Dissolution kinetics of minerals for advanced mineral carbonation

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1. Introduction

- Mineral carbonation is a novel technology which permanently and safely store anthropogenic generated CO_2 in solid Mg- and Ca- carbonates to counter global warming.
- Mineral carbonation involves the dissolution of Mg- and Ca-rich silicates in aqueous solutions, followed by the precipitation of carbonates.
- The release of magnesium and calcium during silicate mineral dissolution is one of the main rate-limiting steps of mineral carbonation.
- However, the kinetics of all the relevant mineral equilibria are essentially unknown under high CO_2 pressure and high temperature condition.

2. Research Background

The two main minerals for mineral carbonation are olivine and serpentine. Olivine has been studied by many researchers duo to its structural simplicity and high reactivity. More recently, serpentine has attracted noticeable interest, due to its widespread distribution and huge availability in nature.

Limitations of research are:

- The optimal reaction temperatures for the mineral carbonation have been found to be between 150°C and 200°C and pressure up to 200 bar. However, almost all kinetics studies have been conducted at temperature between 25°C and 65°C and at ambient pressure.
- The effect of the presence of CO_2 is absent in the majority studies since no suitable reactor system has been designed.

3. Aim and objectives

The aim of this project is to provide kinetics data for mineral carbonation of serpentine at elevated temperature and under high CO_2 pressure and to study effects of catalysts such as acid, base and buffer solution to dissolution.

The objectives of this work are:

- To set up a high temperature and high pressure flow-through reactor with on-line IC analysis system.
- To assess the dissolution rate of serpentine under high temperature and high CO_2 pressure condition.
- To assess the effect of catalyst such as acid, base, buffer solution to dissolution under high temperature and high CO_2 pressure condition.
- Understand the effect of reaction variables on mineral carbonation, such as temperature, pH, the composition of aqueous solution.

4. Methodology

There are two kinds of dissolution rate studies.

- Temperature-dependence rate: determined by integral method using a batch reactor;
- pH-dependence rate: determined by flow-through reactor.

The experiments of temperature-dependence rate have been conducted. After the installation of flow-through reactor, the pH-dependence rate will be studied.

5. Experiment method

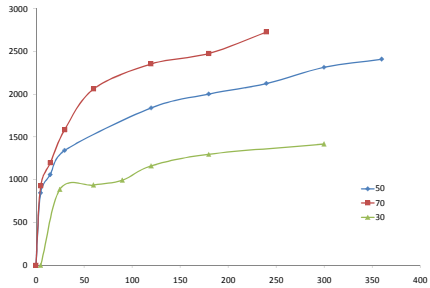
- An open spherical batch reactor heated by a temperature-controlled silicon bath with a magnetic stirrer is used.
- 200 ml of the desired solution (2 M) was added to the reaction vessel. With the temperature set to 30°C, 50°C, and 70°C, 4 g of serpentines was added.
- Solvent Samples were extracted with a syringe from reactor at 5 min, 15 min, 30 min, 1 h, 1.5 h, 2 h, 3 h, 4 h, 5h.
- The Mg, Fe and Si concentrations of the samples were measured using ICP-AES.

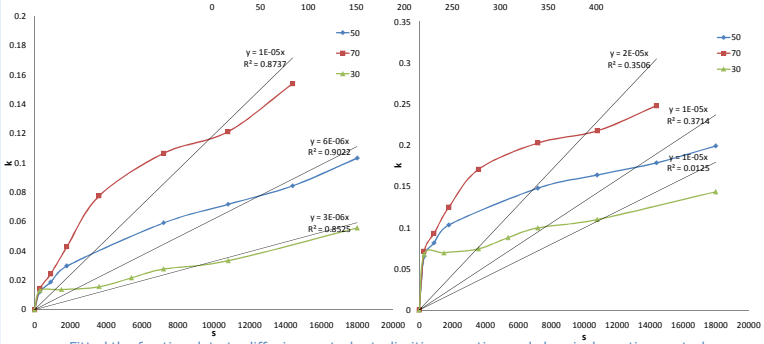
6. Results

- Using the equation below to transfer concentration to fraction:

$$X_{i,j} = \frac{c_{i,j} \bullet V'_i}{m'_{i,j}} = \frac{c_{i,j}[V_{initial} - V_{sample}(j-1)]}{m_{batch}\frac{m_i}{m} - V_{sample}\sum_{2}^{j-1} c_{i,j}}$$

- Left figure indicate ICP-AES results of the magnesium concentration in solvent at different time at 30 °C, 50°C and 70 °C.
- The high temperature condition gives high performance on dissolution.

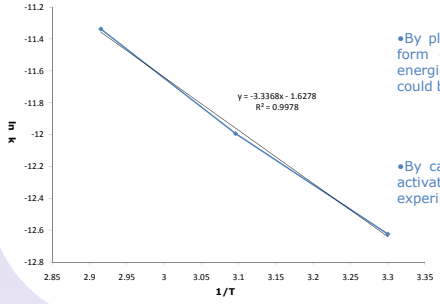




- Fitted the fraction data to diffusion control rate-limiting equation and chemical reaction control rate-limiting equation :

Product diffusion control	$kt = 1-3(1-X_B)^{2/3}+2(1-X_B)$
Chemical reaction control	$kt = 1-(1-X_B)^{1/3}$

- According to the multiple regression correlation coefficients (R^2) got from above figures, the product layer diffusion control shows much better linear relationship than chemical reaction control.



- By plotting the ln k (apparent rate constants) form each experiment to 1/T, the activation energies (E) and the frequency factors (k_0) could be determined by Arrhenius' law:

$$k = k_0 e^{-E/RT}$$

- By calculating the result form left figure, the activation energy of serpentine used in these experiments is 27.74kJ.

7. Conclusions and Future work

- The temperature-dependent dissolution rate will increase with the increasing temperature.
- The transport control is the main rate-limiting step in the process of serpentine dissolution.
- A high temperature and high pressure flow-through reactor with on-line IC analysis system is proposed in order to study the pH-dependence dissolution rate.