesquehonite under these reaction conditions. The saturation indexes for these phases illustrate that the solutions in this study are likely undersaturated. However, the precipitation of magnesium carbonates can be facilitated by mitigating the strong Mg²⁺-H₂O interactions. Research by the petroleum industry has shown that the use of alcohols can inhibit the formation of gas hydrates; however, the alcohols also promote scale formation. An initial evaluation of the effects of methanol and monoethylene glycol indicates that the solubility of two magnesium carbonates, hydromagnesite and magnesite, could be reduced without the consumption of additional reagents.

4.3 Introduction

Ex situ mineral carbonation technology continues to advance; however, elevated costs remain a significant impediment (IPCC, 2005). Research has focused primarily on the rate-limiting step of metal extraction from silicate minerals. The leaching of metals from silicate minerals is a significant challenge and the use of an acidic medium to accelerate leaching can greatly increase the rate and extent of magnesium extraction. However, the pH swing from acidic conditions for dissolution to basic conditions for the carbonation reaction typically requires additional processing and costs. Exacerbating the challenge of shifting between conditions suitable for dissolution and carbonation is the solvation of magnesium ions.

In aqueous solutions, water molecules surround metal ions to minimize the charge imbalance. The high charge-to-radius ratio for magnesium relative to calcium results in a comparatively stable solvation shell. Although dissolved calcium in aqueous solutions can readily react with carbonate ions, magnesium ions are relatively unreactive (Sayles and Fyfe, 1973). The growth rate of magnesite, MgCO_3 , is so slow that effectively it does not form at ambient temperatures and instead, metastable magnesium carbonates predominate (Lippmann, 1973). These metastable phases are stable under ambient conditions and suitable as a carbon sequestration product; however, the higher solubilities of these products necessitate a greater degree of supersaturation. The challenges associated with the carbonation of magnesium ions should be considered in ex situ mineral carbonation approaches that utilize magnesium silicates.

In Chapters 2 and 3, studies on the extraction of magnesium from a relatively stable magnesium silicate, antigorite ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), with carbonic acid were conducted to evaluate the potential for the use of carbonic acid in an ex situ mineral carbonation process. It was demonstrated that mild reaction conditions were capable of extracting magnesium. However, it was concluded that additional improvement in magnesium extraction would be required to achieve a dissolution rate that is commensurate with CO_2 production. Stronger acids have a

demonstrated capability to increase the dissolution rate by many orders of magnitude, but require greater input (e.g., the addition of a base or electrolytic conversion of the acid) for suitable carbonation conditions after extraction (IPCC, 2005; Maroto-Valer et al., 2005; Park and Fan, 2004; Teir et al., 2009; Van Essendelft and Schobert, 2009). Short of a novel process to swing the carbonation conditions, the buffering capacity of magnesium silicates may provide the necessary conditions suitable for the carbonation reaction. Carbonic acid leaching of magnesium from antigorite in a direct aqueous mineral carbonation process may be able to render conditions that are suitable for the formation of magnesium carbonates without the consumption of additional reagents.

4.4 Experimental

A parametric study was conducted utilizing antigorite from the Cedar Hills quarry in southeastern Pennsylvania that was provided by the U.S. Department of Energy, National Energy and Technology Laboratory at Albany, Oregon. Baseline reaction conditions were conducted for three particle size fractions (-38, 38 x 150, 150 x 300 μm) for 24 hr at 50°C, with a solids concentration of 25 g/L of water and reactor pressure of 30 atm. The solutions from the parametric batch experiments were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and the pH of solution was measured with an Orion 720APlus pH meter immediately upon opening the reactor vessel. In this study, the Geochemist's Workbench® software, which is available from Aqueous Solutions LLC in Champaign, IL, was used to evaluate the potential for carbonation of the magnesium ions derived from the leaching experiments. The activities of the aqueous species were calculated with the SpecE8 program and Act2 was used to construct the predominance diagram for the Mg-H₂O-CO₂ system. The activities were calculated with the thermo.dat database, which utilizes an extended form of the Debye-Hückel equation (Bethke, 2006).

Magnesium carbonate solubility experiments were conducted through undersaturation with varying mole fractions of monoethylene glycol and methanol in 125 mL sealed glass vessels that were stirred at 150 rpm with magnetic stirring bars at room temperature for 10 hr. The magnesite sample was synthesized according to the methodology presented by Zhang (2000), by mixing 40 g of hydromagnesite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, with 200 g H_2O in a saturated NaCl solution. The sample was prepared by continuously mixing the solution in a sealed Teflon™-lined Parr reactor for 2 hr at 200°C. Reagent-grade hydromagnesite samples were supplied by Alfa Aesar. X-ray diffraction (XRD) was conducted with a Scintag x2 θ - θ powder diffractometer to characterize the different magnesium carbonate samples as shown in Figures 4.1-4.4. The XRD patterns show that the magnesite sample had a high degree of crystallinity and contains brucite, $\text{Mg}(\text{OH})_2$, as a secondary phase and the hydromagnesite samples contained crystalline as well as amorphous solids. The solutions were filtered with 0.45 μm Whatman® membrane filters, acidified with a 2% HNO_3 solution, and analyzed by ICP-AES.

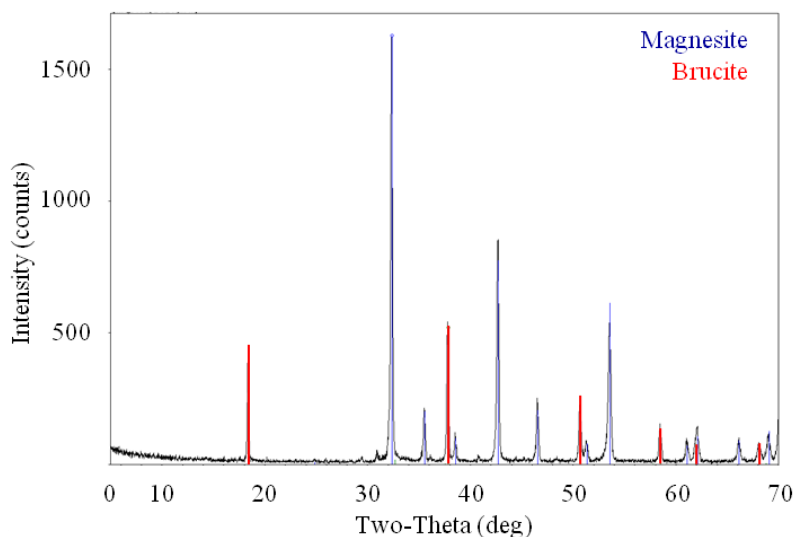


Figure 4.1. XRD of magnesite sample containing brucite

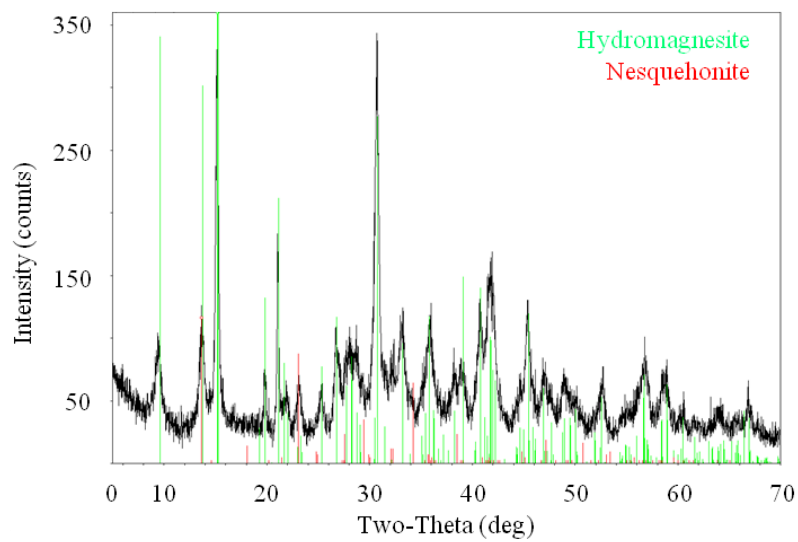


Figure 4.2. XRD of hydromagnesite sample 1 with nesquehonite and amorphous material

