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CO_2 fixation using magnesium silicate minerals part 1: Process description and performance

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ABSTRACT

This paper describes a staged carbonation process for magnesium silicate mineral carbonation. This carbon dioxide capture and storage (CCS) alternative involves the production of magnesium hydroxide, followed by its carbonation in a pressurised fluidised bed (PFB) reactor. The goal is to utilise the heat of the carbonation reaction to drive the $Mg(OH)_2$ production step. The results show that $Mg(OH)_2$ can be produced successfully (up to 78% Mg extraction extent achieved so far) and efficiently from different serpentinite minerals from locations worldwide (Finland, Lithuania, Australia, Portugal…). From the extraction step, ammonium sulphate is recovered while iron oxides (from the mineral) are obtained as by-products. The carbonation step, while still being developed, resulted in $>$50%-wt conversion in 10 min (500 °C, 20 bar) for $>$ 300 μm serpentinite-derived $Mg(OH)_2$ particles. Thus the reaction rate achieved so far is much faster than what is currently being considered fast in the field of mineral carbonation.

1. Introduction

Carbon dioxide capture and storage (CCS) is being considered as one of the options for CO_2 emissions mitigation in many countries, including Finland [1]. Although the storage of compressed CO_2 in geological formations currently receives most attention, the interest towards the alternative option of CO_2 mineralisation is increasing. In Finland, R&D work on this method has been ongoing for many years, motivated by a lack of other CCS options and the fact that the thermodynamics of a CO_2 mineralisation process, when properly optimised, could allow for energy-neutral operation [2–4].

The basic principle behind mineral carbonation can be found in nature, and it is called weathering. When rock, containing a material capable of forming carbonates, such as calcium or magnesium, erodes, small particles are separated and exposed to CO_2 which has been dissolved in rain water. This causes the rock particles to slowly break up, releasing metal ions into the mildly acidic water, which then become available to react with the dissolved CO_2. The result of this is the formation of mineral carbonates. Unfortunately, however, natural weathering is a very slow process that cannot keep up with the increasing atmospheric CO_2 level. Therefore the goal of mineral carbonation has been [5] and still is to increase the reaction rate of mineral carbonation in an environmentally sound way.

There are several ways of increasing the carbonation rate artificially and most of the processes concentrate on precipitating carbonates from aqueous solutions [6]. While the aqueous route might seem more promising at first, with faster carbonation kinetics obtained so far, the energy economy of such an approach is less attractive. This is the main reason why we are studying a gas-solid carbonation process that aims at utilising the heat released from the exothermic carbonation reaction (R5) (see below) at elevated temperatures.

This paper describes a staged carbonation process for magnesium silicate mineral carbonation that involves the production of reactive magnesium in the form of magnesium hydroxide, followed by the carbonation of this in a pressurised fluidised bed (PFB) reactor that is operated at temperatures and pressures up to 600 °C, 75 bar. One specific goal was to operate the PFB at pressures above 74 bar (and 31 °C) where CO_2 is supercritical in order to assess if this has a beneficial effect on the carbonation reaction. However, the final process is likely to require far less severe conditions as will be shown below. A schematic illustration of the process described here can be found in Fig. 1.

Considering the final product, magnesium carbonate: this could find use in various applications, from simple landfill to fine chemicals (depending on purity). $MgCO_3$ is a stable and

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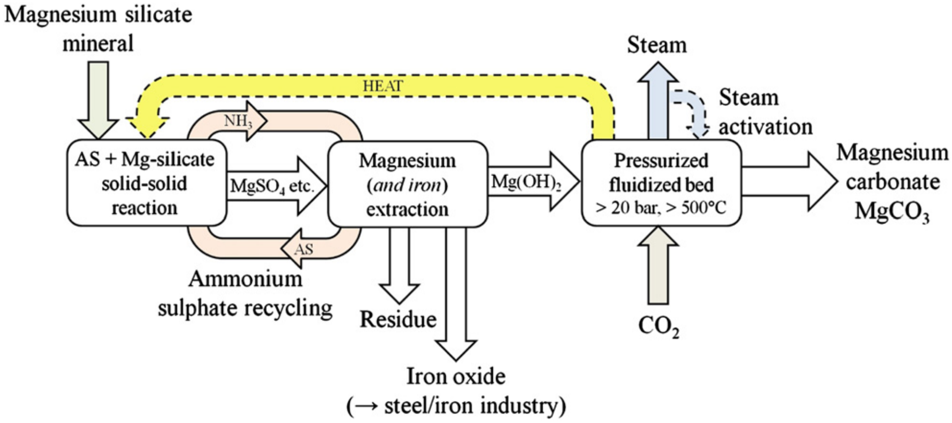

Fig. 1. A schematic illustration of the mineral carbonation process described in this paper.

environmentally benign material [7], but large-scale operation could saturate current markets as a product or by-product (apart from landfill or land reclamation material) in the long run [8]. The focus of this paper (part 1) will be primarily on the process description and on test results. Details regarding the process energy and material streams for a modelled full-scale process are given in part 2 of this paper [9], together with a discussion around the possibility of integration with steel industry.

