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Enhancing Process Kinetics for Mineral Carbon Sequestration

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Abstract

The current low-cost process for mineral carbonation involves the direct carbonation of a slurry of magnesium or calcium silicate mineral with supercritical CO_2. The process is currently limited by the slow reaction kinetics of the carbonation reactions, and in particular the slow dissolution rates of the silicates in weakly acidic conditions. Enhancing the dissolution rate in weakly acidic conditions has been identified as one of the main opportunities for lowering the costs of a direct mineral carbonation process. Serpentine has been identified by its reactivity and abundance as a potential mineral for use in a mineral carbonation process. In this paper we discuss the results of dissolution experiments in which ground serpentine was reacted in weakly acidic aqueous systems containing NH4Cl, NaCl,, sodium citrate, sodium EDTA, sodium oxalate, and sodium acetate. All experiments are carried out at 120ºC and under 20 bars of CO2 in a batch autoclave. It was found that the sodium salts of citrate, oxalate, and EDTA significantly enhance the dissolution of serpentine under weakly acidic conditions.

1. Introduction

Mineral carbon dioxide sequestration is a proposed greenhouse gas mitigation technology whereby CO2 is disposed of by reacting it with calcium or magnesium silicate minerals to form a solid magnesium or calcium carbonate product. The technology has its origins in the 1990's with the initial idea credited to Seifritz [1] and initial development by Lackner et. al at Los Alamos National Laboratory [2].

The technology offers virtually unlimited capacity to permanently store CO_2 in an environmentally benign form via a process that takes little effort to either verify or monitor. These characteristics are unique among greenhouse gas disposal technologies. Energy consumption for initial processes developed, however, is relatively high and it is not currently considered competitive when compared to other sequestration technologies.

Energy consumption associated with the grinding of reactant minerals to fine grain sizes make up 75% of the total energy costs of the process. This is also the main contributor to high cost estimates, a factor of 3-10 times higher than costs associated with the underground injection of CO_2 [3-5]. Increasing the reaction kinetics will allow

for the use of coarser-grained materials (or the achievement of higher carbonation yields at a given grain size), thereby mitigating the demand on grinding and decreasing the overall energy costs per amount of CO_2 sequestered.

2. Background and Motivation

For reasons of mineral availability, cation concentration, and reactivity, the focus of mineral carbonation research has been on rocks rich in the magnesium silicate minerals olivine and serpentine, or the calcium silicate wollastonite.

The reacting of these minerals in aqueous media has received the most attention from researchers. It has been theorized by many that the aqueous carbonation process follows two steps: (1) Dissolution of cations into solution followed by (2) nucleation and growth of carbonate precipitate [6-9]. Most of the evidence for the theory comes from SEM images showing the formation of magnesite and calcite crystals independent of the silicate minerals. At least one study has observed with imaging and EDS analysis that carbonate nanoparticles can form within the silicate mineral, but they do not make up a significant amount of the precipitated carbonate [6].

The dissolution of silicate minerals and the nucleation and growth of carbonate minerals are both pH dependent. On the dissolution side, the solubility of basic silicates such as serpentine and olivine increases as the acidity of the solution is increased. In addition, under currently developed aqueous processes, dissolution is proton-promoted and thus the kinetics of dissolution increases with increasing acidity of the system [10].

On the nucleation and growth side of the process, however, acidity decreases the concentration of carbonate ion in solution, rendering it impossible to precipitate carbonate minerals in an acidic system. Once magnesium and carbonate ion levels are such that a particular level of supersaturation is reached, however, precipitation kinetics do not appear to be limiting [11].

These constraints must be taken into account for the development of a viable process. If silicate dissolution is to take place in an acidic system, conditions must be altered before the formation of solid carbonates can take place. This has led to the research of various "two-stage" or "pH-swing" processes [12, 13].

If dissolution and precipitation are to take place simultaneously, conditions must be such that the system is both undersaturated with respect to the silicate mineral but supersaturated with respect to the carbonate phase. Researchers at NETL (formerly the Albany Research Center) have long been involved in the development of this type of "1-stage" process. They have found that adding sodium bicarbonate to their reacting system significantly enhances the overall carbonate yield as a result of the buffering activity that maintains conditions under which magnesium carbonate species may become supersaturated [3]. As the pH of this system is near neutral, the proton-promoted dissolution is necessarily slow and thus the dissolution of the mineral under these conditions is rate limiting.

As a result of the slow dissolution kinetics under these conditions, pulverization of the reactant mineral is required, consuming energy that constitutes upwards of 75% of the total energy used in the process. Holding all else constant, enhancing dissolution kinetics would allow for the use of coarser grained mineral reactants, which would lead to reduced energy consumption of the mineral grinding stage. A process that could utilize material ground to less than 75 mm, for example, could have a 90% lower energy costs for the grinding stage.