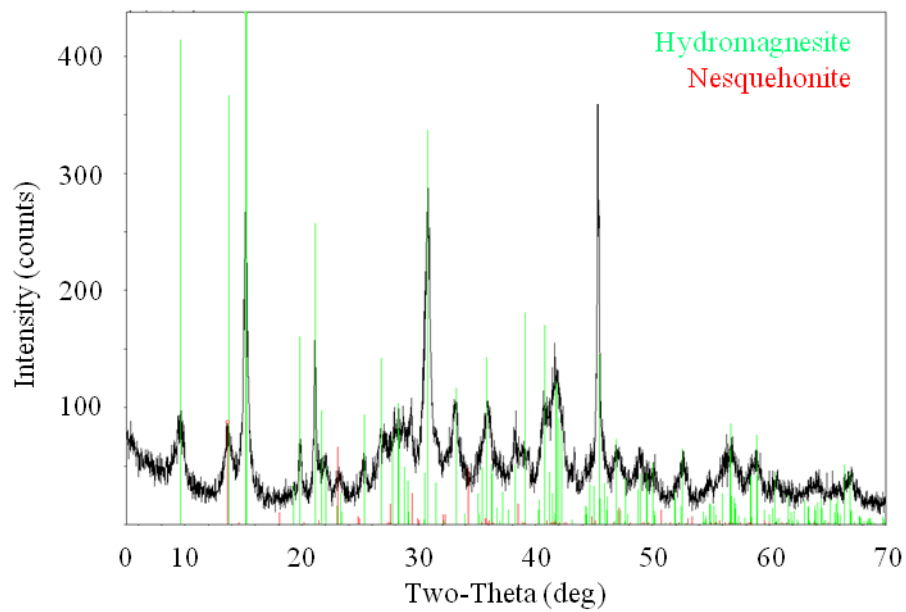


Figure 4.3. XRD of hydromagnesite sample 2 with nesquehonite and amorphous material

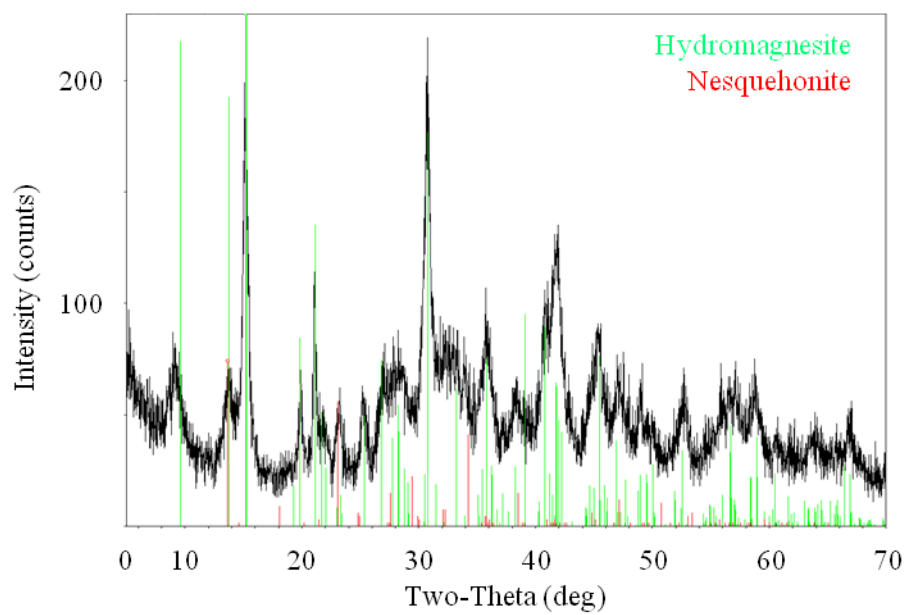


Figure 4.4. XRD of hydromagnesite sample 3 with nesquehonite and amorphous material

4.5 Results and Discussion

4.5.1 Thermodynamic potential for magnesium carbonate precipitation

The experimental conditions, activities, and saturation indexes for magnesite (MgCO_3), nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), and hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), are shown in Table 4.1 for the range of conditions discussed in Chapter 2. The effect of particle size, reactor temperature, CO_2 partial pressure, and solids concentration resulted in magnesium activities, $\alpha_{\text{Mg}^{2+}}$, that ranged by a factor of five. Although this range of experimental conditions resulted in only modest improvements in the extraction of magnesium from antigorite, the bicarbonate activity varied by three orders of magnitude. The sensitivity of the $\alpha_{\text{HCO}_3^-}$ to reaction conditions is significant, as research has indicated that it is the activity of these ions, rather than that of magnesium, that is critical to the precipitation of magnesium carbonates (Lippmann, 1973; Sayles and Fyfe, 1973).

Table 4.1. Reaction parameters and solution conditions for the carbonic-acid leaching of antigorite

