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Flue gas CO_2 mineralization using thermally activated serpentine: From single- to double-step carbonation

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Abstract

This communication explores the carbonation potential of activated serpentine at flue gas conditions. A first series of single-step batch experiments was performed varying the temperature and the slurry density to systematically assess the precipitation regime of the relevant Mg-carbonates and the fate of the Si species in solution. The results suggested that the reaction progress was hindered by a passivating layer of re-precipitated silica, quartz, or carbonates, as well as by equilibrium limitations. Among several strategies that were tested to overcome these limitations, a simple double-step process that is driven by a temperature swing in combination with a low-level CO_2 pressure swing is presented. Exploratory experiments are shown that prove the viability of our process, first by applying a discontinuous method, and secondly by implementing a methodology to cycle the liquid phase continuously between a dissolution reactor and a precipitator. In this way, it was possible to produce highly pure Mg-carbonates that may serve various industries.

1. Introduction

Carbon dioxide (CO_2) mineralization belongs to the family of CO_2 capture and storage technologies that aims at reducing the greenhouse gas emissions from anthropogenic point sources, thus contributing to combat climate change [1]. To this end, a magnesium (Mg) or calcium (Ca) rich precursor material can be dissolved in the presence of CO_2

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in an engineered setting, so as the extracted divalent cations can react with bicarbonate ions to yield Mg/Ca-carbonates. Mineralized in the form of thermodynamically stable, environmentally benign carbonates, the CO_2 is locked outside the atmosphere for millennia to come. Moreover, such carbonates may prove valuable as substitutes for raw materials in various industries, thus combining the element of storage with the element of utilization [2,3]. An energy and cost efficient mineralization process needs to fix CO_2, at the same time while capturing it from the flue gas [4]. In literature, this challenge is mostly tackled by using pH-tuning agents, which require full recovery, and/or by employing rather complex multi-step design to cope with the low reactivity of the precursor materials at flue gas conditions [5,6]. Our approach is to carbonate the Mg-silicate serpentine, the world's most abundant mineralization precursor that can be thermally activated for enhanced reactivity, in an additive-free aqueous medium at low CO_2 pressures.

Our investigations started with a single-step carbonation study [8] that was then refined to monitor the solute concentration and the conversion of the Mg in the feed to carbonates at regular intervals during an experiment. This information was considered crucial to better understand the precipitation dynamics and the fate of the two relevant solutes, i.e. Mg and aqueous silica (Si). This campaign is summarized in the first part of this communication. Given the limitations that were identified for this operation mode, we tested different strategies to improve the processes efficiency [8]. The most promising, i.e. a double-step arrangement that exploits simple thermodynamics was further developed, first in a series of discontinuous experiments before implementing a methodology to cycle the liquid phase continuously.

2. Background: Single-step carbonation

In a first attempt to understand the carbonation potential of the activated serpentine under investigation (see [7] for its detailed characterization), the material was mixed with ultrapure water and exposed to CO_2 at ambient pressure, at temperatures up to $T = 90°C$, and using slurry densities up to $S/L = 20\%$ by weight. The methodology is described in more detail elsewhere [8]. The add on the existing batch system is a sampling port that was installed to the lid of the reactor, enabling to take slurry samples of ~3 mL at regular time intervals at $t = 0.5, 1, 1.5, 2, 3, 4, 6, 8$ h after the start. The samples were filtered immediately, the filtrate was diluted and analyzed for the solutes Mg, Si, and iron (see [7] for the exact methodology), and the solids were dried under vacuum overnight before analyzing them using TGA, XRD, and SEM image analysis [8].

Given the lean operating conditions applied, carbonation experiments in single-step mode yielded an unsatisfactorily low final extent of carbonation, R_x, Mg-extraction, X_{Mg}. This was reported earlier [8] and is can be seen in Fig. 1a,d for two exemplary single-step carbonation experiments at 30°C and 90°C. It was hypothesized that the high pH level that evolves in our batch system could prevent the proton-promoted extraction of Mg from the activated serpentine. In fact, the pH increased initially from $pH(t = 0) ≈ 4$ up to $pH ≈ 9$, and then stabilized at a high level of $pH ≈ 7.5$ during the entire remaining runtime of 8 h (see Fig. 1b,e). Secondly, the precipitation of the Mg-carbonates and/or of silica phases may form a passivating layer on the dissolving serpentine particles, so as further Mg-extraction is hindered by a diffusive barrier. Using carbonate seeds to prevent heterogeneous nucleation on the serpentine surface proofed to be ineffective [8]. Hence, to gain better knowledge about the fate of silica was key.

