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Dissolution of activated serpentine for direct flue-gas mineralization

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Abstract

The dissolution of thermally activated serpentine (75% dehydroxylated) by direct flue-gas mineralization was investigated at far-from-equilibrium (w.r.t mineral dissolution) flow-through operating conditions. Experiments were performed at moderate partial pressures of CO₂ (0.1 bar – 2 bar CO₂) and temperatures (30 °C – 90 °C). Thermal activation enabled the dissolution of serpentine at mildly acidic conditions. Both magnesium and silica were released upon dissolution. However, the silica conversion was under-stoichiometric with respect to magnesium. Fast initial dissolution rates were observed with magnesium conversions reaching 60% in 30min. Experiments were also performed in the absence of CO₂ with identical pH conditions generated with mineral acid (HCl). The dissolution profiles were similar to those obtained under flue-gas atmosphere.

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1. Introduction

A fully operational CCS scheme has to ensure a safe and permanent storage of the captured CO₂. Mineral carbonation enables this by storing CO₂ in a chemically stable carbonate form. Magnesium and calcium silicate rocks found in nature are the main source for Mg and Ca, the metal cations needed for the mineralization process. In aqueous mineral carbonation process, Mg/Ca ions are leached from the silicate rocks and then precipitated as carbonates. The rate limiting step for the mineralization process is the dissolution of the silicate rocks [1, 2]. The relatively simple silicate structure and dissolution mechanism

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of forsterite, the magnesium rich member of olivine group, has resulted in extensive study of its dissolution under various conditions [1-4].

The great abundance of the serpentine group makes it a more attractive feedstock for mineral carbonation than olivine. However, it suffers from slow dissolution kinetics. Thermal activation has shown to accelerate the dissolution kinetics for serpentine [5, 6]. Heat activation is an energy intensive process and adds substantially to the costs. The use of direct flue-gas mineralization in aqueous medium avoids the costs associated with the capture of CO₂ [7]. In such a process, CO₂ is dissolved into an aqueous solution (water and potentially salts), and the resulting carbonic acid and salt species enable the leaching of the Mg ions from the silicate rock. The objective of the present study was to investigate the dissolution kinetics of thermally activated serpentine under flue gas atmosphere.

2. Materials and Methods

Thermally activated serpentine was obtained from Shell Global Solutions International, Amsterdam, the Netherlands. The sample was received as a powder (sub 125 μm), thermally activated according to the provider's standard operating procedure. The thermal activation involved partial dehydroxylation (75% dehydroxylation) of crushed and ground natural crystalline serpentine (mainly lizardite). The density of the activated material was determined by helium pycnometry (Micrometrics, AccuPyc 1330) to be $2629 \pm 2 \text{ kg m}^{-3}$. The powder was dry-sieved into three fractions using 20 μm and 63 μm lab sieves. The size fraction between 20 μm and 63 μm (hereinafter called 20-63 μm fraction) was repeatedly washed with ethanol to remove fines, and then dried overnight in an oven at 60 °C. Light microscope and scanning electron microscope (SEM) images (Fig. 1) were taken to ensure proper sieving and complete removal of fines. The particle size distribution of the 20-63 μm fraction was determined in a 0.15 M NaCl solution using a Coulter counter (Beckman, Coulter Multisizer 3). Distribution data were averaged over nine measurements. The specific surface area of this fraction was $11.24 \pm 0.0165 \text{ m}^2 \text{ g}^{-1}$ as determined by N₂ adsorption multi-point B.E.T method (TriStar 3000). The average composition of the fraction was measured by inductively coupled plasma optical emission spectrometry (ICP-OES Agilent 710-ES) and found to be $(\text{Mg}_{2.56}\text{Fe}_{0.44})\text{Si}_2\text{O}_{6.5}(\text{OH})$.

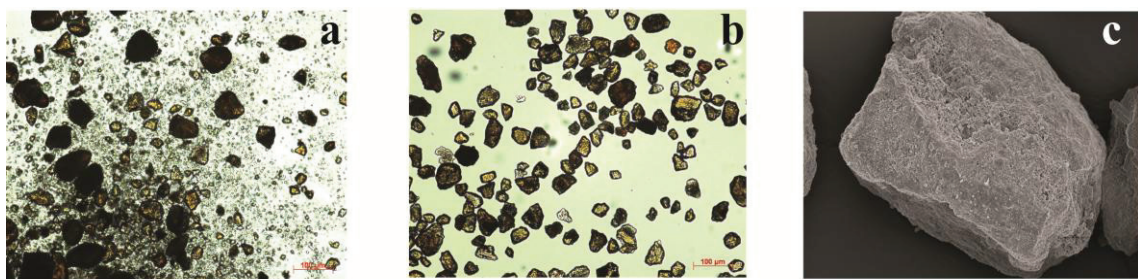


Fig. 1. Thermal activated serpentine. a) sub 125μm particles b) 20-63 μm size fraction after dry sieving and repeated washing with ethanol to remove fines. c) SEM image of a 20-63 μm size fraction particle.