	Particle Size μm	Solids g/L	T °C	P_{CO_2} atm	$\log \alpha_{Mg^{2+}}$	$\log \alpha_{HCO_3^-}$	pH	<i>I</i>	$SI_{Mag}^{(a)}$	$SI_{Nes}^{(b)}$	$SI_{Hyd}^{(c)}$
Baseline	-38				-2.22	-0.86	6.04	0.13	1.15	-2.04	-5.98
	38 x 150	25	50	30	-2.26	-0.85	6.04	0.13	1.12	-2.07	-6.14
	150 x 300				-2.25	-0.87	6.02	0.12	1.09	-2.10	-6.29
1 atm	-38				-1.91	-2.55	5.99	0.06	-0.28	-3.47	-11.49
	38 x 150	25	50	1	-1.96	-2.65	5.90	0.05	-0.52	-3.71	-12.68
	150 x 300				-1.95	-2.57	5.96	0.05	-0.37	-3.56	-11.95
10 atm	-38				-2.09	-1.15	6.18	0.09	1.13	-2.06	-5.65
	38 x 150	25	50	10	-2.05	-1.42	6.02	0.07	0.74	-2.45	-7.49
	150 x 300				-1.97	-1.78	5.79	0.06	0.23	-2.96	-9.91
50 atm	-38				-2.51	-0.42	6.17	0.30	1.43	-1.76	-4.89
	38 x 150	25	50	50	-2.19	-0.94	5.85	0.12	0.91	-2.28	-7.29
	150 x 300				-2.32	-0.76	5.95	0.14	1.06	-2.13	-6.62
25°C	-38				-2.52	-0.45	6.20	0.28	0.79	-1.91	-8.76
	38 x 150	25	25	30	-2.35	-0.8	5.98	0.13	0.39	-2.31	-10.63
	150 x 300				-2.43	-0.66	6.06	0.20	0.53	-2.17	-9.99
100°C	-38				-2.08	-1.31	6.06	0.08	1.96	-2.33	-0.22
	38 x 150	25	100	30	-2.04	-1.58	5.90	0.06	1.57	-2.72	-2.06
	150 x 300				-2.05	-1.58	5.90	0.06	1.56	-2.73	-2.11
5 g/L	-38				-2.59	-1.30	5.78	0.04	0.08	-3.11	-11.15
	38 x 150	5	50	30	-2.42	-2.51	5.15	0.02	-1.59	-4.78	-18.92
	150 x 300				-2.42	-2.52	5.14	0.01	-1.61	-4.80	-19.02
50 g/L	-38				-2.13	-0.60	6.21	0.23	1.68	-1.43	-3.33
	38 x 150	50	50	30	-2.36	-0.36	6.37	0.36	1.84	-1.27	-2.57
	150 x 300				-2.27	-0.46	6.30	0.29	1.76	-1.35	-2.95
100 g/L	-38				-2.32	-0.06	6.60	0.71	2.41	-0.70	0.19
	38 x 150	100	50	30	-2.19	-0.27	6.44	0.46	2.17	-0.94	-0.98
	150 x 300				-2.09	-0.40	6.35	0.36	2.06	-1.05	-1.49
200 g/L	-38				-2.30	0.31	6.92	1.63	3.13	0.02	3.73
	38 x 150	200	50	30	-2.29	0.25	6.87	1.44	3.02	-0.09	3.21
	150 x 300				-2.11	0.04	6.69	0.94	2.81	-0.30	2.20

(a) The saturation index for magnesite, $SI_{Mag} = \log \left[(\alpha_{Mg^{2+}})(\alpha_{HCO_3^-}) / (\alpha_{H^+}) K_{SPMag} \right]$; $K_{SPMag} = 10^{1.81}$

(b) The saturation index for nesquehonite, $SI_{Nesq} = \log \left[(\alpha_{Mg^{2+}})(\alpha_{HCO_3^-})(\alpha_{H_2O})^3 / (\alpha_{H^+}) K_{SPNesq} \right]$; $K_{SPNesq} = 10^{5.00}$

(c) The saturation index for hydromagnesite, $SI_{Hyd} = \log \left[(\alpha_{Mg^{2+}})^5 (\alpha_{HCO_3^-})^4 (\alpha_{H_2O})^6 / (\alpha_{H^+})^6 K_{SPHyd} \right]$; $K_{SPHyd} = 10^{27.68}$

The ability of antigorite to act as a buffer against carbonic acid provides an opportunity to improve upon the carbonation reaction by significantly increasing $\alpha_{HCO_3^-}$. Increasing the solids concentration and decreasing the particle size result in higher pH values and correspondingly higher $\alpha_{HCO_3^-}$. Increasing the solids concentration from 5 to 200 g/L led to an increase in pH from 5.78 to 6.92 and yielded a factor of 40 increase in $\alpha_{HCO_3^-}$. Decreasing the particle size fraction from 150 x 300 μm to -38 μm resulted in a factor of three improvement in $\alpha_{HCO_3^-}$. For the set of experiments that evaluated the effect of CO_2 partial pressure, the pH of solution was essentially invariant as the pressure was increased from 1 to 50 atm in the presence of antigorite. The ability of antigorite to buffer against the increase in CO_2 partial pressure resulted in more than a two order of magnitude increase in $\alpha_{HCO_3^-}$. The potential exists for the CO_2 partial pressure to decrease the pH, potentially leading to the dissolution of carbonate minerals. However, research by Giammar et al., (2005) indicated that dissolution of forsterite, Mg_2SiO_4 , occurred as magnesite precipitated at CO_2 partial pressures that ranged from approximately 87-102 atm.

Figure 4.5 illustrates the effect of the reaction conditions on the degree of saturation with a positive saturation index indicating that the solution is supersaturated. With the exception of experiments conducted at a CO_2 partial pressure of 1 atm and two experiments with a solids concentration of 5 g/L, all of the experiments that were discussed in Chapter 2 resulted in solution conditions that were saturated with respect to magnesite. However, the presence of a precipitate was not observed in any of the experiments visually or by XRD. Although supersaturation is the thermodynamic driving force for precipitation, reaction kinetics associated with nucleation or crystal growth may control the formation of magnesium carbonates.

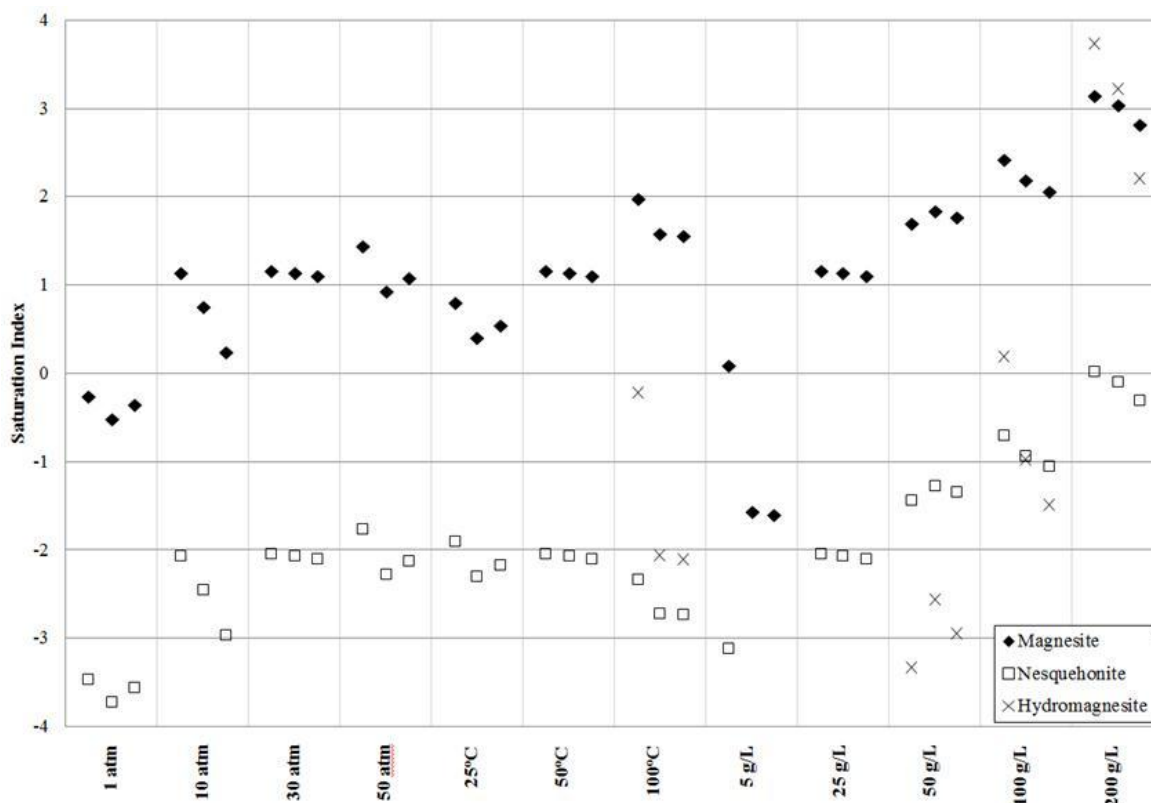


Figure 4.5. Saturation indexes for magnesite, nesquehonite, and hydromagnesite for the different experimental conditions. Baseline reaction conditions were at 50°C, with a solids concentration of 25 g/L, and a CO₂ partial pressure of 30 atm. (Note: The particle size fractions are not labeled explicitly, however the results are presented in order of increasing particle size from left to right [i.e., -38 μm, 38 x 150 μm, and then 150 x 300 μm]).

