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Mechanisms of Aqueous Wollastonite Carbonation as a Possible CO₂ Sequestration Process

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Abstract

The mechanisms of aqueous wollastonite carbonation as a possible carbon dioxide sequestration process were investigated experimentally by systematic variation of the reaction temperature, CO₂ pressure, particle size, reaction time, liquid to solid ratio and agitation power. The carbonation reaction was observed to occur via the aqueous phase in two steps: (1) Ca leaching from the CaSiO₃ matrix and (2) CaCO₃ nucleation and growth. Leaching is hindered by a Ca-depleted silicate rim resulting from incongruent Ca-dissolution. Two temperature regimes were identified in the overall carbonation process. At temperatures below an optimum reaction temperature, the overall reaction rate is probably limited by the leaching rate of Ca. At higher temperatures, nucleation and growth of calcium carbonate is probably limiting the conversion, due to a reduced (bi)carbonate activity. The mechanisms for the aqueous carbonation of wollastonite were shown to be similar to those reported previously for an industrial residue and a Mg-silicate. The carbonation of wollastonite proceeds rapidly relative to Mg-silicates, with a maximum conversion in 15 min of 70% at 200 °C, 20 bar CO₂ partial pressure and a particle size of $<38 \mu m$. The obtained insight in the reaction mechanisms enables the energetic and economic assessment of CO₂ sequestration by wollastonite carbonation, which forms an essential next step in its further development.

Keywords

environment; chemical processes; reaction engineering; precipitation; carbon sequestration; wollastonite

1. Introduction

Various carbon dioxide capture and storage technologies are being studied worldwide in order to mitigate global warming in the relatively short term. Mineral CO_2 sequestration is a chemical storage route in which carbon dioxide is bound in a carbonate mineral (*e.g.*, Lackner, 2002; Park and Fan, 2004; IEA GHG, 2005). The basic concept of this technology is deduced from the natural weathering of Ca/Mgsilicates. For wollastonite (CaSiO₃), the overall weathering reaction can be written as:

$$CaSiO_3(s) + CO_2(g) \rightarrow CaCO_3(s) + SiO_2(s)$$
(1.)

Potential advantages of mineral CO₂ sequestration are the permanent and inherently safe storage of CO₂ due to the thermodynamically stable nature of the carbonate product formed and the vast sequestration capacity because of the widespread and abundant occurrence of suitable feedstock (Lackner, 2002). In addition, carbonation is an exothermic process, $\Delta H_r = -87$ kJ/mol for wollastonite (Lackner et al., 1995), which potentially reduces the overall energy consumption and costs of carbon sequestration. However, natural weathering processes are slow with timescales at atmospheric conditions of thousands to millions of years. For industrial implementation, a reduction of the reaction time to the order of minutes has to be achieved by developing alternative process routes.

Ca/Mg-silicates that are suitable as feedstock for mineral CO_2 sequestration include primary minerals, such as wollastonite (CaSiO₃) and olivine (Mg₂SiO₄), and alkaline solid residues such as steel slag (Huijgen and Comans, 2003). In a previous paper, we have reported the reaction mechanisms of mineral CO_2 sequestration by aqueous steel slag carbonation (Huijgen et al., 2005b). In the present study, we have extended our research to primary minerals. Wollastonite was selected as model feedstock for our carbonation experiments, because Ca-silicates tend to be more reactive towards carbonation than Mg-silicates (Huijgen and Comans, 2003; Lackner et al., 1997), although suitable deposits are limited relative to the world-wide abundance of Mg-silicates (Lackner, 1995). In addition, the choice for a Ca-silicate enables the direct comparison to the carbonation of Ca-rich alkaline solid residues such as steel slag.

Several process routes for industrial mineral CO_2 sequestration have been reported. The so-called aqueous carbonation route (O'Connor et al., 2005) has been selected as the most promising route in a recent review (Huijgen and Comans, 2003; IEA GHG, 2005). In this process, carbonation occurs in a gas-solid-water slurry, which increases the reaction rate substantially when compared to direct gas-solid carbonation. Process steps within the aqueous carbonation route are:

1. Leaching of Ca:

$$CaSiO_3(s) + 2 H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + SiO_2(s)$$
 (2.)

2. Dissolution of CO_2 and subsequent conversion of (bi)carbonate species:

$$\operatorname{CO}_2(g) + \operatorname{H}_2\operatorname{O}(l) \to \operatorname{H}_2\operatorname{CO}_3(\operatorname{aq}) \to \operatorname{HCO}_3^-(\operatorname{aq}) + \operatorname{H}^+(\operatorname{aq})$$
 (3.)

