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Mineral carbonation process for CO₂ sequestration

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Abstract

The most promising route for mineral carbonation is the aqueous process using naturally occurring silicate minerals. The overall carbonation reaction consists of the dissolution of MgO- or CaO-bearing silicates such as olivine, serpentine, and wollastonite, followed by the precipitation of carbonates such as magnesite and calcite. In this paper, we report the experiments to investigate both the dissolution and the precipitation processes, separately. Olivine dissolution kinetics has been studied under several temperature and CO₂ pressure, and by varying the solution composition. The experiments were performed in a flow-through reactor at 90–120–150°C. The pH was adjusted using either acids (e.g., HCl, citric acid) or LiOH, and by changing the CO₂ pressure while the salinity was varied by adding NaCl and NaNO₃. To estimate the dissolution rate for each experiment, a population balance equation (PBE) model coupled with a mass balance was applied. The obtained values were regressed over a pH range from 2 to 8, using a linear model of the form $\log(r) = -n \text{pH} - B$, where r is the specific dissolution rate ($\text{mol cm}^{-2} \text{s}^{-1}$). The experiments to study the kinetics of magnesite precipitation were performed in batch using the H₂O-CO₂-Na₂CO₃-MgCl₂ system at 90, 120, and 150°C and at 100 bar of CO₂ pressure. The solution composition and solid phases were monitored with in-situ Raman spectroscopy. At the conditions applied, we observed two mechanisms: direct precipitation of magnesite and simultaneous precipitation of magnesite and hydromagnesite followed by the transformation of the latter into the former.

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"Keywords: mineral carbonation, olivine dissolution, magnesium carbonate precipitation."

1. Introduction

Evidence of man-made climate change has been accumulating over the past decades. Rising carbon dioxide concentrations due to anthropogenic emissions are scientifically proven to be the main cause for it. One way to reduce carbon dioxide emissions is to capture CO₂ from large point sources like power plants and to store it permanently, either underground or as mineral carbonates [1].

Mineral carbonation is the reaction of gaseous CO₂ with e.g. naturally occurring magnesium and calcium silicates such as olivine, serpentine, and wollastonite. The reaction products are carbonates and silica, naturally occurring,

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environmentally benign, stable solid materials. Olivine and serpentine deposits can be found worldwide and are large enough to fix the CO₂ that could be produced from the combustion of all fossil fuels resources.

Fig. 1 shows a sketch of the mineral carbonation process.

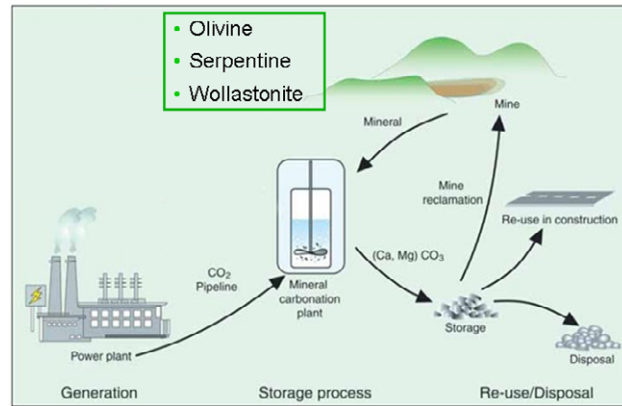


Figure 1. Sketch of a mineral carbonation scheme. Figure modified from ref. [1]