3. Experimental Work on Enhancing the Dissolution of Serpentine in Weakly Acidic Environments

Experimental work described in this study has focused on enhancing the dissolution of serpentine in weakly-acidic solutions. Specifically, serpentine has been reacted in solutions with dissolved salts at varying concentrations under a CO_2 atmosphere and at 120ºC. "Neutral" salts were chosen, such that the pH of the system is minimally affected by their presence.
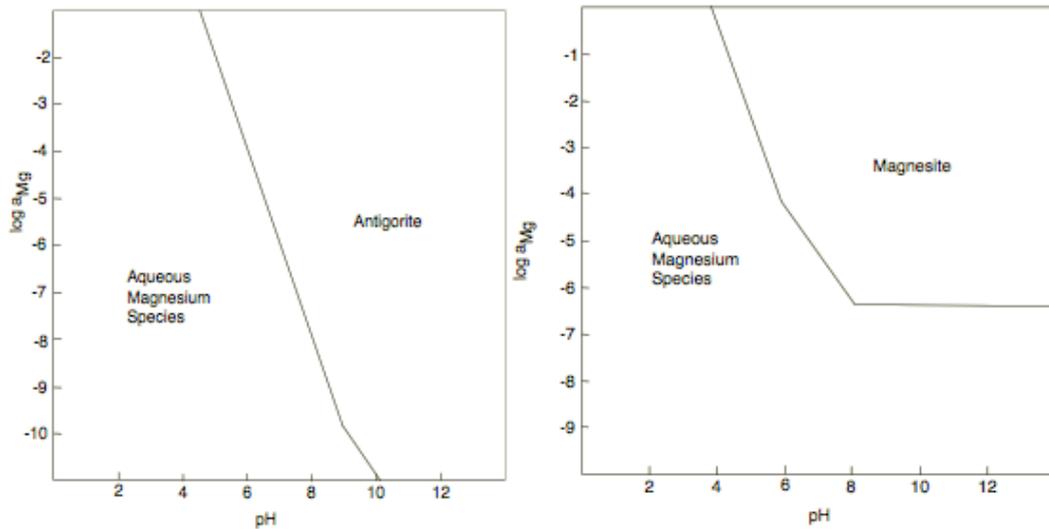
Figure 1. Solubility diagrams for antigorite serpentine (left) and magnesite (MgCO3, right) as a function of pH and magnesium ion activity in solution. Modelled using Geochemist Workbench software. Systems modelled at 120ºC under 20 atmospheres of CO2 fugacity. Solution of the antigorite system is in equilibrium with solid amorphous silica.

3.1. Materials and Methods

Starting material was raw antigorite serpentine from Belvidere Mountain in Vermont, ground to 90% below 75 microns in diameter but otherwise untreated. Analysis for major oxide content was performed by SGS Mineral Services using X-ray fluorescence and is given in Table 1.

About 3 grams of serpentine is reacted in 1 liter of fluid with dissolved NaCl, NH4Cl, sodium citrate, sodium oxalate, sodium EDTA, or sodium acetate in a Parr 4520 batch autoclave with temperature, pressure, and stirring control. Experiments have been performed under 20 bars of pressure, at 120ºC with a carbon dioxide atmosphere.

Salts are dissolved fully in solution, after which time the serpentine sample is added and the clock started. The reactor is closed and pressurized with CO_2 from a gas cylinder. Heating is also initiated, taking about 45 minutes to reach 120ºC. Experiments last from 6 to 24 hours and samples are drawn periodically during the experiment through a dip tube with a stainless steel .2 mm filter on the submerged end. The first sample is taken as the system reaches the steady-state temperature. Samples were weighed to maintain a mass balance on the solution. Each sample results in a solution loss of about 5 grams and no more than 10% of the solution is drawn throughout any given experiment.

Samples are analyzed for magnesium content using a Buck Instruments AA flame spectrophotometer.

Major Oxide	Weight Percentage
SiO2	37.9
Al2O3	1.02
CaO	0.53
MgO	39.1
Na2O	0.05
K2O	0.01

Fe2O3*	7.78

* All Fe as Fe2O3

3.2. Experimental Results

In experiments with no salts in solution, but 20 bars of CO_2 pressure, there is an initial rapid dissolution of about 6% of the material, followed by a reduced dissolution rate. In experiments with 1M NaCl, 1M NH_4Cl, or 0.5M sodium acetate, there is a rapid initial phase of dissolution followed by a dissolution rate too slow for detection with our experimental procedure. The extent of the initial rapid phase of dissolution is dependent on the salt being used, with NH_4Cl leading to more dissolution than NaCl, but it is not clear that the rate is affected. There is no detectable difference in dissolution rate after the initial rapid dissolution stage. These results mirror results obtained by Bales and Morgan [14], although in that study serpentine is dissolved for hundreds of hours so that a dissolution rate in the latter slow stage can be observed.

