

Serpentine and single stage mineral carbonation for the storage of carbon dioxide

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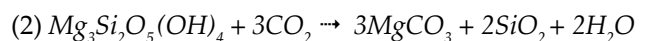
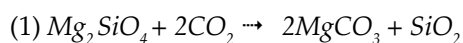
ABSTRACT

Mineral carbonation is the formation of stable calcium, magnesium, and iron carbonates from the reaction between the metals in common minerals and carbon dioxide. The benign and long-term nature of this CO₂ sequestration option has led to ongoing research efforts. Magnesium silicates such as olivine and serpentine have been the focus of mineral carbonation research for the sequestration of CO₂ for over a decade. The aqueous carbonation route has received more attention over simpler solid-gas reactions due to reaction kinetics and carbonation conversion efficiencies. However, the removal of magnesium from the magnesium silicate matrix remains as a challenge for the aqueous carbonation scheme. Strong acids such as sulfuric and hydrochloric acid have been used to improve upon the rate limiting step of magnesium removal. Although the use of an acid-accelerating medium can improve the reaction kinetics and reduce the reaction pressures and temperatures, it requires an additional step. Reagents are required to raise the pH to support carbonation, therefore imparting costs to the reaction process that, to date, are prohibitive. Our preliminary investigations have demonstrated that serpentine has the intrinsic ability to buffer against the acidic conditions resulting from the dissolution via carbonic acid, while leaching magnesium into solution for subsequent carbon storage.

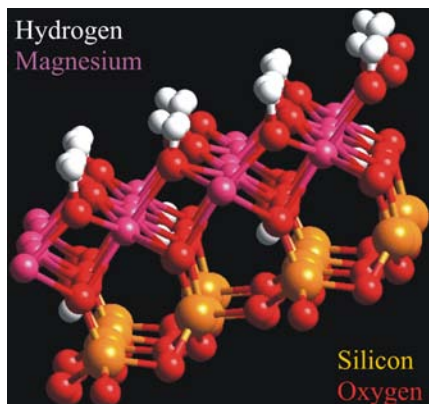
Keywords: Carbon Dioxide, Sequestration, Serpentine

INTRODUCTION

The process of mineral carbonation is based on the formation of geologically stable and benign magnesium or calcium carbonate from the reaction between CO₂ and magnesium or calcium silicates. These siliceous minerals exist in sufficient quantity to sequester the CO₂ from the combustion of all the world's known fossil fuel resources [1]. (IPCC, 2005). Olivine (Reaction 1) and serpentine (Reaction 2) have been the focus of mineral carbonation research for the sequestration of CO₂ for over a decade due to their natural abundance, geologically accessible deposits, and high magnesium content [2].



An aqueous carbonation route, where captured CO₂ is firstly dissolved in solution, has been the focus of research efforts [3,4,5,6] over simpler solid-gas reactions [7,8] due to reaction kinetics and carbonation conversion efficiencies. However, the removal of magnesium from the magnesium silicate matrix remains as a challenge for the aqueous carbonation scheme. Strong acids such as sulfuric and hydrochloric acid have been used to improve upon the rate limiting step of magnesium removal [3,4,6]. Although these accelerating mediums have been successful in extracting magnesium, a pH swing is required to facilitate the carbonation reaction [6]. This increase in pH requires the consumption of a base to compensate for the acid utilized in the extraction process.

Figure 1. Molecular structure of serpentine.

The Albany Research Center has conducted extensive research into aqueous mineral carbonation, favoring olivine over serpentine due to a greater reactivity [5]. Tests achieved nearly a 100% carbonation conversion at 185°C and 115 atm P_{CO_2} . However, the addition and possible consumption of sodium bicarbonate as a buffer was utilized to improve the carbonation efficiency and accelerate the reaction. Considering the potential scale for a CO_2 sequestration operation, the consumption of acids and/or bases quickly affects the feasibility of any proposed process.

Our investigations have demonstrated that serpentine has the intrinsic ability to provide a significant buffering capacity against the acidic conditions resulting from the dissolution of carbonic acid. Although challenges associated with the leaching and subsequent carbonation of magnesium from serpentine with carbonic acid are present, the economic advantage of avoiding additional reagents is promising.

EXPERIMENTAL

Serpentine from the Cedar Hills quarry in SE Pennsylvania and olivine from Twin Sisters, Washington were provided by the Department of Energy – Albany Research Center (ARC) for dissolution and carbonation studies. The serpentine consisted of a -4 mm parent sample that underwent grinding in a rotor mill for 30 seconds. The olivine sample was 80% passing -38 μm (-400 mesh) that underwent magnetic separation from a separation pilot-plant study.

