REACTIVITY OF SERPENTINE IN CO_2-BEARING SOLUTIONS: APPLICATION TO CO_2 SEQUESTRATION

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Introduction

Fossil fuels produce CO_2, which is a significant greenhouse gas that contributes to global warming. Environmentally benign use of fossil fuels requires that CO_2 be captured and sequestered. The reactivity of CO_2 with minerals is important to several sequestration strategies. These include aboveground mineralization in which mined rock is reacted with CO_2 to form permanent carbonates and belowground geologic sequestration in which the amount of *in situ* mineralization is an important factor in repository performance. As part of a general investigation of mineral reactivity in the H_2O-CO_2 system, we have investigated the reactivity of serpentine [$Mg_3Si_2O_5(OH)_4$] with H_2O and CO_2 as a function of pH and the addition of potential catalyzing agents (weak acids). Serpentine is a prime candidate for aboveground mineralization but could also occur as a caprock for the injection of CO_2 belowground.

Experimental

Mineral reactivity studies were conducted in an externally heated, stirred batch reactor (1.8 L Parr autoclave) with a high-pressure CO_2 atmosphere applied using a gas-booster pump. All of the experiments described were conducted at 150 ºC and 2300 psi (15.9 MPa) for periods of 2 to 10 hours. The reactor included a sampling device for extracting fluids during the course of the experiment. Speciation and equilibrium calculations for the fluids were conducted using the Geochemist's Workbench software package with activity coefficients based on the Debey-Hückel equation. The software database was modified to include a more accurate representation of the solubility of CO_2 at elevated pressure.

Results and Discussion

Thermodynamic calculations indicate that in CO_2-rich fluids serpentine should react to produce magnesite ($MgCO_3$) and silica at moderate temperatures and pressures, including those used in our experiments. Many of our experiments were conducted in de-ionized water (DI) or systems containing 1 m NaCl or 1 m NaCl + 0.64 m $NaHCO_3$. None of these simple systems yielded detectable magnesite (0.1-0.2 wt%) over the course of the experiments, and x-ray diffraction analysis of the run products showed that the serpentine was unchanged.

However, experiments with strong acid (HCl) completely destroyed the serpentine and produced solutions rich in Mg^{2+} but from which no carbonate could be directly formed. Back-scattered electron imagery showed that the acid leached the Mg^{2+} from the serpentine, leaving behind a husk of amorphous silica. The leaching effect is highly desirable because it produces an insoluble residue of silica that could be easily separated with the magnesite, if the Mg^{2+} could be precipitated with CO_2.

In an attempt to preserve the aggressive effects of HCl but operate at more moderate pH, the reactivity of serpentine with a series of weak organic and inorganic acids was investigated (Table 1). Some of these acids re also known to be effective chelating agents. None of these experiments with weak acids produced magnesite, although many produced solutions very rich in total Mg. Because of a lack of thermodynamic data, it was not possible to calculate the equilibrium speciation for these solutions. We suspect that many of these solutions contained Mg-ligand complexes that could not be displaced by the carbonic acid generated by the dissolution of CO_2. In other cases, a precipitate formed that was less soluble than magnesite under our experimental conditions.

Table 1. Organic and Inorganic Acids Used to Enhance Serpentine Reactivity

Solution†	Dissolution Extent	Comment
Citric Acid	Large increase	Mg-citrate too strong
EDTA	Large increase	Mg-EDTA too strong
Oxalic acid	Large increase	Mg-oxalate insoluble
Phosphoric acid	Large increase	Mg-phosphate insoluble
Formic acid	Large increase	Solution too acidic
Ascorbic acid	Moderate increase	No carbonate
Maleic acid	Moderate increase	No carbonate
Tartaric acid	Moderate increase	No carbonate
Glycine	Moderate increase	No carbonate
Pthalic acid	Moderate increase	No carbonate
Malonic acid	Moderate increase	No carbonate
Aspartic acid	Moderate increase	No carbonate
Iminodiacetic acid	Small increase	No carbonate
Acetic acid	Small increase	No carbonate
Asparagine	Small increase	No carbonate
Salicylate	Small increase	No carbonate

