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Dissolution kinetics of thermally activated serpentine for mineralization at flue gas conditions

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Abstract

This communication gives an overview of our study on the dissolution kinetics of thermally activated serpentine (dehydroxylated serpentine). Firstly, we had studied the far-from-equilibrium dissolution kinetics of 75% dehydroxylated lizardite particles in a liquid and gas flow-through reactor at moderate temperatures ($30^{\circ}\text{C} < T < 120^{\circ}\text{C}$) and low CO_2 partial pressures ($0.1 \text{ bar} < p_{\text{CO}_2} < 2 \text{ bar}$). Over 80% of the Mg was leached from the dehydroxylated lizardite particles. We then followed it up by developing a non-steady state dissolution kinetics model. The model uses surface complexation mechanisms to describe the specific dissolution rates. The model was able to describe the evolution of the non-stoichiometric aqueous concentration profiles of magnesium and silica accurately, taking into account the dynamic evolution of the reactor pH at non-steady state dissolution conditions. The kinetic parameters could be used to compare the dissolution performances of differently activated minerals in their application as potential feed materials for an ex situ mineral carbonation process.

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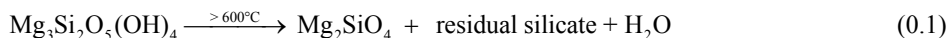
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1. Introduction

Avoiding emissions of the greenhouse gas CO₂ to the atmosphere, by its safe and permanent storage is required for all options within the carbon dioxide capture and storage (CCS) scheme. Proper monitoring of the stored CO₂ is critical in the case of geological storage, i.e. when the captured CO₂ is not processed in a carbonation plant, but sent to suitable storage reservoirs (depleted oil and gas fields, saline aquifers). Any onshore geosequestration project might face the opposition of local residents, under whose premises the CO₂ plume would spread. Barriers such as public perception, regulatory issues, well bore integrity and risk of induced seismicity is slowing down the deployment of subsurface CO₂ storage and in turn is helping alternative sequestration techniques to gain momentum. Only ex-situ mineral carbonation allows for a sequestration process, where the carbon is rapidly converted to its chemically most stable form, a solid carbonate.

Traditionally, aqueous mineralization was studied at high temperature with the acidifying help of high CO₂ partial pressures to extract alkaline earth metals from a solid feed, which then form carbonates by precipitation. Recent developments in mineralization research have seen process concepts that accept dilute CO₂ streams as input, thus avoiding the cost associated with a preliminary capture step. Usually, these concepts employ pH-tuning agents, which require full recovery, and/or a rather complex multi-step design to deal with the low reactivity of the solid feed at flue gas conditions. More simply, the CO₂ absorption, feed dissolution, and carbonate precipitation could take place simultaneously in a single reactor without additives. This, however, requires special feed materials, such as alkaline industrial residues (fly ashes, cement kiln dust etc.) or the magnesium (Mg) silicate serpentine in its activated form. Alkaline residues are highly reactive, but suffer from limited availability. Natural serpentine is abundant worldwide, but needs to be thermally pretreated to maximize its reactivity [1].

When serpentine is heated to temperatures higher than 600 °C, it dehydroxylates to form forsterite and a residual silicate (0.1). This process also results in distortion of the crystal lattice resulting in a particle with high porosity. The faster dissolution kinetics of forsterite together with its high porous surface area could result in rapid dissolution rates for activated serpentine, even at lean operating conditions. However, heat activation is considered to be an energy intensive process. Based on actual measurements on Australian serpentinites, Balucan et al. [2] have recently estimated the energy requirement for their best case heating strategy to be as low as 0.57 GJ t⁻¹ serpentinite. In comparison, the energy penalty for CO₂ capture in a post-combustion plant using amine absorption is in the range of 2.7–3.3 GJ t⁻¹ CO₂, excluding compression [3].



We have studied the far-from-equilibrium dissolution kinetics of 75% dehydroxylated lizardite particles at low temperatures (30°C < T < 120°C) and CO₂ partial pressures (0.1 bar < p_{CO2} < 2.0 bar). In the following sections, we will present a brief summary of the experimental and modelling analysis of the dissolution kinetics. A detailed description of the experiments and modelling approach can be obtained from Werner et al. [4] and Hariharan et al. [5] respectively.

2. Experimental Study

Lizardite was crushed and ground to a sub 125 μm size fraction and then thermally activated at 610°C by Shell Global Solution International. This resulted in a net 75% dehydroxylation. XRD analysis of this material was carried out in our laboratories that revealed a distorted crystal lattice. BET nitrogen adsorption analysis revealed that the particles revealed the presence of pores in the dimensions of meso – to macro pores.