4.5.2 Kinetic limitations of the Mg-H₂O-CO₂ system

The reactivity of metals in solution is affected by the hydration structure and dynamics of water interactions (Di Tommaso and de Leuw, 2010). The variation in ionic radii between magnesium and calcium result in differences between the metal-water interactions, with magnesium having a relatively rigid and well-defined inner-solvation sphere. The weaker Ca²⁺-OH₂ interactions increase the Ca²⁺-CO₃²⁻ and Ca²⁺-HCO₃⁻ interactions, resulting in lower solubility of calcium carbonate and a lack of metastable calcium carbonate phases. Simulations and laboratory studies have shown that the inter-atomic distance between magnesium and oxygen ions in water is approximately 2.1 Å, versus 2.4 Å for calcium ions, with water

exchange rates of $5 \times 10^5 \text{ s}^{-1}$ and $4 \times 10^{11} \text{ s}^{-1}$, respectively (Lightstone et al., 2001; Lightstone et al., 2005). These studies have also shown that the coordination number for magnesium ions in aqueous solution is fixed at six water molecules, whereas the coordination number for calcium ions shifts between six, seven, and eight. Consequently, the interactions between magnesium and carbonate or bicarbonate ions are limited, the formation of magnesite is suppressed, and metastable reaction products tend to predominate under ambient conditions. At temperatures below 60°C , it is energetically favorable for water molecules to be incorporated into the crystal structure of magnesium carbonates (Lippmann, 1973).

Magnesite is the thermodynamically stable magnesium carbonate phase at all temperatures and CO_2 partial pressures; however, the kinetics of nucleation or crystal growth can dictate the predominance of metastable magnesium carbonates. The stability fields for magnesite and two metastable magnesium carbonates, hydromagnesite and nesquehonite, are shown in Figure 4.6. As these minerals are metastable with respect to magnesite, the degree of supersaturation would be less. Table 4.1 and Figure 4.5 illustrate that precipitation of these phases is not expected for most of these experiments. The calculated saturation index of hydromagnesite for several of the experiments conducted with a high solids concentration was as high as 3.73, which even exceeded the saturation index for magnesite. As previously discussed, magnesite is the thermodynamically stable phase and therefore the saturation index of hydromagnesite cannot exceed that of magnesite. Uncertainty in the geochemical calculations, coupled with the sensitivity of the saturation index for hydromagnesite due to the exponential terms, likely led to this result.

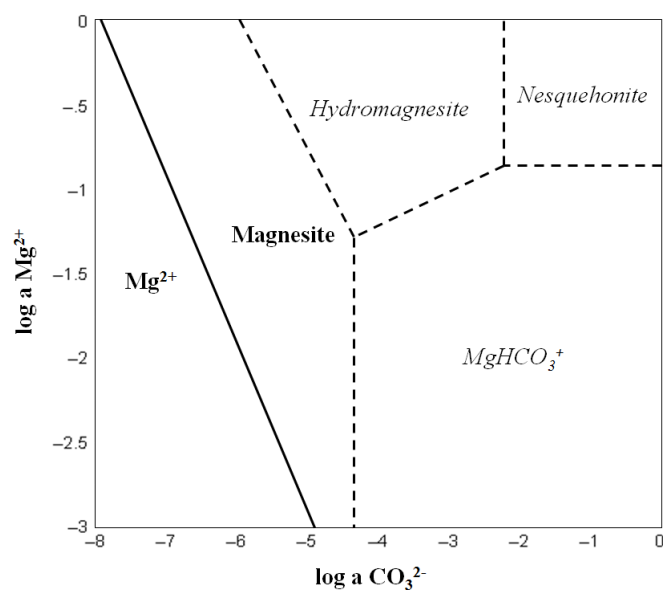


Figure 4.6. Stability diagram for the Mg-H₂O-CO₂ system at 25°C and a pH of 7 with the metastable magnesium carbonates, hydromagnesite and nesquehonite, denoted with italics.

4.5.3 Uncertainty in the prediction of magnesite carbonate precipitation

The complexity of the Mg-H₂O-CO₂ system provides experimental challenges that have resulted in uncertainty and variability in thermodynamic data (Christ and Hostetler, 1970; Hänchen et al., 2008; Königsberger et al., 1999; Langmuir, 1965). Accordingly, a relatively high degree of uncertainty exists in predicting the stability fields for magnesium carbonates. The saturation indexes for several of the experiments conducted with a high solids concentration have an additional degree of uncertainty as they were also calculated with the thermo.dat dataset. The extended form of the Debye-Hückel equation would be expected to deviate at ionic strengths greater than approximately 0.1 M due to the effect of short-range electrostatic interactions (Stumm and Morgan, 1996). However, it was selected over the Pitzer approach due to limitations with the derived virial coefficients for calculating the activities and saturation indices for the Mg-H₂O-CO₂ system at temperatures greater than 25°C (USGS, 2011).

The calculated degree of supersaturation is an oversimplification of the relative contributions of $\alpha_{Mg^{2+}}$ and $\alpha_{HCO_3^-}$. Researchers have noted that beyond a certain threshold, $\alpha_{Mg^{2+}}$ does not promote the formation of magnesium carbonates and it can actually inhibit the reaction (Lippmann, 1973; Sayles and Fyfe, 1973). Accordingly, Figure 4.5 may overestimate the potential for the precipitation of magnesium carbonates in these experiments.

Uncertainty also exists in the calculated $\alpha_{HCO_3^-}$ values, which were based on CO_2 partial pressures and the ionic strength of solution. The pH was measured immediately upon opening the reactor vessel, though the pH of solution increases as $CO_2(g)$ is released during depressurization. The $\alpha_{HCO_3^-}$ is sensitive to pH and due to limitations with in situ pH measurements for a pressurized vessel, the pH and therefore the $\alpha_{HCO_3^-}$ may have both been overestimated. The $\alpha_{HCO_3^-}$ is critical to the formation of magnesium carbonates, however, field and laboratory observations have indicated that the reaction can be improved upon by reducing the influence of the solvation sphere.