†NaOH was used in many of the solutions to moderate the pH

Thermodynamic Analysis. Measured solution compositions were used to make equilibrium calculations for experiments in DI, NaCl-$NaHCO_3$, and Na-acetate (Figure 1). These three cases span a range of pH and ionic strength. The DI experiment produced the lowest calculated pH and highest activity of Mg^{2+}, and the NaCl-$NaHCO_3$ experiment produced the highest pH and lowest activity of Mg^{2+}. All of the experiments had solutions that were calculated to be at saturation or supersaturated with magnesite, although none yielded magnesite identifiable by x-ray diffraction.

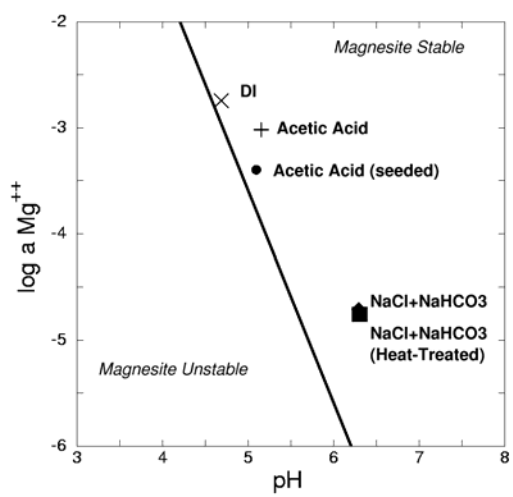

Figure 1. Thermodynamic calculations of solution activities based on measured solution compositions for batch reactor experiments at 150 ºC, 2300 psi total pressure $_{CO2}$ (approximated as with a fugacity of 12.5 Mpa). All of the experiments are saturated or supersaturated with magnesite.

These results suggested a nucleation barrier to the formation of magnesite. However, the Na-acetate experiment was repeated with the addition of 20 wt% magnesite seeds. The x-ray diffraction result

(19.8 wt% magnesite) was indistinguishable from no reaction. In addition, the solution composition was not significantly different than in the unseeded experiment (Figure 1).

The experiment with magnesite seeds indicates that nucleation of magnesite is not rate limiting. This is consistent with experiments on other Mg-oxide phases (see below) that generate magnesite.

Kinetics of Dissolution. The lack of observable precipitation could be explained if the rate of serpentine dissolution was sufficient to reach saturation but insufficient to produce a measurable quantity of magnesite. Carey et al.[1] obtained rates of dissolution for serpentine at far from equilibrium condtions (and in the absence of CO_2), including activation energies, that allow prediction of the evolution of Mg concentration in the batch reactor experiments (Figure 2). These calculations show that as much as 5-10 wt% magnesite could be produced based solely on the dissolution rate of serpentine. These calculations are conservative since the observed concentration of Mg is higher than the predicted concentrations. Consequently, a purely dissolution-limited process does not explain the lack of magnesite.

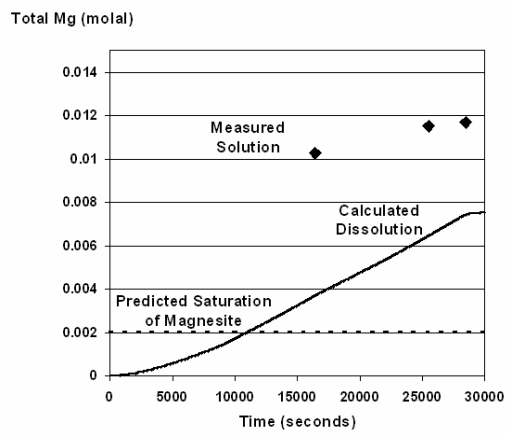

Figure 2. Measured solution compositions for batch reactor experiments at 150 ºC, 2300 psi total pressure CO_2 compared with the Mg concentration at saturation of magnesite and a calculated dissolution path based on the kinetic measurements of Carey et al[1].