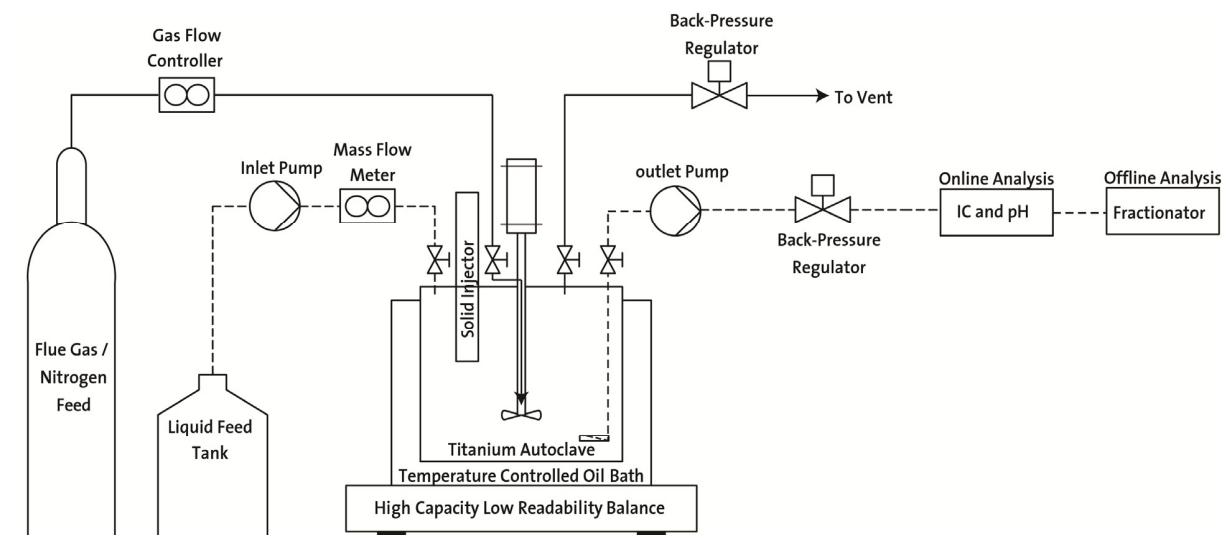


Figure 1: Simplified scheme of the continuous liquid and gas flow-through experimental setup

Far-from-equilibrium dissolution kinetics was measured in a continuous gas and liquid flow-through stand-alone setup. A simplified scheme of the setup is shown in Figure 1. The interesting feature about this experimental setup is the solid particle injector. Typically, in order to study dissolution kinetics in a pressurized reactor, particles are pre-loaded into the reactor, and then the reactor solution is allowed to reach equilibrium with respect to temperature T and gas solubility. During this start-up period, a significant amount of activated serpentine can dissolve. This may not be of considerable importance when steady state dissolution rates are measured. However this information lost due to the start-up period is quite significant for our study, where we aim to maximize our dissolution rates by operating at non-steady state conditions. In order to tackle this limitation, we developed a solid particle injector that can inject activated serpentine particles encapsulated in ice into a well equilibrated reactor. For a detailed description of the experimental setup and the particle properties, we refer to [4].

Figure 2 shows typical concentration profiles of Mg^{2+} (c_{Mg}) and aqueous Si (c_{Si}) measured downstream of the reactor. These profiles can be integrated in order to yield the extents of dissolution (X) w.r.t. Mg and Si. We also measure the pH downstream at atmospheric pressure conditions. However, this measured value does not represent the actual pH of the reactor solution as CO_2 degases during the pH measurement, resulting in a higher measured pH. Hence the actual reactor pH is instead calculated from a CO_2 speciation model and/or with a geochemical equilibrium software package EQ3/6 [6]. Detailed analysis of the experimental results can be found in Werner et al [4].

3. Kinetic Modeling

A non-steady state model was developed that describes the far- from-equilibrium dissolution kinetics of thermally activated serpentine at the operating conditions considered in this study [5]. The modeling approach involved the following sequential steps:

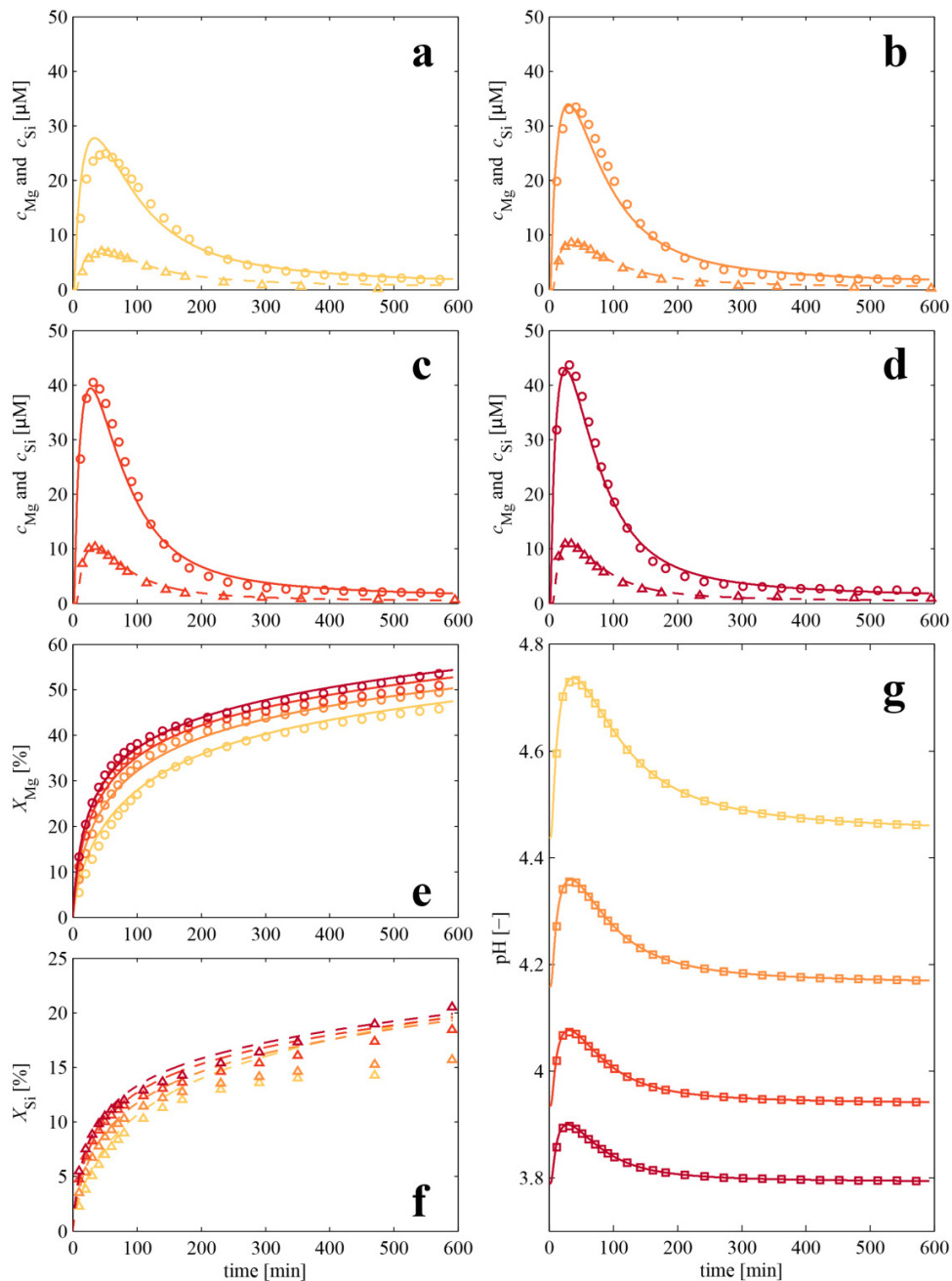


Figure 2: Simulated (lines) and experimental (points) dissolution profiles assuming the homogeneous particle structure for dehydroxylated lizardite at 30°C under flue gas atmosphere. Concentration profiles of Mg^{2+} (solid line and circles) and $Si(aq)$ (broken line and triangles) for experiments at p_{CO_2} of 0.10 bar (a), 0.36 bar (b), 1.00 bar (c) and 2.00 bar (d) respectively; the corresponding extent of dissolution with respect to Mg^{2+} (e) and $Si(aq)$ (f); the simulated pH profiles (g) with simplified speciation model (solid lines) and EQ3/6 (squares). The different colors in (e) - (g) corresponding to the different p_{CO_2} experiments in accordance with the concentration profile plots (a) - (d).

- 1) Assumptions were made regarding the dehydroxylation kinetics of lizardite particle, which resulted in descriptions for the physical morphology and chemical compositions of the dehydroxylated particles.
- 2) Specific dissolution rates for the different chemical species in dehydroxylated lizardite were described using surface complexation model and empirical models from literature.
- 3) The reactive surface areas for each particle were computed at each time instant of particle dissolution.
- 4) The pH of the bulk reactor solution was computed with a simplified CO₂ speciation model that approximates activity coefficients to unity.
- 5) A liquid flow-through reactor equation was used to compute the time varying reactor composition.

An example of a typical simulation result is shown in Figure 2. In general, the developed was able to accurately capture the complex dissolution profiles observed for dehydroxylated lizardite [5].

In a real flue gas mineralization process, however, the dissolution of the dehydroxylated lizardite will be at near-equilibrium conditions. The model developed, at the moment, does not yet account for near-equilibrium effects on the dissolution process. Nevertheless, the far-from-equilibrium model enables us to understand the intrinsic dissolution kinetics of dehydroxylated lizardite independent of equilibrium limitations.

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