2. Material and method

The dissolution experiments with natural San Carlos gem-quality olivine crystals ($\text{Mg}_{1.82}\text{Fe}_{0.18}\text{SiO}_4$) were performed in a 300 ml high pressure flow-through titanium reactor at 90-120-150°C within a pH range from 2 to 8.5 [2]. A stirring rate of 700 rpm was applied in all experiments. The feed consisted of distilled water, using either acids, such as HCl and citric acid, or LiOH to set the pH. It was fed to the reactor at a constant rate of 10 ml min⁻¹. The runs were performed having a liquid volume of 160-180 ml under a 20 bar N₂-atmosphere. The olivine size fraction was 90-180 μm. We also investigated the effect of CO₂ and salts on the dissolution kinetics. In this case, the experiments were carried out at 120°C and within a pH range from 3 to 8. pH and solution compositions were varied by changing the CO₂ partial pressure (between 1 and 180 bar) and by adding LiOH, NaCl, and NaNO₃. Pressure was maintained by feeding either N₂ or CO₂ from a buffer tank via front pressure regulator.

The magnesium concentration in the outlet solution was measured on-line by means of an ion chromatograph (CS12A column, Dionex). The silica concentration was measured spectrophotometrically using the Molybdate Blue method.

Precipitation of magnesium carbonate from the H₂O-CO₂-Na₂CO₃-MgCl₂ system was investigated in a high pressure titanium reactor at 120°C and partial pressure of CO₂ of 100 bar. The reactor was first filled with an aqueous solution of Na₂CO₃, sealed and heated to the desired temperature, then pressurized with CO₂ and kept at constant pressure. All the experiments were continuously monitored by means of in-situ Raman spectroscopy. Upon equilibration of the reactor solution with the CO₂ atmosphere, indicated by the stabilization of the Raman signal, supersaturation with respect to Mg-carbonate was achieved by adding a solution of MgCl₂. The addition of MgCl₂ marked the start of the induction period. The onset of precipitation, i.e. the end of the induction period, was defined as the time of the first detection of solid particles in the Raman signal. At the end of a precipitation experiment, the solid reaction products were filtered, washed with deionised water and dried in an oven at 60°C for about 12 hrs, then characterized using SEM/EDX (Bruker axs, model D8 Advance) and X-ray diffraction (Zeiss, model LEO 1530).

The simulation package EQ3/6 v8.0 [3] was used to estimate the pH during both dissolution and precipitation experiments and the supersaturation ratios at the experimental conditions. The EQ3/6 database employs an extended

Debye-Hückel equation to calculate aqueous activity coefficients. The CO₂ fugacity was calculated using the Redlich-Kwong equation of state, solved by the non-iterative model developed by Spycher *et al.* [4].

3. Silicate carbonation

Mineral carbonation is best carried out in an aqueous solution. While the overall reaction is exothermic and thus a naturally occurring process (silicate weathering), its kinetics is very slow. Rate-limiting is the silicate dissolution. Three examples of the overall carbonation reaction for common natural silicates are given herein:



4. Mathematical model for olivine dissolution

A 1-D population balance equation (PBE) model was formulated to model the dissolution of olivine particles [5]:

$$\frac{\partial n}{\partial t} - D \frac{\partial n}{\partial L} = 0, \quad (1)$$

where n is the particle size distribution (PSD), i.e. the unscaled number distribution density of a population of olivine particles. In eq. 1, neither the occurrence of particle breakage nor agglomeration is considered. Moreover, a size-independent dissolution rate, D (m s⁻¹), is assumed and defined below. L is the characteristic length of a given particle (m). The PBE was coupled with the mass balance of olivine in solution for a flow-through reactor model:

$$V \frac{dc}{dt} = 3k_v \rho D \mu_2 - Qc, \quad (2)$$

where c represents the concentration of olivine equivalent (mol l⁻¹), V is the liquid volume in the reactor (l), k_v is the particle volume shape factor (-), ρ is the olivine molar density (mol m⁻³), μ_2 is the second moment of the PSD (m²), and Q the outlet flow rate (l s⁻¹).

The initial conditions are given by

$$n(0, L) = n_0(L), \quad (3)$$

$$c(0) = c_0, \quad (4)$$

where $n_0(L)$ is the initial PSD (-), and c_0 is the olivine equivalent present in the first sample (mol l⁻¹).

