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Analysis of the effect of temperature, pH, CO₂ pressure and salinity on the olivine dissolution kinetics

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Abstract

The dissolution kinetics of olivine has been extensively studied under several temperatures, CO₂ pressures, and solution compositions. Dissolution is an important mechanism in the aqueous mineral carbonation process. The overall carbonation reaction consists of dissolution of mineral silicate, e.g. olivine, serpentine and wollastonite, followed by carbonate precipitation, thus fixing CO₂ into naturally occurring stable solids, such as magnesite and calcite. The slowness of the dissolution kinetics hinders the overall carbonation reaction and in order to make the process technically and economically feasible, such a reaction should be sped up by finding the optimum operating conditions. Experiments were performed in a flow-through reactor at 90–120–150°C. The pH was adjusted by adding either acids (e.g., HCl, citric acid) or LiOH, and by changing P_{CO₂}. The salinity was changed by adding NaCl and NaNO₃. From the experimental data, the dissolution rate was estimated by using the population balance equation (PBE) model coupled with a mass balance, and the obtained values were regressed with a linear model $\log(r) = -n \text{ pH} - B$, where r is the specific dissolution rate (mol s⁻¹ cm⁻²).

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1. Introduction

Evidence of global warming has been accumulating over the past decades and global warming is now recognized as a fact by the scientific community. Rising carbon dioxide concentrations due to anthropogenic emissions are believed to be the main cause for it. One way to reduce carbon dioxide emissions is to capture CO₂ emitted from point sources like power plants and to store it indefinitely, either underground or in the ocean or as mineral [1].

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

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

Figure 1 shows a sketch of a mineral carbonation process.

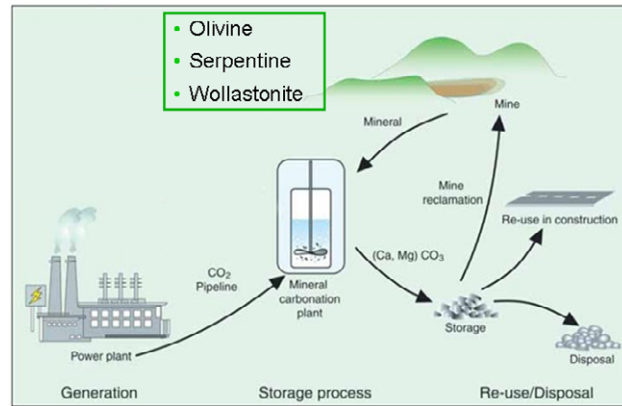


Figure 1. Sketch of a mineral carbonation process. Figure modified from ref. [1]

2. Material and method

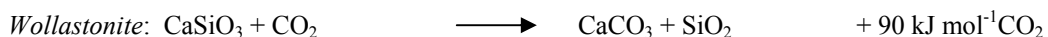
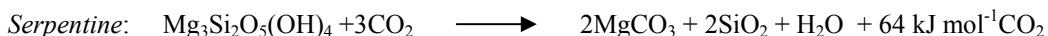
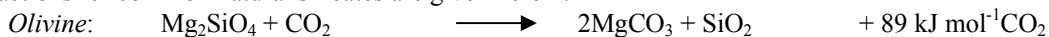
The dissolution experiments with natural San Carlos gem-quality olivine crystals ($Mg_{1.82}Fe_{0.18}SiO_4$) were performed at 90-120-150°C and in the pH range 02-8.5 in a 300 ml high pressure flow-through titanium reactor [2]. A stirring rate of 700 rpm was used in all experiments. The feed consisted of distilled water, with the pH set by adding either acids, such as HCl and citric acid, or LiOH. It was fed to the reactor at a constant rate of 10 ml min⁻¹, and the runs were performed using a liquid volume of 160-180 ml under a 20 bar N₂-atmosphere. The crystal size fraction was 90-180 μm. We also investigated the effect of CO₂ and salts, and in this case the experiments were carried out at 120°C, with pH values between 3 and 8 and solution compositions varied by changing CO₂ partial pressure, between 1 and 180 bar, and by adding LiOH, NaCl, and NaNO₃.

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

The simulation package EQ3/6 v8.0 [3], with a database employing an extended Debye-Hückel equation for the aqueous activity coefficients, was used to estimate the pH. The CO₂ fugacity, needed as an input parameter for EQ3/6, was calculated using the Redlich-Kwong equation of state solved by the non-iterative model developed by Spycher *et al.* [4].

3. Silicate carbonation

The carbonation reaction is best carried out in an aqueous solution. It is thermodynamically favored and exothermic with the rate-limiting step being the silicate dissolution. Three examples of the overall carbonation reactions for common natural silicates are given herein:



4. Mathematical model

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 unscaled number distribution density of the individual constant-shape particles of olivine assuming neither breakage nor agglomeration and a size-independent dissolution rate, D , (m s^{-1}) defined below. L is the characteristic length of a given particle (m). This equation 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 is the concentration of olivine (mol l^{-1}), V is the liquid volume in the reactor (l), k_v is the volume shape factor, (-), ρ is the olivine mole density (mol m^{-3}), μ_2 is the second moment of the distribution (m^2), Q is the outlet flowrate (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 particle size distribution of olivine particles (-), 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 , of a given particle:

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

where r is the specific dissolution rate ($\text{mol cm}^{-2} \text{s}^{-1}$) given by:

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

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

5. Results

The specific dissolution rate values, r , were estimated from the experimental data by fitting the concentration patterns with the model described above. The logarithm of the r values were regressed over pH, and the estimated regressed functions are given in Figure 2 together with the experimental data. In the case of the investigations in presence of CO_2 and salts, $\log(r)$ values showed a similar behavior to the ones without CO_2 , indicating that CO_2 , NaCl , and NaNO_3 did not significantly affect olivine dissolution kinetics.

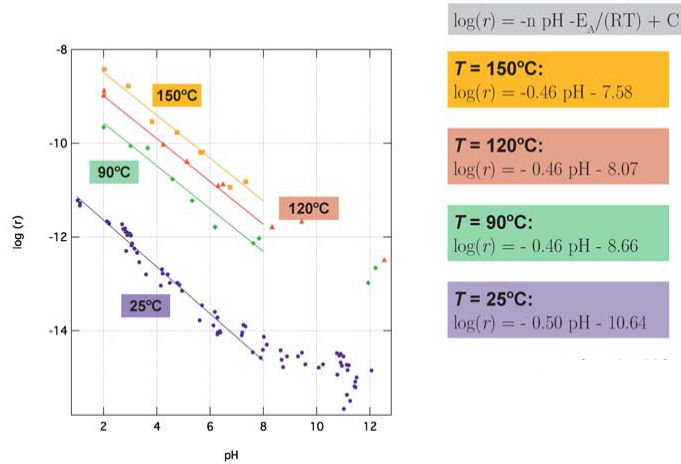


Figure 2. Logarithm of the specific dissolution rate r as a function of pH and at different temperatures. In violet literature data by Prokovsky and Schott [6] for comparison.

6. CONCLUSION

Dissolution rate of olivine was studied at the operating conditions relevant for mineral carbonation process. In particular, the effect on the dissolution kinetics of temperature, pH, P_{CO_2} , and salinity was investigated.

The experiments were modelled by using a population balance equation model coupled with a mass balance equation. The logarithm of the estimated specific dissolution rate values were regressed linearly over pH. We observed that this model can be applied to a wide variety of operating conditions and in presence of salts and CO_2 and that its slope was always around 0.5 indicating that always the same mechanism occurs.

7. References

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8. Acknowledgments

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