4.5.4 Mitigation of the kinetic limitations within the Mg-H₂O-CO₂ system

The carbonation reaction is dependent on the ligand exchange of bicarbonate ions with the solvation sphere associated with magnesium ions; accordingly, the potential for magnesium carbonate precipitation can be improved upon by reducing the Mg^{2+} -H₂O interactions. By increasing the ionic strength of solution, reaction temperature, and the presence of alcohol, the formation of magnesium carbonates can be promoted. Laboratory experiments have demonstrated a catalytic effect associated with ionic strength for the formation of magnesium carbonates, which is consistent with observations of magnesite deposits that are associated with highly saline solutions (Hänchen et al., 2008; Sayles and Fyfe, 1973). The decrease in the activity of water with increasing ionic strength promotes the formation of magnesium carbonates by increasing the interaction between magnesium and bicarbonate ions. An increase

in reaction temperature also increases the likelihood of magnesium and carbonate/bicarbonate ion interactions by dramatically increasing the ligand exchange rate and promoting nucleation (Giammar, et al., 2005; Hänchen et al., 2008; Sayles and Fyfe, 1973).

The oil and gas industry uses alcohols, such as methanol (MeOH), and ethylene glycol (MEG), to inhibit the formation of gas hydrates in natural gas pipelines; however, an adverse side effect of these reagents is an increase in scale formation (Kan, et al., 2002). The presence of alcohols results in a decreased activity of water that reduces the solubility of carbonates. Exploiting the effects of alcohols in aqueous solution may alleviate challenges associated with the precipitation of magnesium carbonates in an ex situ mineral carbonation process.

An initial evaluation of the solubility of three different hydromagnesite samples and one magnesite sample with respect to the mole fraction, χ , of MeOH is illustrated in Figure 4.7. In addition, the solubility of magnesium in an aqueous solution with MEG is evaluated for one hydromagnesite sample. All of the magnesium carbonate samples demonstrate an inverse relationship between solubility and the concentration of alcohol in solution, with MeOH having a greater effect than MEG. These results are consistent with research conducted on scale formation in the presence of MeOH and MEG (Kan, et al., 2002). Contamination of these samples with brucite or the presence of an amorphous fraction is not ideal. However, these artifacts do not affect these initial findings that the use of alcohols can improve an ex situ mineral carbonation process without the consumption of additional reagents or the need for chemical regeneration.

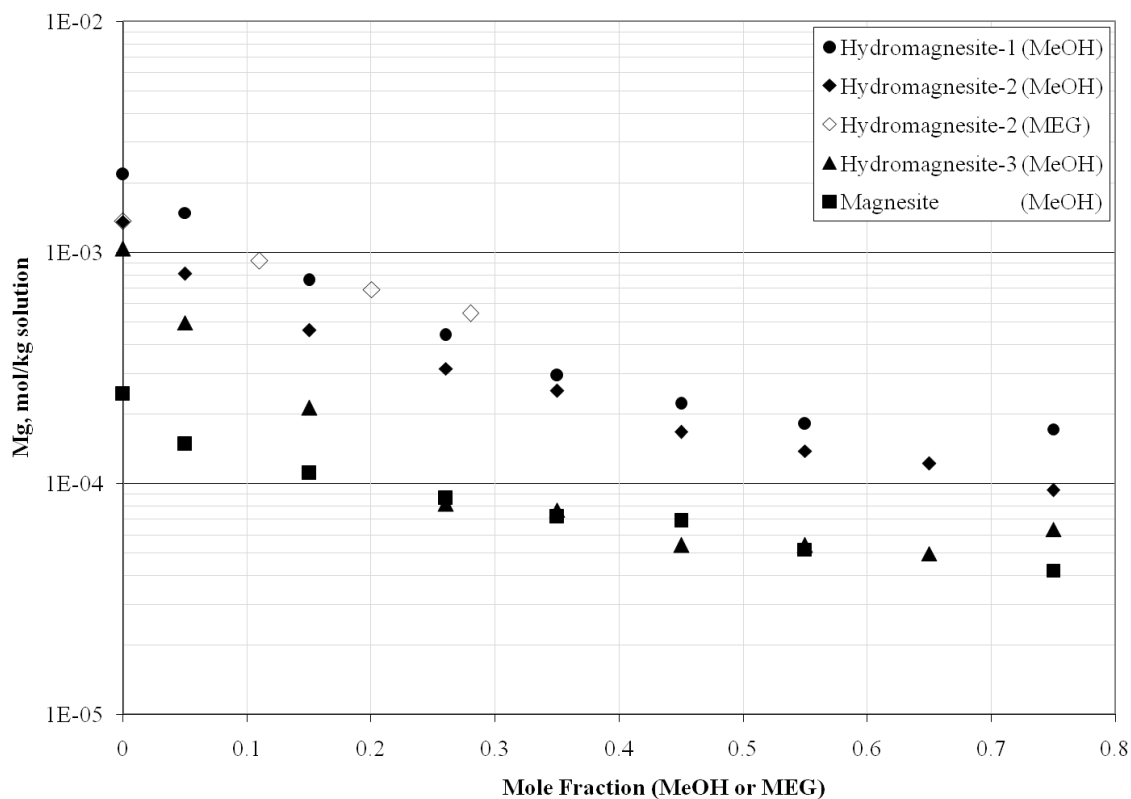


Figure 4.7. Concentration of magnesium in solution with respect to the mole fraction of methanol or monoethylene glycol.

4.6 Conclusions

The challenges associated with both dissolution and precipitation should be considered for any ex situ mineral carbonation process. The use of carbonic acid in a mineral carbonation process is attractive in that it is capable of extracting magnesium and rendering conditions that may be suitable for carbonation without additional reagents. The dissolution of antigorite via carbonic acid was relatively insensitive to particle size, reactor temperature, CO_2 partial pressure, and solids concentration, as the range of magnesium activities varied by a factor of five for these reaction conditions. Mild reaction conditions were able to extract a degree of magnesium, however, it is likely the activity of carbonate and bicarbonate ions that is critical to the carbonation reaction. The $\alpha_{\text{HCO}_3^-}$ varied by three orders of magnitude for the range of

parameters evaluated in this study due, in large part, to the buffering capacity of antigorite. However, the formation of magnesium carbonates was not observed in this series of experiments even with a high degree of magnesite supersaturation. Uncertainty in thermodynamic data and measured parameters (e.g., $\alpha_{HCO_3^-}$), reaction kinetics, the contribution of magnesium ions to the carbonation potential, and the solvation of magnesium ions all likely contributed to the lack of observed precipitates. The stable coordination number and relatively slow water exchange rate for magnesium leads to kinetic limitations. The opportunity exists to improve upon the carbonation reaction by increasing the ionic strength, increasing the reaction temperature, and by the addition of alcohols. The use of MeOH and MEG provides an opportunity to reduce the solubility of magnesium carbonates without the consumption of additional reagents, as the concentration of magnesium in solution decreased by as much as one order of magnitude.