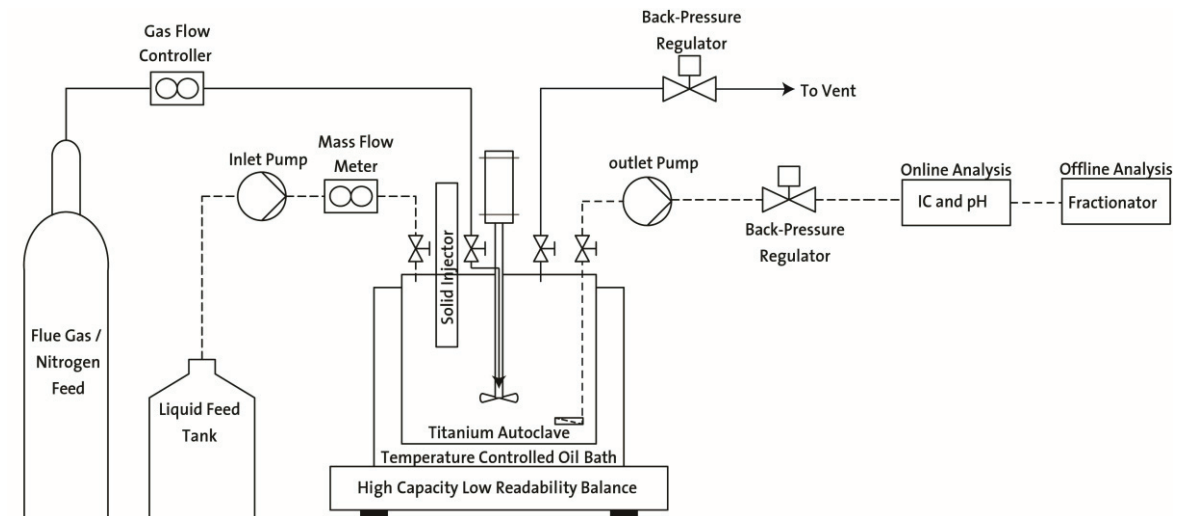


Fig. 2.: Simplified scheme of the experimental setup

A stand-alone process setup with good control and monitoring of the process conditions was built. The experimental setup is as described in [8]. The probe for in-situ Raman spectroscopy measurements was replaced by a gas-tight, tailor-made solid particle injection system. A simplified schematic diagram of this setup is shown in Fig. 2. Gas mixtures of CO_2 and N_2 were used to represent the flue gas atmosphere for the experiments. In order to exclude the effects of any impurities in the system, Milli-Q™ water purged with N_2 gas in the feed tank was used as the liquid feed.

Dissolution studies were performed with 2.5% and 10% CO_2 in N_2 gas atmosphere to attain different partial pressures of CO_2 ($p_{\text{CO}_2} = 0.1 \text{ bar} - 2 \text{ bar}$), and at different temperatures ($T = 30 - 90 \text{ }^\circ\text{C}$) in a 300 ml titanium autoclave stirred at 700 rpm. The residence time for the liquid and the synthetic flue gas were set at 34 and 10 min respectively, and only 5 mg of activated serpentine was dissolved in each experiment. These operation settings were chosen in order to study the far-from-equilibrium dissolution kinetics of activated serpentine. Prior to start of a dissolution experiment, the reactor was brought to equilibrium by having controlled liquid and gas flows. The temperature and pH of the reactor solution was monitored continuously, and steady state was reached in less than an hour. Serpentine particles of the chosen size fraction were then carefully weighed, encapsulated in a small ice beaker (0.7 mL volume) and injected into this equilibrated, pressurized autoclave via the solid particle injection system. This enabled the monitoring and measurement of initial, far-from-equilibrium dissolution kinetics of the activated serpentine. The instantaneous pH, magnesium and silica concentrations in the reactor were measured over the entire duration of the experiment. Instantaneous magnesium concentrations were measured with an ion-chromatography system with a sampling period of 10 min. Total silica concentrations were determined from fractionated samples using molybdate blue method. Experiments were also performed with mineral acid (HCl) in nitrogen atmosphere in order to compare the dissolution kinetics and reaction rate parameters with those observed under flue gas atmosphere.