In experiments with 0.1M citrate, EDTA, or oxalate in solution, dissolution proceeds rapidly achieving greater than 60% dissolution within 2 hours and greater than 80% in 7 hours. Near 100% dissolution is achieved sometime between 10 and 20 hours. Dissolution rate in the citrate solution is unaffected by the presence of .5M NH_4Cl. There is no discernible difference in rate between solutions with these three organic salts.
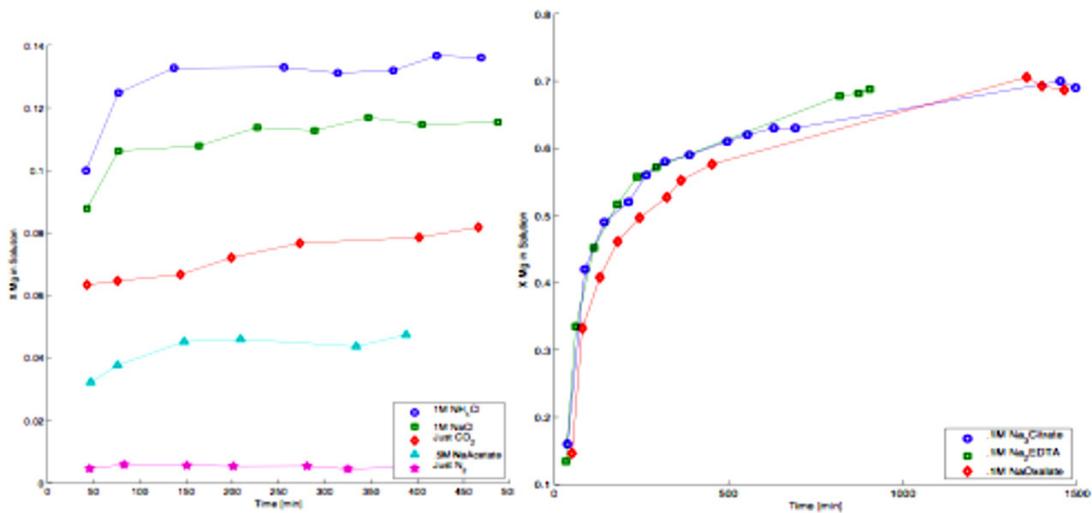

Figure 2. Dissolution experiment results. Fraction of magnesium leached from mineral into solution is shown as a function of time for dissolution experiments of antigorite serpentine in inorganic salts and sodium acetate (left), as well as sodium salts of citrate, EDTA, and oxalate (right).

4. Discussion

While it is clear from the dissolution experiments in inorganic and acetate salt solutions that the presence of these salts has an effect on the initial stage of dissolution, the cause of the effect is not clear. At the high concentrations of salts being used, the pH of the solutions is slightly affected, and may in turn be affecting the initial dissolution. It has also been postulated in mineral dissolution literature that the surface structure of ground minerals is altered relative

to the bulk particles, and may contain cations more easily dissolved than the interior 'unaltered' structure. In any case, because of low overall dissolution yields resulting from an inability to affect the latter slow stage of dissolution, dissolution of serpentine in these systems is of little interest for an industrial scale mineral carbon sequestration process.

Enhanced dissolution in citrate solutions has been previously observed for silicate minerals [10]. In addition, studies have been performed showing that the citrate ion enhances dissolution kinetics for silica by lowering the activation energy to dissolution [15, 16]. It is clear from this experimental work that the dissolution rate enhancement that the citrate, oxalate, and EDTA provide is comprehensive, leading eventually to 100% dissolution of the minerals. Furthermore, the sodium salts of citrate, oxalate, and EDTA, as with the inorganic salts, have a small impact on the overall pH of the system and thus should be compatible for use with the direct carbonation process. Indeed, the studies showing the catalytic effect of citrate on silica dissolution have found that the enhancement is most pronounced at neutral to weakly basic conditions, also optimal for the precipitation of carbonate minerals

Further work is being performed to derive the organic ion promoted dissolution rate laws as a function of ion concentration and pressure. In addition, work has begun on understanding the conditions under which carbonate mineral will precipitate from solutions containing these dissolved organic salts.

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