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CHAPTER 5. SUGGESTIONS FOR FUTURE WORK

The reliance on carbonic acid to extract metals from silicate minerals provides challenges as well as many opportunities for process advances. The following recommendations are suggested for future work:

As the optimization of magnesium extraction and of carbonation conditions occur under opposing conditions, a counter-current series of reactors would facilitate both the extraction of magnesium from antigorite and the carbonation of a magnesium- and carbonate-rich solution, as shown in Figure 5.1. Solution feedback mechanisms could be minimized at the tail end of the process to maximize the extraction of magnesium and an increased solids concentration at the front end would promote the carbonation reaction. The percolation of $\text{CO}_2(\text{g})$ through aqueous solution under ambient conditions would preclude the need for sophisticated processing technology to accommodate elevated reactor pressures and the simplicity of this approach would provide a wide range of potential processing improvements.

Extraction could be potentially improved upon with the use of concurrent grinding, which may result in the ongoing creation of reactive surface sites. The addition of catalytic reagents (e.g., inorganic and organic salts, methanol) may be able to promote the dissolution reaction and/or the formation of carbonates. In addition, novel pretreatment options, such as the use of microwave technology for hydrated minerals like antigorite, may result in significant improvement in the rate of extraction by increasing the defect density in the crystal structure.

This research focused on a relatively recalcitrant silicate mineral. A study conducted on broader set of magnesium silicate minerals, under similar reaction conditions, would provide additional insight into the potential for a direct carbonation process. Additionally, a study

evaluating different samples of antigorite from the Cedar Hills quarry and other quarries would provide information on the significance of mineral variability.

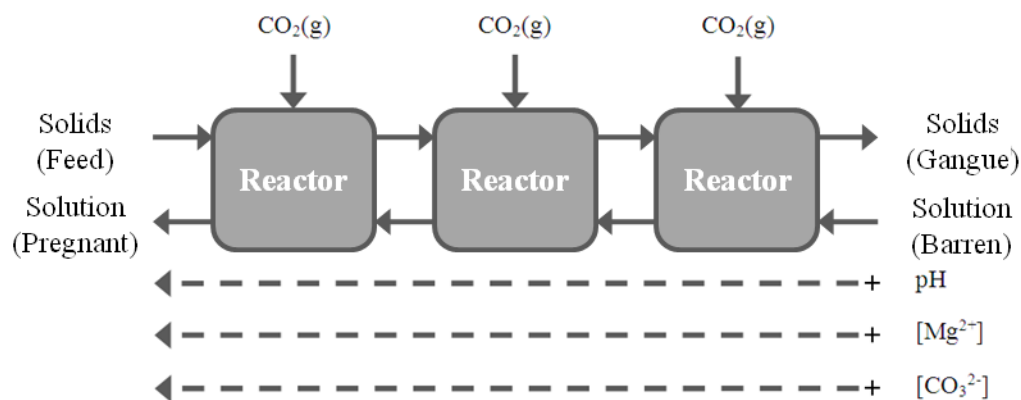


Figure 5.1. Counter-current series of reactors to promote the extraction and carbonation of magnesium ions from antigorite

Researchers at the National Energy Technology Laboratory in Albany, Oregon observed that the overall mineral carbonation reaction was significantly improved by the addition of NaHCO_3 . It was interpreted that NaHCO_3 acted as an effective CO_2 carrier while providing slightly alkaline conditions. The researchers hypothesized that the bicarbonate ion was regenerated, not consumed. If NaHCO_3 could be regenerated within an ex situ mineral carbonation process without external inputs, it would be a significant improvement to the overall process. However, a series of informal experiments by this author indicated that the addition of NaHCO_3 or Na_2CO_3 resulted in consumption of the reagent without an evident pathway for regeneration. A series of experiments with the addition of $\text{NaHC}^{14}\text{O}_3$ would demonstrate whether the bicarbonate ion was regenerated or consumed during the reaction.

An initial study on the addition of alcohols to $\text{Mg-H}_2\text{O-CO}_2$ system demonstrated a reduction in the solubility of several magnesium carbonate samples. A more comprehensive experimental matrix (e.g., different alcohols, a wider array of magnesium carbonates without

amorphous material, varying ionic strengths, reaction times, and temperatures) coupled with additional analytical techniques (e.g., titration of solutions to determine bicarbonate and carbonate ion concentrations) and geochemical modeling would better define the carbonation envelope for an Mg-H₂O-CO₂-alcohol system. The potential improvement in the carbonation reaction with the addition of alcohols should not be limited to mineral carbonation routes that rely on the use carbonic acid. Provided that the challenges associated with the use of strong acids can be met, the addition of alcohol could improve other ex situ mineral carbonation routes.

The evaluation in Chapter 4 on the use of alcohols to reduce the solubility of magnesium carbonates was conducted from undersaturation. A series of carbonation experiments conducted from oversaturation (i.e., by adding known quantities of magnesium and carbonate or bicarbonate ions) with and without the addition of alcohols would help resolve the conditions that are required for the formation of magnesium carbonates in an ex situ mineral carbonation process. Experimental conditions such as pH, reagent concentrations, and especially atmospheric contamination of CO₂ would need to be carefully controlled to minimize experimental uncertainties, as the degree of saturation is very sensitive to these parameters.

In addition to the use of alcohols to improve upon the carbonation conditions for magnesium ions, the use of seeding may also reduce the solubility of magnesium carbonates. The addition of a seed material such as magnesite may effectively reduce solubility, as the activation energy for two-dimensional crystal growth is less the energy required for three-dimensional nucleation. The use of different magnesium carbonates as seed crystals may promote the formation of certain magnesium carbonates outside of their typical environment

(i.e., the addition of magnesite to a supersaturated solution may promote the formation of magnesite at temperatures below that at which it is typically observed to form).

CHAPTER 6. SUMMARY AND CONCLUSIONS

Ex situ mineral carbonation provides a benign and long-term option for the storage of CO₂. Over the past two decades multiple process routes have been explored with aqueous mineral carbonation garnering the most attention due to the relatively high reaction rates. However, the extraction of metals from silicate minerals continues to be a challenge. Extensive pretreatment stages, elevated reactor temperatures and pressures, and the use of acidic media to accelerate mineral dissolution have limited the development of ex situ mineral carbonation technology. Further, optimization of the dissolution reaction has often come at the cost of the carbonation reaction. The use of strongly acidic media to digest silicate minerals necessitates an additional processing stage to regenerate the acid or the addition of basic reagents to provide conditions suitable for the carbonation reaction. The use of carbonic acid process provides an option that may be able to circumvent more costly processing routes. To gain insight into the potential for the use of carbonic acid in an ex situ mineral carbonation process, research has been conducted to evaluate: (i) the susceptibility of antigorite to various reaction conditions through a parametric study; (ii) the rate and mechanisms by which magnesium is released from antigorite; and (iii) the conditions for the carbonation of magnesium ions derived from the carbonic acid leaching of antigorite.