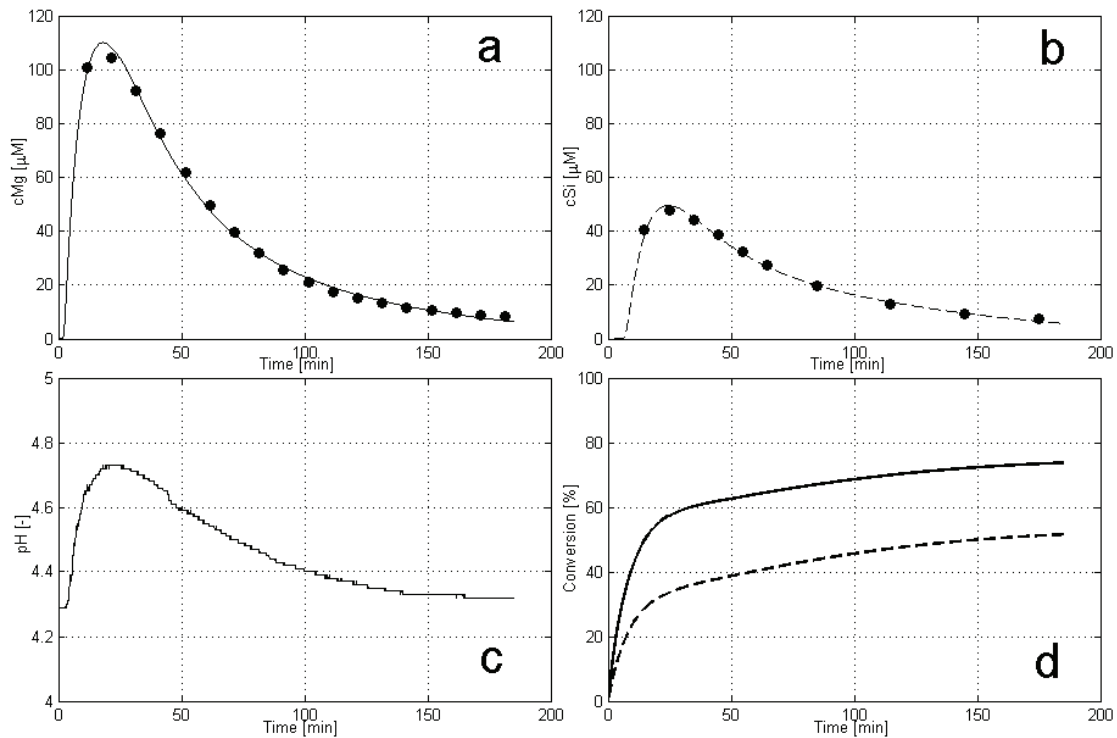


Fig. 3.: Dissolution profile for activated serpentine in flue gas atmosphere. $p_{CO_2} = 2.0$ bar, $P = 20.0$ bar, $T = 90$ °C, $m_f = 5.0$ mg. (a) downstream magnesium concentration profile (b) downstream silica concentration profile (c) downstream pH profile (d) upstream conversion profiles for (continuous line) magnesium and (broken line) silica.

3. Results and Discussion

Dissolution of thermally activated serpentine was studied at different p_{CO_2} levels and temperatures. The measured downstream concentration profiles of magnesium and free silica, and the pH for an experiment under flue-gas atmosphere is shown in Fig. 3. In the magnesium and silica concentration profile plots (Fig. 3a, b), the circular markers (●) indicate the experimental downstream concentration measurements. The lines in these plots have been produced by joining the experimental data points and accounting for a delay in concentration profile evolution due to the dead-volume of downstream piping network. The pH is measured downstream in an open system. Hence the pH measured would be higher than the reactor pH due to downstream CO_2 degassing. The conversion with respect to magnesium and silica (Fig. 3d) has been calculated upstream at the reactor.

In a CO_2 -water system, the resultant acidity is insufficient to dissolve natural serpentine [9]. However, thermally activated serpentine dissolves rapidly in moderate flue-gas operating conditions. The dissolution rate is observed to be fast in the first 30 min where a magnesium conversion (X_{Mg}) of over 60% is reached. This is followed by a slow dissolution rate phase and this transition is clearly observed in the conversion plots. Unlike natural serpentine, a significant amount of silica is released upon mineral