The dissolution rate, D , is defined as the rate of change of the characteristic length, L :

$$\frac{dL}{dt} = -D \propto -r. \quad (5)$$

D is proportional to the specific dissolution rate, r (mol cm⁻² s⁻¹), which is commonly used in geochemical literature. The rate law applied here is of the form:

$$r = a_{\text{H}^+}^n A e^{\left(\frac{E_a}{RT}\right)}, \quad (6)$$

where $a_{\text{H}^+}^n$ is the activity of protons (mol l⁻¹), A the pre-exponential factor, E_a represents the activation energy estimated for the olivine dissolution reaction equal to 52.9 ± 6.9 kJ mol⁻¹ [2], R is the gas constant (kJ mol⁻¹ K⁻¹), and T the temperature (K).

5. Results

5.1. Olivine dissolution kinetics

To estimate the specific dissolution rate values, r , the model described above was fitted to the measured concentration patterns. The logarithms of the r values were regressed over pH as shown together with the experimental data in Fig. 2. In the presence of CO₂ and salts, the $\log(r)$ values showed no significant differences to experiments performed under a N₂ atmosphere without additional salts. This indicates that CO₂, NaCl, and NaNO₃ do not affect the olivine dissolution mechanism and kinetics.

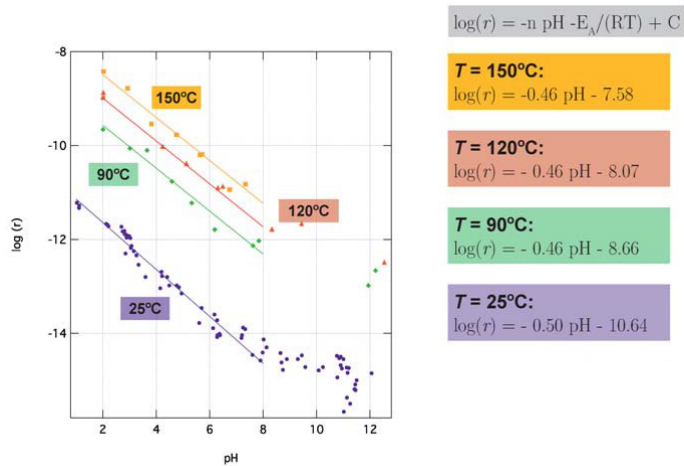


Figure 2. Logarithm of the specific dissolution rate r as a function of pH and at different temperatures. Results and regression for 25°C was taken from literature data for comparison [6].

5.2. Magnesite precipitation

In Fig. 3, the precipitation experiments are reported on the composition diagram $[\text{Mg}^{2+}]$ vs. $[\text{Na}^+]$ [7]. Throughout experiment B, no precipitation was observed, while during experiments A, C, and G, direct precipitation of magnesite occurred. The Raman spectra collected during experiment A is reported in Fig. 4. Initially, the HCO_3^- Raman signal was intense, but as soon as MgCl_2 was dosed, the peak decreased and a magnesite peak appeared. The experiments D, E, F, and H were characterized by the simultaneous precipitation of magnesite and hydromagnesite, followed by the transformation of the latter into the former. For illustration, Fig. 5 shows the Raman spectra recorded during experiment D.