A parametric study was conducted to evaluate the effects of reaction time, particle size, partial pressure of CO₂, reactor temperature, and solids concentration on the extraction of magnesium from antigorite and the subsequent buffering of solution. The influence of highly reactive sites was evident in both the rapid rate of decay in the extraction of magnesium with time and the minor improvement (up to 12% increase in magnesium release to solution) observed with particle size reduction. Reactor temperatures up to 100°C and CO₂ partial

pressures up to 50 atm provided for improvements in magnesium release of 31% and 17%, respectively. The effect of solution feedback mechanisms appears to have been important for this set of experimental conditions, as a reduction in the concentration of solids from 100 g/L to 5 g/L produced a 50% improvement in the fraction of magnesium removed from antigorite. Although the greatest fraction of magnesium extracted under any of the conditions investigated (24 hr at 50 atm, 100°C, 5 g/L, for particles less than 38 μm) was 13%, approximately 8% magnesium extraction occurred within 24 hr at 1 atm, 25°C, and 25 g/L for all particle sizes. As the stoichiometric requirement of antigorite to carbon dioxide is already 2.1:1 (wt. basis), a process with a 13% magnesium recovery would not be practicable. However, the ability of carbonic acid to extract magnesium from antigorite under minimal reaction conditions affords a wide range of potential processing options. In addition to the extraction of magnesium that was observed in this series of experiments, antigorite was shown to be capable of buffering the solution to a pH of 6.92 for an experiment conducted with a solids concentration of 200 g/L, which corresponded to an increase in the bicarbonate ion activity by a factor of 40 relative to a solution with 5 g/L.

The rate of CO_2 production from a typical coal-fired power plant requires the release of metals at a rate in excess of steady-state dissolution rates, for even the more soluble silicate minerals. However, the creation of reactive sites during grinding provides an opportunity for the use of carbonic acid in an ex situ mineral carbonation process. In Chapter 2, it was demonstrated that mild reaction conditions with carbonic acid were capable of extracting magnesium from a common silicate. In Chapter 3, a kinetic investigation was conducted to evaluate the rate and mechanisms controlling the extraction of magnesium from antigorite in carbonic acid at early time periods to better understand the potential use of carbonic acid in an ex situ mineral carbonation process. The initial rate of dissolution reflected a rapid proton-metal exchange consistent with the hydrolysis of reactive sites on the surface of the antigorite

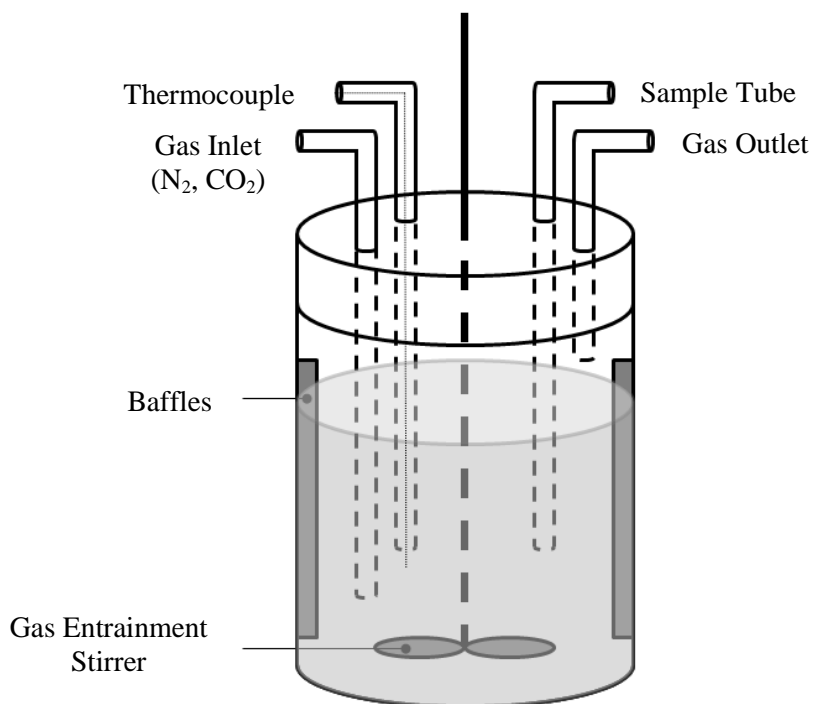
particles. The rate of magnesium release decayed from almost 10^{-6} mol/m²/s to approximately 10^{-8} mol/m²/s for the various particle size fractions that were investigated, as the most reactive sites were readily depleted within 24 hr. Due to the scale of CO₂ emissions, the rate of magnesium release would need to be increased to avoid an impracticable capital expenditures and operating costs. Although additional improvement in extraction of magnesium would be required, the use of carbonic acid provides conditions that may be suited to the formation of magnesium carbonates.

In addition to the challenges associated with the extraction of magnesium from silicate minerals, the precipitation of magnesium carbonates is not trivial. The use of carbonic acid is an attractive process as it is both capable of extracting magnesium and rendering conditions that may be suitable for carbonation without the consumption of additional reagents. Although mild reaction conditions within the parametric study yielded solutions that were supersaturated with respect to magnesite, the presence of magnesium carbonates was not observed. Uncertainty in thermodynamic data and measured parameters (e.g., $\alpha_{HCO_3^-}$), reaction kinetics, the contribution of magnesium ions to the carbonation potential, and the solvation of magnesium ions all likely contributed to the lack of observed precipitates. The stable coordination number and relatively slow water exchange rate for magnesium leads to kinetic limitations. The addition of alcohols such as MeOH and MEG demonstrated an opportunity to improve upon the carbonation conditions. As the Mg²⁺-H₂O interactions were reduced by the presence of these alcohols, the solubility of several magnesium carbonates samples were shown to have decreased by approximately one order of magnitude.

Due to the scale of CO₂ emissions from coal-fired power plants, significant challenges are associated with every option for CO₂ storage. For ex situ mineral carbonation, supplying metals at a rate consistent with CO₂ production is the key obstacle. However, optimization of the overall process is critical due to contrasting conditions for the extraction of magnesium and the

carbonation of magnesium ions. The use of carbonic acid provides a process route that has the potential to span both the dissolution and carbonation reactions. It has been demonstrated that additional advances in the rate and extent of magnesium extraction with carbonic acid and the conditions for the carbonation of magnesium ions would be required for a large-scale process. This research has only evaluated a small subset of a larger matrix of experimental conditions pertaining to the use of carbonic acid in an ex situ mineral carbonation process. Accordingly, significant opportunities for improvement in this approach exist.

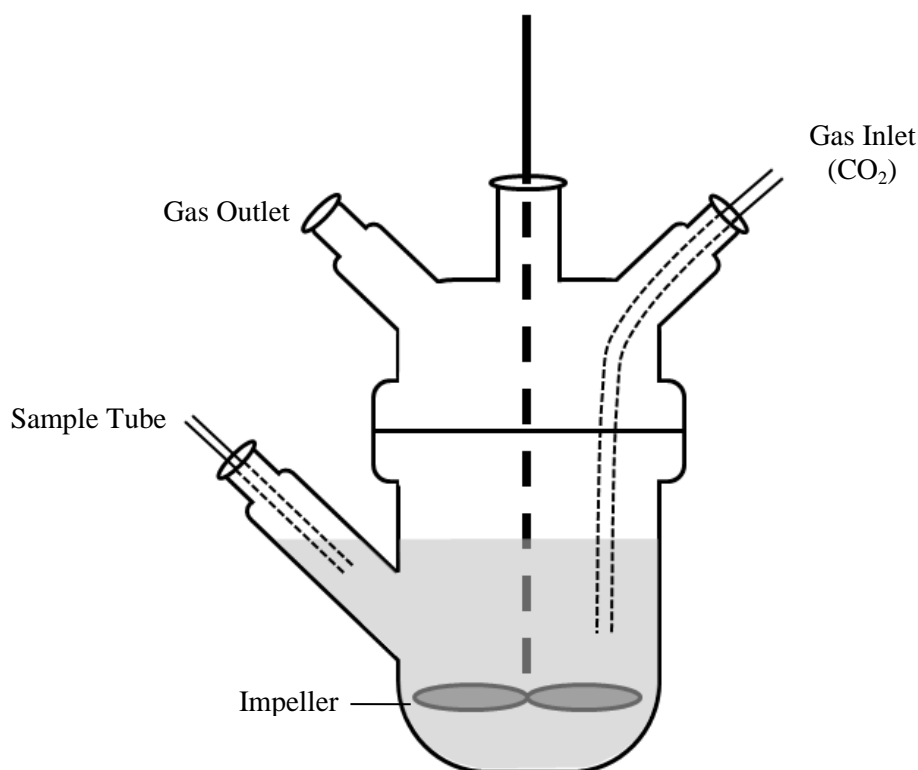
Appendix A. Design of Experiments for the Parametric Study and Reactor Diagram