3. Nucleation and growth of calcium carbonate:

$$\operatorname{Ca}^{2+}(\operatorname{aq}) + \operatorname{HCO}_3^-(\operatorname{aq}) \to \operatorname{CaCO}_3(\operatorname{s}) + \operatorname{H}^+(\operatorname{aq})$$
 (4.)

A limited number of studies on wollastonite carbonation for CO_2 sequestration has been published so far (Kojima et al., 1997; Wu et al., 2001; O'Connor et al., 2005). These studies have demonstrated that (1) the leaching of Ca from the CaSiO₃ matrix (eq. 2) is the rate-limiting reaction step at the conditions applied and that (2) this step can be enhanced by e.g. increasing the specific surface area of the wollastonite. However, two of these studies (Kojima et al., 1997; Wu et al., 2001) focus on carbonation at low CO_2 pressure and low temperature and reported reaction times are, consequently, much too long for industrial application. O'Connor et al. (2005) have studied the carbonation of various silicate minerals at elevated temperature and pressure, including a limited number of experiments with wollastonite, which confirm the higher reactivity of Ca- relative to Mg-silicates.

In the present paper, we present an experimental study on the mechanisms of wollastonite carbonation at elevated temperature and pressure in support of the development of a rapid carbon dioxide sequestration process. The rate-determining reaction steps are identified and compared to those reported earlier for other feedstock. Finally, routes for further research on aqueous wollastonite carbonation are indicated.

2. Materials and Methods

2.1 Wollastonite characteristics

Wollastonite with size class <7 mm (Casiflux A 7020) was obtained from Ankerpoort B.V., Maastricht, The Netherlands. The particle size distribution of the wollastonite was determined by laser diffraction (Malvern Mastersizer 2000) (Figure 1). Scanning Electron Microscope (SEM) analysis of a wollastonite sample (<106 μ m) showed needle-shaped particles consistent with its crystal structure. X-ray powder diffraction (XRD) (Bruker, D8 advance) identified (Fe)-wollastonite, with best fitting formula (Ca_{0.96}Fe_{0.04})SiO₃ and traces of lime (CaO) and calcite (CaCO₃), but no crystalline

SiO₂ (Figure 2). The calcium carbonate content of the fresh wollastonite (<106 µm), expressed in terms of CO₂, was determined by TGA-MS (see below, eq. 5). The lime content was estimated from the amount of dissolved Ca at pH = 8.5 in the pH_{stat} leaching curve of the fresh wollastonite (see also below). The total composition of the wollastonite was determined by grinding a sub-sample to <106 µm. A part of the ground sub-sample was digested with concentrated HNO₃/HClO₄/HF (in proportions of 5:0.5:4.5) in an autoclave at 190 °C for 10 h. The rest of the sample was digested in a lithium metaborate smelt at 1150 °C during 30 min (1 g at 0.1 g sample). Element concentrations in the resulting solutions were measured by ICP-AES. Table 1 shows the determined composition of the wollastonite (*i.e.*, if all calcium is carbonated). The resulting product would contain 24.8 wt% CO₂. The carbonation degree (ζ_{Ca}) of the starting material is 2.4% of the total amount of Ca, based on eq. 6 below.

The pH of a wollastonite-water slurry at a liquid to solid ratio of 10 kg/kg was determined at 10.6 (open to the atmosphere, after 24 h). This value is in good agreement with the natural pH of wollastonite (10.7) as calculated with The Geochemist's Workbench 4.0 (GWB) (Bethke, 2002). The leaching characteristics of Ca and Si from fresh (and carbonated) wollastonite were measured in a pH_{stat}-system. Eight suspensions of ground wollastonite (<106 μ m) and nanopure-demineralised water at a liquid to solid ratio of 10 kg/kg were stirred at room temperature in closed Teflon reaction vessels. For seven vessels, the pH was controlled automatically within ±0.2 pH of a pre-set pH value by the addition of HNO₃ and NaOH. In one vessel, leaching occurred at the native pH of the sample (i.e., not adjusted by the addition of acid or base). After 48 h, the final pH of the suspensions was determined and the

suspensions were filtered over 0.2 μ m membrane filters. The clear filtrates were acidified with concentrated HNO₃ (pH < 3) and analysed for Ca and Si by ICP-AES. Solubility products of CaSiO₃ (wollastonite), amorphous SiO₂ and calcite (CaCO₃) were used to calculate the solubility curves of these minerals, as shown in Figure 3.