The experiments with slurry sampling provided valuable insight into the peculiar precipitation regime of both Mg and Si at flue gas conditions. In the case of the Mg-carbonates, we observed a change from the precipitation of a more soluble carbonate at temperatures below ~60°C, namely nesquehonite ($MgCO_3.3H_2O$), to the formation of a less soluble but thermodynamically more stable carbonate at higher temperatures, namely dypingite or hydromagnesite ($(MgCO_3)_4Mg(OH)_2.zH_2O$, $4 ≤ z ≤ 5$). The same was found to be true in the case of silica, where our data suggested the re-precipitation of Si in the form of amorphous silica below 90°C, but experiments at 90°C yielded the more stable, less soluble form of quartz (SiO_2). This T-effect can be appreciated from Fig. 1c and Fig. 1f when comparing the measured concentration data with the solubility levels of the kinetically relevant solid phases at the given temperatures, i.e. nesquehonite/amorphous silica at 30°C (Fig. 1c) and hydromagnesite/quartz at 90°C (Fig. 1f). Solubility data has been calculated using the geochemical equilibrium software package EQ3/6 [8,9]. Importantly, at 30°C prior to the onset of precipitation (1 h < t_{onset} < 1.5 h), the measured Mg concentration was 1.7 times higher than the solubility of

nesquehonite at this temperature (Fig. 1c), and over 50 times higher than the corresponding solubility of hydromagnesite at 90°C (Fig.1f).
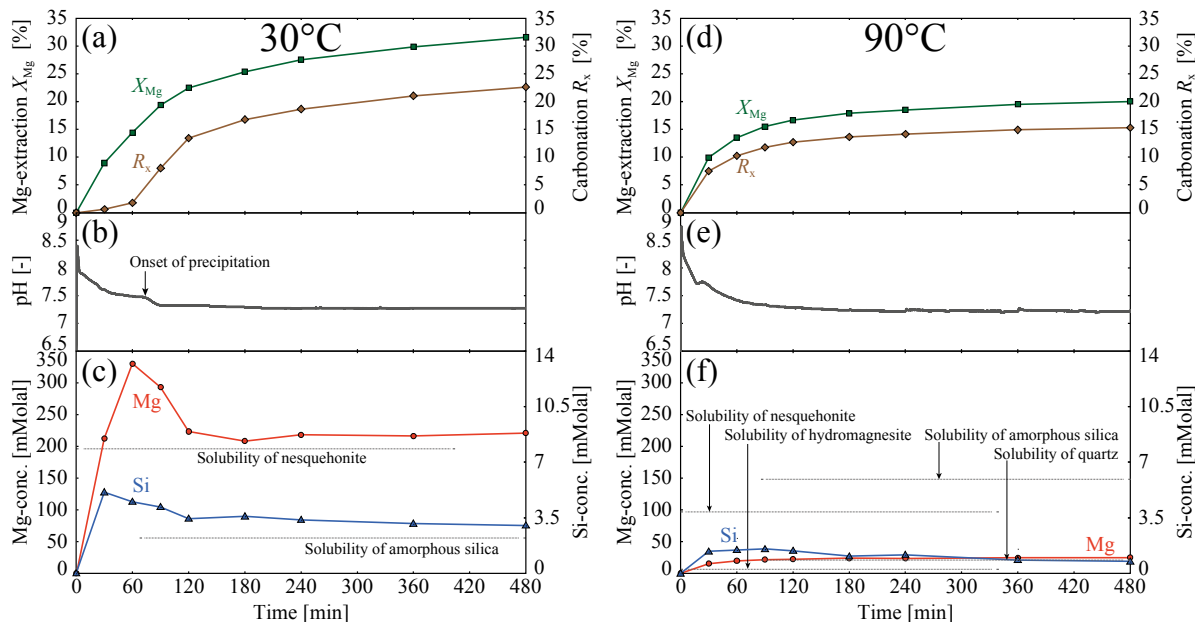

Fig. 1. Two exemplary single-step carbonation experiment at $T = 30°C$ (left column) and $90°C$ (right column), $pCO_2 = 1$ bar, and $S/L = 20\%$ wt.: (a,d) the Mg- and Si-concentration profiles; (b,e) the pH profile (pH($t = 0$) ≈ 4, i.e. outside the range of the figure axes); (c,f) the extent of Mg-extraction and carbonation. The dashed lines in (a,b) indicated the solubility levels of the kinetically relevant solid phases at each temperature; for comparison, also the solubility of nesquehonite and amorphous silica shown in (d).