Experimental procedure for the Parametric Study of Carbonic Acid Leaching of Antigorite for Mineral Carbonation	
Parent Sample	The U.S. Department of Energy, National Energy Technology Laboratory in Albany, Oregon provided a parent sample of antigorite (80% finer than 4 mm) from the Cedar Hills quarry in southeastern Pennsylvania.
Sample Preparation	The parent sample was ground for 30 s in a cup-and-puck mill in 150 g batches.
	The samples were dry sieved for 20 min using a sieve shaker to -38, 38 x 150, 150 x 300, and +300 μm . The samples were then wet sieved with 750 mL of water for the 150 x 300 and +300 μm and 1500 mL of water for the 38 x 150 μm material, followed by 30 min of oven drying at 105°C. The samples were then dry sieved again for 30 min.
Dissolution Reaction	Dissolution experiments were carried out in a Series 4561 300 mL stirred Parr reactor (see diagram above).
	Antigorite samples, according to Table 2.3, were placed in the reactor with 200 mL of ultrapure Millipore water (18.2 M Ω ·cm).
	After sealing the reactor, the reactor was charged with N ₂ (g) to 6.8 atm and purged (three times) to reduce atmospheric contamination.
	The reactor was then heated with a mantle according to the prescribed temperatures in Table 2.3.
	The reactor was then charged to the prescribed pressures in Table 2.3 with bone dry CO ₂ (g). Additional CO ₂ (g) was added as necessary to maintain the appropriate pressure throughout the experiment.

Experimental procedure (continued)	
Dissolution Reaction	The dissolution reaction was conducted for the prescribed time and at a stirring speed of 150 RPM with a gas-entrainment stirrer and baffles. t
Analyses	After the reaction period, the reactor was depressurized and the pH of solution was immediately taken with an Orion 720APlus pH meter once the reactor was opened.
	The solutions were filtered with 8 μm Whatman® Grade 40 ashless quantitative filter paper and samples of the filtrates were acidified with a 10% HNO_3 solution.
	Solids were dried overnight at 105°C and weighed.
	Ion concentrations of the filtrate samples were analyzed by ICP-AES.

Appendix B. Design of Experiments for the Kinetics Investigation and Reactor Diagram



Experimental procedure for the Study on Kinetics of Magnesium Extraction from Antigorite via Carbonic Acid Leaching	
Parent Sample	The U.S. Department of Energy, National Energy Technology Laboratory in Albany, Oregon provided a parent sample of antigorite (80% finer than 4 mm) from the Cedar Hills quarry in southeastern Pennsylvania.
Sample Preparation	The parent sample was ground for 30 s in a cup-and-puck mill in 150 g batches.
	The samples were dry sieved for 20 min using a sieve shaker to -38, 38 x 150, 150 x 300, and +300 μm . The samples were then wet sieved with 750 mL of water for the 150 x 300 and +300 μm and 1500 mL of water for the 38 x 150 μm material, followed by 30 min of oven drying at 105°C. The samples were then dry sieved again for 30 min.
Dissolution Reaction	Dissolution experiments were carried out in parallel 200 mL CSTRs (see diagram above and Figure 3.3).
	2.5 g of antigorite sample were placed in the reactors with 100 mL of distilled water.
	Bone dry CO ₂ (g) was percolated through the vessels at flow rate of 30 mL/min
	The experiments were conducted at room temperature, for 24 hrs, at 300 rpm.

Experimental procedure (continued)	
Analyses	The pH of solutions were periodically taken throughout the experiments with an Orion 720APlus pH meter.
	Samples of solution were taken periodically, alternating between the duplicate
	Approximately 0.5 mL of solution was periodically extracted from the CSTRs, filtered with 0.45 μm Whatman® membrane, and acidified with 7 mL of a 2% HNO_3 solution. Note: sampling alternated between the duplicate experiments to minimize the change in solids concentration throughout the experiment. The filtrates were then analyzed by ICP-AES.
	Solids were dried overnight at 105°C and weighed.
	Solid samples were then digested using a lithium metaborate fusion technique and analyzed by ICP-AES.

**Appendix C. Design of Experiments for the Mitigation of Kinetic Limitations within the
Mg-H₂O-CO₂ System with the Addition of Alcohols**

Experimental procedure for the Mitigation of Kinetic Limitations within the Mg-H₂O-CO₂ System with the Addition of Alcohols	
Reagents	Reagent-grade hydromagnesite and ethylene glycol, ACS-grade methanol, and distilled water were used in these experiments.
Sample Preparation and Characterization	The magnesite sample was synthesized by mixing 40 g of hydromagnesite with 200 g distilled H ₂ O in a saturated NaCl solution. The sample was prepared by continuously mixing the solution in a sealed Teflon™-lined Parr reactor for 2 hr at 200°C.
	X-ray diffraction was conducted with a Scintag x2 θ - θ powder diffractometer to characterize the different magnesium carbonate samples (see Figures 4.1-4.4).
Solubility Experiments	The methanol experiments were conducted at mole fractions ranging from 0 to 0.75 and the ethylene glycol experiments ranged from 0 to 0.28.
	The experiments were carried out in 125 mL sealed glass jars at room temperature for 24 hr. The solutions were stirred at 150 rpm with a magnetic stirrer bar.
Analyses	The solutions were filtered with 0.45 μ m Whatman® membrane filters, acidified with a 2% HNO ₃ solution, and analyzed by ICP-AES.

VITA

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George Alexander was born in Franklin, Pennsylvania in 1977. He received a Bachelor of Science degree from The Pennsylvania State University in Geo-Environmental Engineering in 1999. In 2003, the author returned to Penn State and received a Master of Science degree in Energy and Geo-Environmental Engineering. Beginning in 2005, he spent two years abroad at the University of Nottingham as a research and teaching associate before returning to Penn State. While completing a Doctor of Philosophy Degree in Energy and Geo-Environmental Engineering, the author has continued to work at the United States Nuclear Regulatory Commission as a Systems Performance Analyst in the Division of Waste Management and Environmental Protection since 2008.