2.2 Carbonation experiments

Three representative wollastonite batches were ground quantitatively to a specific sieve size class by a tungsten-carbide vibratory ring pulveriser (<38, <106 and <500 μ m). Figure 1 shows the resulting particle size distributions that were measured by laser diffraction. Homogeneous samples of each batch were taken with a sample splitter. For each carbonation experiment, a (ground) wollastonite sample was suspended in nanopure-demineralised water in a 450 ml AISI316 autoclave reactor (Limbo 350, Büchi Glas Uster). The suspension was stirred using a three-bladed pitched turbine (D= 32×10^{-3} m) in order to suspend the solid wollastonite particles and disperse the CO₂ gas. The reactor was heated to a specific reaction temperature and, subsequently, CO₂ was added directly into the slurry with the help of a compressor (a Haskel AG75 gas booster) until a pre-determined CO₂ pressure was reached. Subsequently, the pressure and temperature were kept at their set-point by replenishment of the consumed CO_2 and cooling of the reaction heat, respectively. After the reaction time had expired, the CO_2 addition was stopped and the autoclave was cooled down and depressurised (Figure 4). The suspension was immediately filtered quantitatively over a 0.2 µm membrane filter, the solid was dried and, finally, the carbonate content was analysed by Thermal Gravimetrical Analysis (TGA-MS) to determine the conversion of the reaction.

The following process variables, which potentially influence the carbonation reaction, were varied systemically: (1) reaction time (t), (2) reaction temperature (T), (3) CO₂ partial pressure (p_{CO2}), (4) particle size of wollastonite feedstock (d), (5) liquid to solid ratio (L/S) and (6) agitation power determined by the stirring rate (n). Ranges of process conditions were chosen such that a wide range of conversions resulted (t = 5 - 60 min, T = 25 - 225 °C, $p_{CO2} = 1 - 40$ bar, d = <38 - <7000 µm, L/S = 2 - 10 kg/kg, n = 100 - 2000 rpm). The stirring rate, as adjusted experimentally, corresponds with a power input of 1×10^{0} , 1×10^{2} , 8×10^{3} W/m³, for n = 100, 500 and 2000 rpm, respectively, assuming a power number (N_p) of 1 for all Reynolds numbers (calculations for 150 ml water at 200 °C).

TGA-MS analyses were performed in duplicate in a Thermal Gravimetrical Analysis system (Mettler-Toledo TGA/SDTA 851e) coupled with a Mass Spectrometer (Pfeiffer, Thermostar) (TGA-MS). Samples (10-20 mg) were heated in aluminium oxide ceramic cups under an oxygen atmosphere at 40 °C/min from 30 to 1000 °C with one stop at 105 °C for 15 min (Figure 4). The TGA measured the weight loss caused by drying (30-105 °C) and by thermal decomposition of carbonates (105-1000 °C). The MS simultaneously analysed the evolved gas for CO₂ and H₂O. The amount of CO₂ sequestered as calcium carbonate of a sample was defined on the basis of its dry weight ($m_{105°C}$) and the weight loss between 105 and 1000 °C ($\Delta m_{105-1000°C}$):

$$CO_{2}[wt\%] = \frac{\Delta m_{105-1000^{\circ}C}[kg]}{m_{105^{\circ}C}[kg]} \times 100$$
(5.)

The carbonation degree (ζ_{Ca}) was determined by the carbonate content measured by TGA-MS, the total calcium content (Ca_{total}) and the carbonate content (CO_{2,0}) of the

fresh wollastonite, assuming only Ca had been carbonated during the carbonation process and no significant mass had been lost due to leaching in the reactor.

$$\zeta_{Ca}[\%] = \frac{CO_{2}[wt\%] \times \frac{100 - CO_{2,0}[wt\%]}{100 - CO_{2}[wt\%]} \times \frac{MW_{Ca}[kg/mol]}{MW_{CO_{2}}[kg/mol]}}{Ca_{total}[kg/kg]}$$
(6.)

If the absolute difference in carbonation degree between the duplicate analyses was larger than 2%, a third TGA-analysis was performed and potential outliers were identified with Grubb's statistical test. The resulting mean carbonate content and ζ_{Ca} are given in this paper. For a more detailed description of the experimental procedure see Huijgen et al. (2005b).