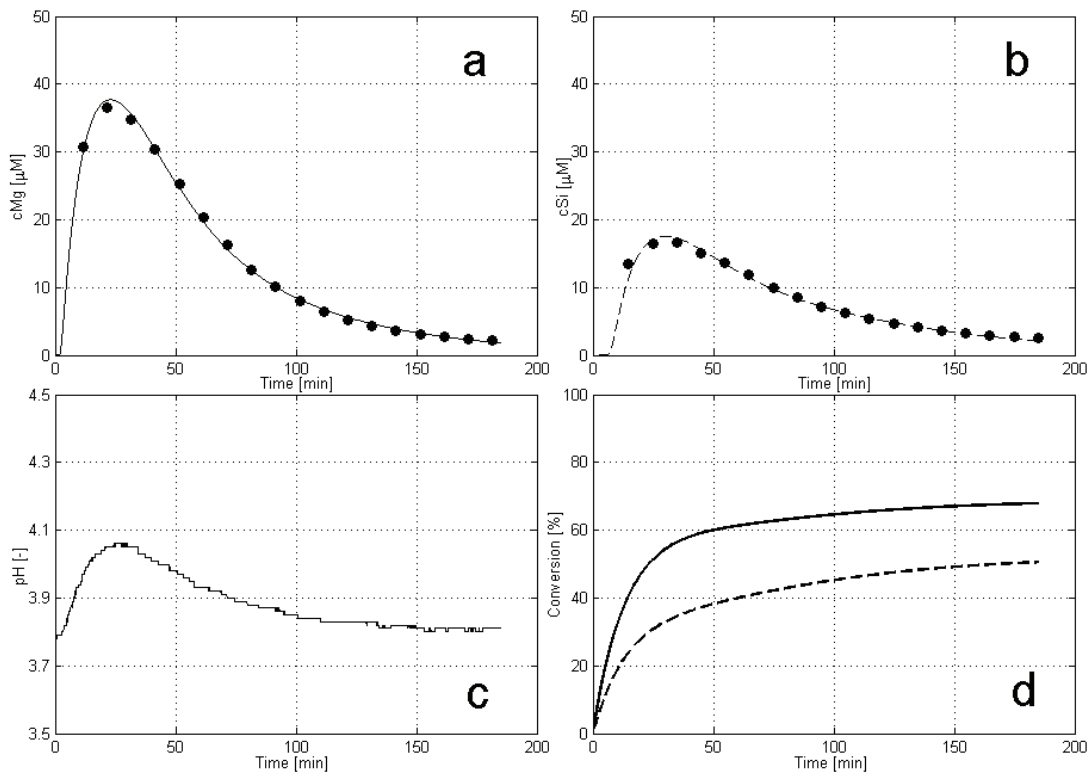


Fig. 4 Dissolution profile for activated serpentine in HCl under nitrogen atmosphere. $\text{pH} = 3.8$, $T = 90\text{ }^{\circ}\text{C}$, $m_f = 2.0\text{ mg}$. (a) downstream magnesium concentration profile (b) downstream silica concentration profile (c) downstream pH profile (d) upstream conversion profiles for (continuous line) magnesium and (broken line) silica.

dissolution. The removal of the silica diffusive barrier probably results in the higher magnesium conversions. However, the silica conversion is found to be under-stoichiometric with respect to magnesium. Hence, only a part of silica gets released into the bulk solution.

The initial dissolution rate (magnesium based) of activated serpentine was found to increase with T and p_{CO_2} . The influence of p_{CO_2} on the dissolution rate is related indirectly through the pH of the aqueous system. Far-from-equilibrium dissolution rates of minerals are dependent on the pH of the system [10]. Hence dissolution kinetics should be identical for experiments performed with mineral acid in the absence of CO_2 . Fig. 4 shows the dissolution profiles for experiments performed with mineral acid (HCl) as the liquid feed with inlet pH identical to the initial pH of the flue-gas system. The small differences in the profiles are due to the differences in the instantaneous pH in the reactor for the two systems.

4. Conclusions

The dissolution profiles of thermally activated serpentine under flue-gas atmosphere were measured. Thermal activation enabled the rapid dissolution of serpentine under mild acidic conditions. The dissolution profiles were found to be dependent on the instantaneous pH of the aqueous system. The dissolution kinetics is characterized by a short initial phase with fast mineral dissolution rates followed by a phase with slow dissolution rates. The conversion with respect to magnesium reaches 60% in 30 min in a flue-gas system. The silica conversion is under-stoichiometric with respect to magnesium, thereby indicating only a partial leaching of the silica diffusive barrier. A model that can describe the non-stoichiometric dissolution profiles is being developed. Such a model would be essential in designing an optimized continuous process.

Nomenclature

p_{CO_2}	partial pressure of $CO_2(g)$ in the reactor [bar]
P	total pressure in the reactor [bar]
T	reaction temperature [$^{\circ}C$]
m_f	amount of activated serpentine of 20-63 μ m fraction dissolved [mg]
X_{Mg}	extent of dissolution with respect to the amount of magnesium leached [%]

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