Carbonation experiments were carried out in a 300 mL Parr – 4651 stirred reactor after being purged three times at 3 atm to remove any air from the reactor. The scanning electron microscopy (SEM) image was obtained on an FEI Quanta 600.

RESULTS AND DISCUSSION

Buffering Capacity of Serpentine. The pH of solu-

tion is a fundamental challenge to producing carbonates and the scale of potential industrial applications for mineral carbonation prohibits the consumption of a base. However, the use of serpentine as the magnesium precursor potentially circumvents the typically required base. Figure 1 shows the octahedral brucite, $\text{Mg}(\text{OH})_2$, layers and SiO_4 tetrahedra layers responsible for the buffering capacity of serpentine.

The dissolution of carbon dioxide proceeds according to Equations 1-4. The oxygen atoms in the brucite layers are able to be protonated, thereby buffering the solution, polarizing the Mg-O-Si bonds, and removing the magnesium ions from the serpentine matrix for their subsequent carbonation.

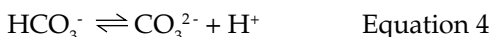
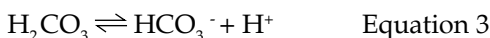
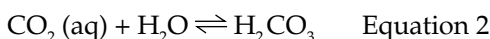
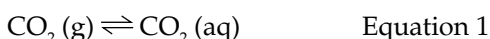
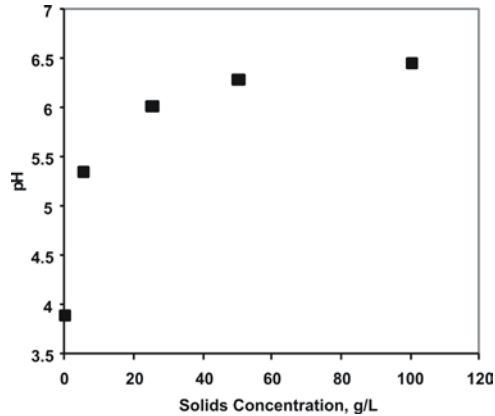


Table 1 shows the baseline experiment with a P_{CO_2} of 37 atm, resulting in an acidic aqueous solution with a pH of 3.70 due to the formation and dissociation of carbonic acid, whereas Experiments 1 and 2 demonstrate the buffering capacity of olivine and serpentine. Experiment 1 yielded a final pH of 6.58 versus Experiment 2 at 5.47. The corresponding bicarbonate ion concentrations for the serpentine and olivine solutions at a P_{CO_2} of 37.4 atm were 2.25M and .17M, respectively. Although olivine has been traditionally favored for greater reactivity, the increased buffering capacity for serpentine is advantageous.

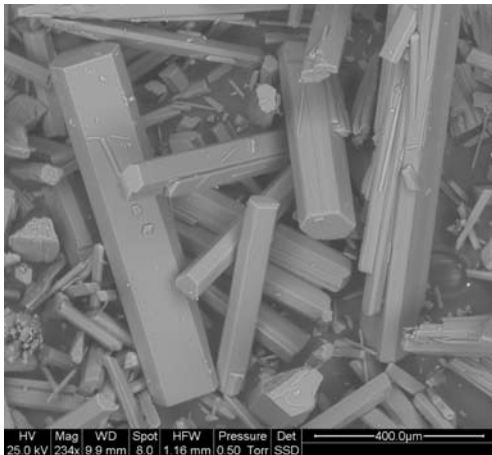
Table 1. pH Response to the Dissolution of Carbon Dioxide.

Experiment	Serpentine (M)	Olivine (M)	P_{CO_2} (atm)	pH
Baseline	--	--	37.4	3.70
1	0.5	--	37.4	6.58
2	--	0.5	37.4	5.47

An increase in the solids concentration of serpentine can further reduce the effect of P_{CO_2} on pH as more oxygen atoms in the brucite layers can be protonated. The buffering capacity of serpentine is immediately clear in Figure 2 with an increase in solids loading there is the corresponding increase in pH. Although the pH increase appears modest, it corresponds to a 20-fold increase in the concentration of carbonate ions.