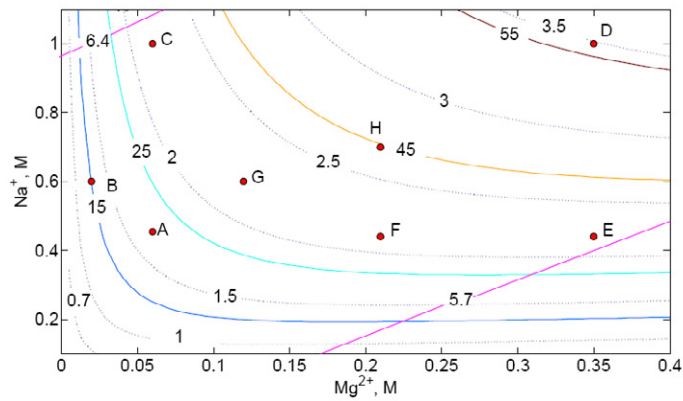


Figure 3. Composition diagram $[\text{Na}^+]$ vs. $[\text{Mg}^{2+}]$ for the precipitation experiments. Dotted contour lines indicate the supersaturation ratio with respect to hydromagnesite; continuous contour lines indicate the supersaturation ratio with respect to magnesite; the two continuous lines with a positive slope indicate the pH values; the big dots symbolize the solution composition used during the experiments.

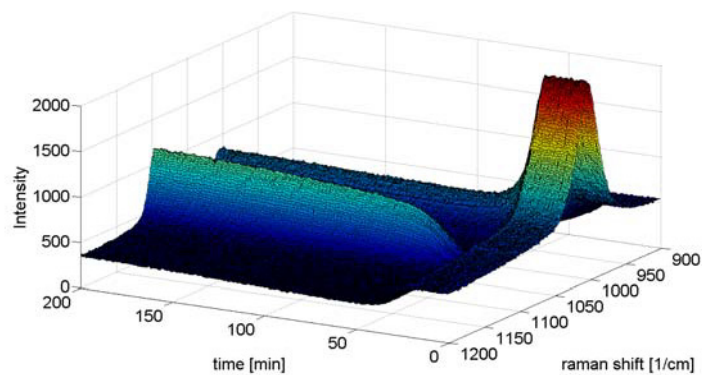


Figure 4. Raman spectra recorded during experiment A.

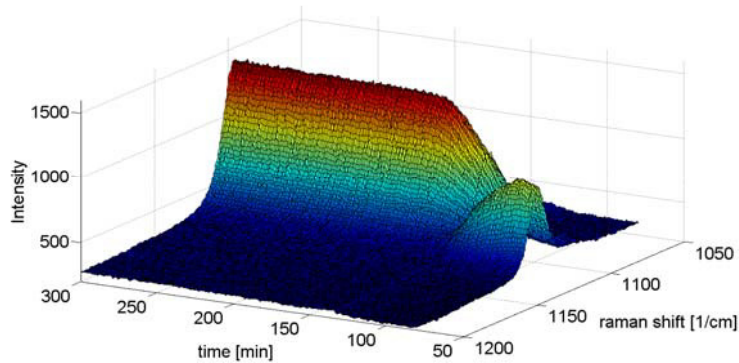


Figure 5. Raman spectra recorded during experiment D.

6. CONCLUSION

The dissolution rate of olivine and the precipitation mechanism of magnesium carbonate were studied at operating conditions relevant for the aqueous mineral carbonation process.

The effect of temperature, pH, P_{CO_2} , and salinity on the dissolution kinetics was investigated using a flow-through reactor. All experiments were modeled using a population balance equation model coupled with a mass balance equation. The logarithm of the estimated specific dissolution rate values were linearly regressed over a pH range from 2 to 8. We found that the thus obtained rate law can be applied to a broad variety of operating conditions, as well as in the presence of salts and CO_2 . Its slope was always around 0.5, indicating no differences in the dissolution mechanism for all conditions applied.

The effect of supersaturation and solution composition on the precipitation mechanism of magnesium carbonates was investigated. The kinetics was found to be controlled by the supersaturation with respect to magnesite, S_M while the Mg^{2+} -concentration controls the two precipitation mechanisms. Direct precipitation of magnesite at low $[Mg^{2+}]$, and simultaneous precipitation of magnesite and hydromagnesite, at higher $[Mg^{2+}]$, with the latter transforming into the former over time.

7. References

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8. Acknowledgments

Financial support from the *Fondation Claude and Giuliana*, Basel, Switzerland, is gratefully acknowledged.