2. Stepwise carbonation of magnesium silicates

One of the features of CO_2 mineralisation using magnesium silicates is that the overall chemical reaction is exothermic, for example for serpentine $3MgO\cdot 2SiO_2\cdot 2H_2O$, carbonation $\Delta H = -52$ (at 0 °C) to -49 (at 800 °C) kJ/mol CO_2 ($\sim$1.2 MJ/kg CO_2), with $\Delta G < 0$ for $T < 500$ °C. For forsterite $2MgO\cdot SiO_2$ the values found are $\Delta H = -106$ (0 °C) to -93 (800 °C) kJ/mol CO_2 (2.4–2.1 MJ/kg CO_2), with $\Delta G < 0$ for $T < 340$ °C. However, the direct carbonation of magnesium silicates is too slow, too energy demanding or otherwise economically unviable, although work on improving the rate of processes based on pressurised aqueous solutions is still ongoing [10]. Here, the process consists of three steps: magnesium extraction, $Mg(OH)_2$ production and $Mg(OH)_2$ carbonation. The following section presents each step in some detail.

2.1. *Step 1: Extracting Mg from serpentinite*

The method for extracting magnesium from serpentinite (and other magnesium silicate minerals), being developed at Åbo Akademi University (ÅAU), consists of heating the serpentinite to between 400 °C and 500 °C together with ammonium sulphate (AS) salt [11]. This causes the magnesium to form magnesium sulphate (R1), which can be further converted to $Mg(OH)_2$ (R4).

$$Mg_3Si_2O_5(OH)_4(s) + 3(NH_4)_2SO_4(s) \leftrightarrow$$
$$3MgSO_4(s) + 2SiO_2(s) + 5H_2O(g) + 6NH_3(g) \qquad (R1)$$

The reaction described by (R1) is endothermic and for this reason, the carbonation step has to be sufficiently effective to compensate for the heat input required. In reality we also have to consider the other minerals typically present in serpentinite, minerals containing significant amounts of iron and calcium. Assuming that iron is in the form of FeO and calcium in the form of $CaSiO_3$ two additional reactions take place when subjected to AS at elevated temperatures:

$$FeO(s) + (NH_4)_2SO_4(s) \leftrightarrow FeSO_4(s) + 2NH_3(g) + H_2O(g) \qquad (R2)$$

$$CaSiO_3(s) + (NH_4)_2SO_4(s) \leftrightarrow$$
$$CaSO_4(s) + SiO_2(s) + 2NH_3(g) + H_2O(g) \qquad (R3)$$

For the rock material composed of serpentine, calcium silicate and iron oxide the energy requirements for extraction of magnesium are of course somewhat higher than for pure serpentine, as a result of reactions (R2) and (R3) requiring energy as can be seen from Table 1. Reaction enthalpy data and the temperature range at which the reactions may occur ($\Delta G < 0$) are given in Table 1. The heat required for a typical serpentinite rock (Finnish rock with 84%-wt serpentine, 13%-wt FeO, and 3%-wt $CaSiO_3$) is given by R1+R2+R3 and was calculated by linear addition based on molar fractions.

A more detailed analysis of the reaction between serpentinite material and AS salt was made by Nduagu et al. [12], analysing the equilibrium product mix composition. The results, obtained with HSC Chemistry 5.11 software for the mixture reacting at an AS/Mg mole ratio 4:3 are shown in Fig. 2. It shows that $MgSO_4$ is the main solid product at temperatures above 200 °C, while above 450 °C the production of SO_3, basically from AS thermal decomposition, becomes significant.

Also, it was experimentally found that a longer reaction time ($\sim$1 h) at a somewhat higher temperature ($\sim$ 500 °C) increases extraction of iron relative to magnesium compared to shorter times ($\sim$20 min) and lower temperatures (400–450 °C). A detail that is not considered here is that the levels of extraction of Mg, Ca and Fe are different – see part 2 of this paper [9] for that.

2.2. *Step 2: $Mg(OH)_2$ production*

After the first process step, in which serpentinite rock is thermally treated with ammonium sulphate (AS) at 400–500 °C, atmospheric pressure, during 10–60 min (depending on the

Table 1
Reaction enthalpies and thermodynamics.

Reaction	ΔH_{373K} (kJ/mol)	ΔH_{873K} (kJ/mol)	$\Delta G < 0$ range (°C)
R1	243/mol Mg	174/mol Mg	>200
R2	183/mol Fe	149/mol Fe	>180
R3	131/mol Ca	91/mol Ca	>50
R1 + R2 + R3	264/mol Mg	220/mol Mg	>190
R4	−6/mol Mg	113/mol Mg	<136
R5	−56/mol Mg	−60/mol Mg	no limit[a]
R6	80/mol Mg	71/Mol Mg	>265
R7	101/mol Mg	94/Mol Mg	>304

[a] Whole range 100–600 °C.