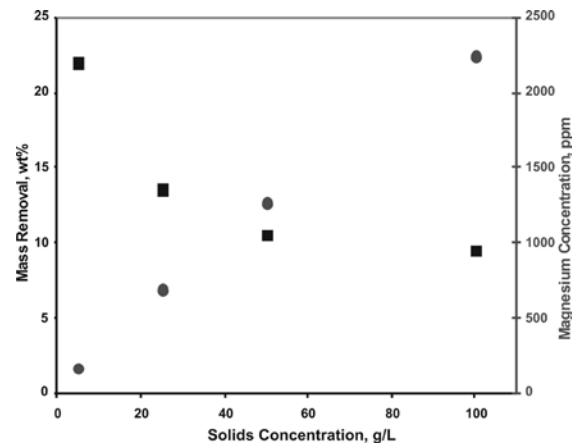
Figure 2. Effect of solids concentration on pH.

Additionally, nesquehonite, a hydrated magnesium carbonate ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), was observed to precipitate in the serpentine solution after remaining outside the reactor overnight under ambient conditions, whereas no precipitate could be observed for the olivine solution. So not only was serpentine capable of buffering against carbonic acid, a degree of magnesium was able to be leached out.

Figure 3. SEM image of nesquehonite.

Formation of Magnesium Carbonates. In addition to increasing the bicarbonate and carbonate ion concentrations to facilitate the carbonation reaction, the magnesium ion concentration should also be maximized. However, the graph in Figure 4 demonstrates the trade-off between $[\text{Mg}^{2+}]$ and mass removal with respect to solids concentration for $-38 \mu\text{m}$ serpentine particles, at 50°C , for 24 hours with a P_{CO_2} of 30 atm.

The theoretical minimum requirement of tons of serpentine to tons of carbon dioxide is already 2.1:1 and to not drive it further, as much magnesium as feasibly possibly needs to be extracted. A balance will need to be struck between maximizing magnesium extraction and providing a high enough magnesium ion concentration for the carbonation reaction.

Figure 4. Dissolution of serpentine versus solids concentration.

Mineral carbonation faces carbonation challenges in addition to the dissolution of serpentine. There are challenges specific to the magnesium ion even though there are many similarities with calcium including atomic similarities and identical crystal structures for each carbonate. However, carbonation differences between the two metals come about from different atomic radii. Magnesium being a smaller ion leads to a greater charge to ionic radius ratio which manifests itself in the hydration of the metal ion.

Through primarily electrostatic interactions, metal ions exist in aqueous solution as hydrated ions. The charge on the magnesium ion is balanced by 6 water molecules, whereas the coordination number for calcium rapidly fluctuates between 6 and 8 [9,10]. This fluctuation in coordination number greatly facilitates ligand interactions (Rode et al., 2005), which is a prerequisite for carbonation.

The Mg-O bond is just over 2.03 angstroms where for Ca-O it is 2.46, resulting in a stronger attraction which can be seen in the water exchange rate [11]. This water exchange is critical for interactions between magnesium and carbonate ions and calcium has a water exchange rate that is 6 orders of magnitude greater than magnesium ($\text{Ca}^{2+} = 4 \times 10^{11} \text{ s}^{-1}$ and $\text{Mg}^{2+} = 5 \times 10^5 \text{ s}^{-1}$) [9,10].

Not only does this lead to difficulties in carbonating magnesium, it also leads to metastable products. Calcium reacts with carbonate ions to form calcium carbonate, whereas magnesium has metastable products that are kinetically favored. Although CO_2 is still being sequestered in these metastable products, they are not as stable at ambient conditions and they also require 2.6 times the volume of magnesite.

CONCLUSIONS

- A single-stage reaction utilizing the inherent pro-

perties of serpentine results in conditions suitable for carbonation without the consumption of additional reagents. As serpentine is able to buffer against acidic conditions (which are required for the leaching of magnesium ions from serpentine) from the dissociation of carbonic acid, the dissolution of serpentine therefore appears to be the underlying strategy for the production of magnesium carbonates in a single-stage process.

- The advantages of serpentine over olivine are apparent as the pH for a typical serpentine-carbonation solution is 6.58 compared to 5.47 for a solution containing olivine. Additionally, an increase in solids concentration of serpentine can provide a 20-fold increase in the concentration of carbonate ions.
- The utilization of mineral carbonation will depend on the cost-effectiveness of this technology, which will be dependent on the trade-offs between solids concentration and the reaction temperature, time, pressure, and particle size.

ACKNOWLEDGEMENTS

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