In the discussion of the results below, it is assumed that carbonation occurs exclusively during the reaction time (*i.e.*, at elevated temperature and pressure) and not during heating, cooling or depressurisation of the reactor (Figure 4). First, the effect of the heating period on the carbonation degree is assumed to be negligible since (1) CO_2 is absent during heating of the reactor and (2) the amount of Ca that is leached during heating is probably relatively limited, because leaching is expected to proceed orders of magnitude faster after the addition of CO_2 due to the resulting pH decrease. Second, the effect of the cooling time is neglected since preliminary experiments have shown that carbonation rates have been reduced substantially at the end of the reaction time and these rates probably decrease even further during cooling due to the lowering of the reactor temperature. Therefore, although the heating and cooling times (max. 23 min and 15 min, respectively, at T = 225 °C) are significant compared to the reaction time (typically 15 min), their effect on the carbonation degree is neglected. Third, the amount of calcite that precipitates during the depressurisation of the autoclave is assumed to be negligible. Although

depressurisation results in an increase of the supersaturation of calcite (*i.e.*, due to a pH increase), the amount of extra calcite that can precipitate during depressurisation is small. First, a limited fraction of the Ca is dissolved at the moment of depressurisation. Analysis of an aqueous solution sample taken directly from the autoclave at 20 bar CO₂ pressure and 150 °C (d < 106 μ m, t = 15 min, L/S = 5 kg/kg, n = 500 rpm), using a sampling device with an in-line filter, showed that only 1% of the Ca was dissolved at the moment of depressurisation. Second, it is unlikely that significant amounts of additional Ca dissolve during depressurisation given the short time involved (typically, 1-2 min) and the increasing pH. Summarizing, we suggest that carbonation occurs exclusively during the reaction time at elevated temperature and pressure (Figure 4).

3. **Results and discussion**

3.1. Reaction mechanisms

A reference carbonation experiment at T = 150 °C, $p_{CO2} = 20$ bar, d < 106 µm, n = 500 rpm, L/S = 5 kg/kg and t = 15 min resulted in a Ca-conversion of 35% and a native pH decrease to 9.1. Figure 4 shows the development of the temperature and the pressure during the reference carbonation experiment. A TGA-MS curve of the carbonation product is shown in Figure 5. XRD (Figure 2) and SEM-EDX analyses (Figure 6) of fresh and carbonated wollastonite samples identified the reactants and products given in equation 1, with calcite as the only crystal form of calcium carbonate detected. The pH_{stat} leaching curves of fresh and carbonated wollastonite (Figure 3) confirm the formation of calcium carbonate and silica. For carbonated

wollastonite, the leaching of Ca and Si seems to be controlled by the solubility of calcite and amorphous SiO_2 , respectively. Figure 3 also shows that the leachates are not in equilibrium with wollastonite.

The dependency of the carbonation degree on the process variables is shown in Figure 7. The effect of the individual process variables on the degree of carbonation is discussed below.

Reaction time. The carbonation rate decreases as the reaction time elapses (Figure 7.I). The SEM-micrographs suggest that this effect is caused by physical barriers that develop during the carbonation process (Figure 6). The scanning electron micrographs of a 35% and a 72% carbonated wollastonite sample (Figures 6.I and 6.II) show rhombohedral calcite crystals (Figure 6.III) that have precipitated during the carbonation of the needle-shaped wollastonite particles. These calcite crystals have been identified both at the surface of the wollastonite particles and as separate phases (Figure 6.IV). In addition, SEM-EDX analyses on the carbonated products show the formation of a Ca-depleted SiO₂-rim at the edges of the unconverted wollastonite (Figure 6.IV). This observation suggests preferential (incongruent) Ca-leaching relative to Si. Incongruent Ca leaching from CaSiO₃ is confirmed by the strong preferential dissolution of Ca relative to Si observed between pH 8 and 4 in the pH_{stat} experiment (Figure 3), given that 97% of the Ca in the fresh wollastonite ore is present as CaSiO₃ (Table 1). At these pH values, the leaching of Si seems to be controlled by the solubility of less-soluble amorphous silica.