3. Double-step carbonation

Based on these findings, it was clear that the dissolution step must be separated from the precipitation step. A continuous removal of the extracted Mg from the dissolution reactor should help to keep the pH therein at a level that allows for ongoing Mg-extraction. The higher the Mg-concentration in the dissolution reactor, the higher the alkalinity and correspondingly the higher the amount of CO_2 that can dissolve, i.e. be captured than can be captured into this solution. Bringing the Mg- and CO_2-enriched solution to a higher temperature triggers precipitation, which brings down the Mg concentration close to the level corresponding to the solubility of the Mg-carbonate that is kinetically relevant at the higher temperature. The Mg- and CO_2-depleted solution can then be brought back in contact with the partially dissolved activated serpentine sample to proceed with the Mg-extraction and CO_2 uptake at the lower temperature. Such a temperature swing can be combined with a pCO_2 swing (higher pCO_2 during dissolution, lower during precipitation) to exploit the fact that the solubility of carbonates decreases not only with increasing temperature but also with decreasing pCO_2. The higher pCO_2 during dissolution provides acidity and thus fosters the Mg-extraction, whereas the higher T during precipitation causes CO_2 to degas and thus keeps the pCO_2 at the desired lower level.

3.1. Discontinuous double-step carbonation

The combined T-pCO_2-swing double-step process was first tested in a discontinuous manner as follows. After dissolving a given amount of feed at 30°C and 1 bar pCO_2 for one hour ($t_{diss} < t_{onset}$, cf. Fig. 1c), the slurry was filtered and the solids were stored for subsequent dissolution steps. The filtrated was then quickly heated to 90°C at a reduced

$p\text{CO}_2$ of 0.025 bar. After the Raman signal used to monitor the precipitation progress indicated that no further precipitation is taking place, the product slurry was collected, filtered, and the filtrate was quenched back to the lower temperature. The quenched solution was then mixed with the partly reacted feed from the first dissolution step and the same procedure was repeated several times. In between each step, a small liquid sample was taken and diluted to analyzed the Mg-concentration. Fig. 2 shows the Mg-concentration data of one exemplary experiment with three dissolution (D) and precipitation (P) cycles. Also shown are the solubility curves of nesquehonite and hydromagnesite (calculated), and arrows to visualize the evolution of the Mg-concentration during the different steps (conceptual). Note that at the start of the precipitation step, the Mg-concentration was up to 250 times higher than the solubility of hydromagnesite, yielding a substantial driving force for precipitation. The liquid analysis revealed while the precipitation efficiency was close to 100% (all Mg in the rich solution was converted into a carbonate), the dissolution efficiency was generally low (see Table 1).
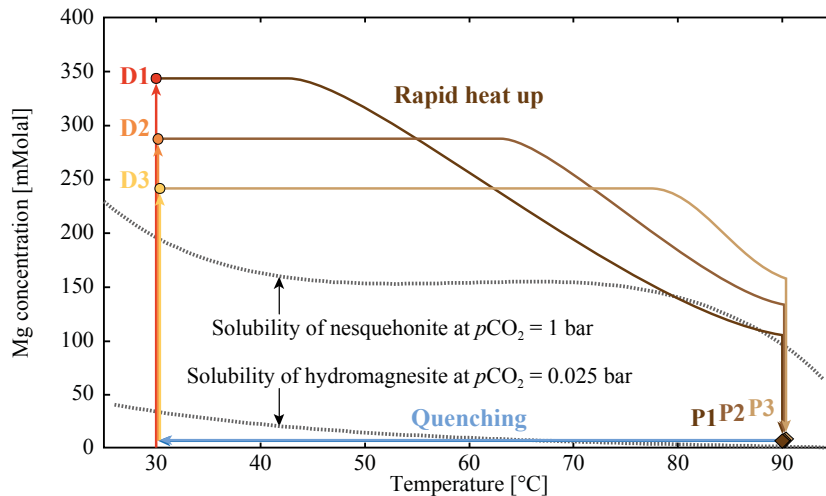

Fig. 2. Exemplary double-step carbonation experiment in discontinuous mode (batch switching). Mg concentration after dissolution at $T = 30°C$, $p\text{CO}_2 = 1$ bar (orange, circles) and after precipitation at $T = 90°C$, $p\text{CO}_2 = 0.0025$ bar (brown, diamonds). The arrows connecting the data points indicate the conceptual evolution of the Mg concentration during dissolution (D) and precipitation (P) and quenching.