Observations of the Reactivity of Other Mg-Oxides. The reactivity of serpentine can be compared with other Mg-bearing silicates and oxides. Periclase (MgO) and brucite [$Mg(OH)_2$] are readily carbonated; forsterite ($MgSiO_4$), with structurally isolated SiO_4 tetrahedra, carbonates to a significant degree; enstatite ($MgSiO_3$), with structural chains of SiO_4 tetrahedra, carbonates slowly; while serpentine, which consists of sheets of SiO_4 tetrahedra, is unreactive. These observations indicate that the greater the degree of silica polymerization, the less reactive is the Mg-silicate.

Methods of Inducing Reactivity in Serpentine. Three energy-intensive methods have been identified that allow carbonation of serpentine. Heat-treatment to 650 ºC dehydroxylates serpentine, disrupting the structure, and permits significant carbonation over a several hour period. Although the heat-treated serpentine can be carbonated, the resulting solution composition is indistinguishable from an experiment using raw serpentine (Figure 1). If the serpentine is heated to 840 ºC and the structure is allowed to recrystallize (to forsterite, enstatite and amorphous residue), then the degree of reactivity is reduced. Intense mechanical grinding, which renders serpentine nearly x-ray amorphous, also permits substantial carbonation[2]. These observations indicate that structural disruption of serpentine enhances reactivity.

A third method for inducing reactivity utilizes a strong acid (e.g., concentrated HCl) to leach the Mg^{2+} from the serpentine, followed by neutralization of the solution with a strong base (e.g., NaOH) to saturate the solution with magnesite. By analogy with thermal and mechanical treatments, it appears that a strong acid can effectively "disrupt" the structure (i.e., render the Mg^{2+} accessible).

None of these methods are likely to be a solution for CO_2 sequestration. They require too much energy or consume too much material. If the cost of sequestration becomes too high, alternative forms of energy become economically favorable.

Conclusions

The exact kinetic factors limiting the reactivity of serpentine remain obscure. Our observations indicate that rate of dissolution of serpentine cannot explain the limited reactivity. We have also shown that nucleation and growth of magnesite occurs in other Mg-oxides and in thermally or mechanically treated serpentine and so limitations due to magnesite cannot explain the lack of carbonation of serpentine.

Our data suggest two possible explanations. We note that Mg-oxides, Mg-silicates with a lower degree of silica polymerization, and thermally and mechanically treated serpentine yield magnesite. On dissolution in water, all of these compounds produce (or are likely to produce) more Mg^{2+} than serpentine does and, upon exposure to CO_2, will be more supersaturated with magnesite than serpentine. In other words, the driving force for the conversion of these materials to magnesite is greater than that for unaltered serpentine. Perhaps, this greater degree of supersaturation overcomes some kinetic barrier, such as the release of Mg^{2+} from the structure or the growth of the Mg-carbonate.

Our second suggestion is that serpentine reacts differently because of the greater degree of silica polymerization (or effectively the lower ratio of Mg to Si). In this model, only the near-surface Mg is accessible for dissolution and precipitation of magnesite. Further growth of magnesite relies on extracting Mg from greater depths in the serpentine crystal where it is effectively shielded by a silica-rich carapace on the serpentine crystal. As a consequence, only a miniscule amount (unmeasurable by x-ray diffraction) of magnesite is produced. Thermal and mechanical treatment of serpentine disrupts the crystal structure thus yielding defects in the silica-enriched carapace. These defects allow for diffusion of Mg^{2+} and the growth of magnesite. The effectiveness of acid may arise from the ability of H^+ ions to penetrate the silica carapace and reasct with the interior Mg-oxy-hydroxy octahedra. This reaction may induce intracrystalline swelling thereby disrupting the carapace. Weak acids promote dissolution (Table 1) but their effectiveness appears to be limited by the reduced concentration of H^+ and the formation of stable Mg-ligand complexes.

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