Table 1. Data for an exemplary discontinuous double-step carbonation experiment with three cycles.

Step	D1	P1	D2	P2	D3	P3
Temperature [°C]	30	90	30	90	30	90
$p\text{CO}_2$ [bar]	1	0.0025	1	0.0025	1	0.0025
Time [min]	60	60	90	30	120	30
Final Mg conc. [mMolal]	343.8	7.4	287.0	8.1	241.8	9.1
Efficiency [%]	13.8	98.7	11.1	97.9	7.2	96.5
Photograph of the solids collected						

3.2. Semi-continuous double-step carbonation

With the goal of performing double-step experiments with a continuous exchange of the liquid phase, two reactors of the same type as described above were interconnected in such a way that the liquid phase can be pumped simultaneously from the dissolution reactor into the precipitator and vice versa. This was realized using a double-head peristaltic pump and two dip tubes in each reactor. Filters were attached to the lower end of the dip tube to keep the serpentine in the dissolution reactor and the carbonate product in the precipitator.

Already the first test with this upgraded set-up yielded very promising results. Fig. 3 compares the best-case single-step efficiency in terms of X_{Mg} and R_x with that of the first semi-continuous experiment operated at 5% slurry density, 30°C, and 1 bar pCO_2 in dissolution reactor, while the precipitator was kept at 90°C under a pure nitrogen atmosphere. The operating conditions were then tuned in an exploratory manner to further improve the process efficiency. This included temperature ramps in the dissolution reactor to mimic consecutive dissolution steps at increasing temperature, a reduction of the slurry density, as well as the addition of seeds in the precipitator. The third pair of bars shown in Fig. 3 corresponds to one experiments under improved operating conditions. As from this comparison, the double-step strategy with a simple temperature and pCO_2 swing indeed offers substantial room for optimization.
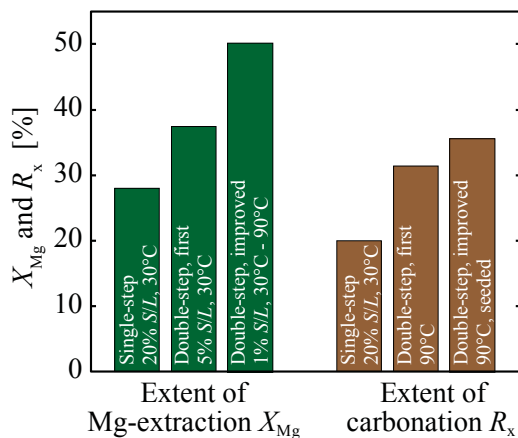

Fig. 3. Comparison of the extent of Mg-extraction and carbonation between the best-case single-step experiment, our first semi-continuous double-step experiment, and another double-step experiment with improved operating conditions as annotated inside the bars.

4. Concluding remarks

A comprehensive study of the relevant operating parameters for the direct flue gas CO_2 mineralization using activated serpentine led to the proposal and experimental investigation of a simple double-step process, which is driven by a temperature swing in combination with a low level CO_2 pressure swing. Our test experiments provided the proof of principle that a combined T-pCO_2-swing is indeed a feasible route to flue gas mineralization. Instead of natural minerals, the our double-step process may also successfully treat anthropogenic materials that have undergone a thermal process, for instance alkaline slags or ashes, which usually require remediation.

Considering the lean T- and pCO_2-conditions applied to carbonate a natural mineral in this study, the efficiency levels reached so far represent a remarkable starting point. To give a reference, the Albany group around O'Connor, i.e. the group pioneering research on CO_2 mineralization, reached a maximum carbonation efficiency of 40% when exposing heat treated lizardite to temperatures and CO_2 pressures as high as 155°C and 115 bar, respectively [10,11]. Furthermore, such levels were only reached when using smaller particles (sub 38 µm instead of sub 125 µm as used in our work) and chemical additives (0.64 M $NaHCO_3$ plus 1 M $NaCl$).

Starting from the positive results of the exploratory experiments presented herein, we have worked on further assessing the feasibility of our double-step process via illustrative simulations and more experiments. These, together with the complete single-step carbonation study, will be presented elsewhere [12].

Nomenclature

pCO_2	partial pressure of CO_2 [bar]
R_x	extent of carbonation [%]
S/L	slurry density (solid to liquid ratio) [% wt.]
t	time [min]
T	temperature [°C]
X_{Mg}	extent of Mg-extraction (dissolution) [%]
z	degree of hydration of a basic-hydrated Mg-carbonate [−]

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