The observations discussed above show that (1) carbonation actually takes place via the aqueous phase according to equations 2-4 and (2) (further) carbonation is hindered by the Ca-depleted SiO_2 -rim formed during the process, at some locations

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accompanied by precipitated CaCO₃ particles on the wollastonite surface. Therefore, we consider the leaching of Ca from unconverted wollastonite (eq. 2) to consist of the following steps: (1) diffusion of protons through the SiO₂ layer at the particle surface towards the unconverted CaSiO₃ core, (2) calcium release from the CaSiO₃ matrix, leaving solid SiO₂ behind and (3) diffusion of Ca ions (and H₂O formed) through the SiO₂ layer towards the solid/liquid interface. Subsequently, Ca²⁺ (aq) reacts with (bi)carbonate, either directly at the solid/liquid interface or in the bulk solution (eq. 4).

Particle size. Figure 7.V shows the influence of the volume-based mean particle size (D[4,3]) on the Ca-conversion at 150, 200 and 225 °C. Grinding the wollastonite sample as received to <38 μ m (D[4,3] = 16.1 μ m) results in an increase of the conversion from 12 to 60% at 150 °C and 20 bar CO₂. The conversion corresponds roughly with the reciprocal square root of the volume-based mean particle size at all temperatures ($\zeta \propto D[4,3]^{-n}$ with n between 0.45 and 0.56). Probably, the specific surface area of the wollastonite particles controls the overall reaction rate, which can be demonstrated by the dependence of the wollastonite conversion on the surface-area based mean particle size (D[3,2]), *i.e.*, $\zeta \propto D[3,2]^{-n}$, resulting in n = 0.85, 0.72 and 0.93 at 150, 200 and 225 °C, respectively. The exponential factor n approximates the theoretical value of n = 1 even closer (0.93 - 1.11), when the low conversions obtained with the <7000 μ m particle size are left out of consideration, since the relative experimental error is largest for these experiments. In brief, size reduction is a key process step in increasing the reaction rate by means of an increase of the specific surface area.

Stirring rate. The conversion is not influenced by the agitation power at high stirring rates (*i.e.*, \geq 500 rpm), which are typically used in the experiments (Figure 7.VII). However, lowering the stirring rate from 500 to 100 rpm at 150 °C and 20 bar CO₂ results in a large decrease of the conversion, suggesting that processes in the boundary layer at either the solid/liquid or gas/liquid interface become rate-determining at low stirring rates (*e.g.*, transport of leached Ca from the wollastonite interface into the water phase).

Liquid to solid ratio. The influence of the liquid to solid ratio (Figure 7.VIII) seems to suggest that the conversion slightly increases if the system becomes more diluted. However, the effects are small compared to the (absolute) experimental error of the carbonation experiments, which was determined at 5% for steel slag carbonation in our experimental set-up (Huijgen and Comans, 2005a). Based on the limited number of observations with regard to the effect of the L/S ratio, it is uncertain whether the observed slight increase in the conversion is significant.

Reaction temperature and CO₂ pressure. At 20 bar CO₂ pressure, the carbonation rate increases with reaction temperature between 25 and 150 °C (Figure 7.II). However, after a further increase of the temperature, the conversion stabilises and, subsequently, decreases, resulting in a maximum conversion around 200 °C. This behaviour is probably a result of two opposite temperature effects; raising the reaction temperature increases reaction and mass transfer rates (*e.g.*, leaching of Ca), but on the other hand reduces the activity of (bi)carbonate in water. A simulation of demineralised water saturated with CO₂ at $p_{CO2} = 20$ bar showed a decrease of the log activity for CO₃²⁻ from -10.3 at 25°C to -11.1 at 225 °C and for HCO₃⁻ from -3.3 to

-4.2 (GWB). The decrease of the (bi)carbonate activity apparently becomes dominant above 200 °C causing a net decrease of the conversion. This effect can also be demonstrated in a pressure dependency plot (Figure 7.III). At 150 °C, the conversion remains constant between 10 and 40 bar; the (bi)carbonate activity is sufficient. Only a further decrease of the CO₂ partial pressure below 10 bar reduces the (bi)carbonate activity such that a decline of the reaction rate results. At 200 and 225 °C, however, increasing the CO_2 pressure from 20 to 40 bar results in a rise of the conversion. Apparently, at 20 bar, a deficiency of (bi)carbonate activity occurs when the temperature is increased from 150 to 200 °C. In the GWB simulation discussed above, the log HCO₃⁻ activity at 150 °C and 20 bar CO₂ is -3.8. At 5, 10 and 40 bar CO₂, the calculated temperatures at which the same activity occurs are 85, 116 and 179 °C, respectively. The calculated p,T-dependency of the HCO₃⁻ activity seems consistent with the observed conversion patterns shown in Figure 7.II. The reaction temperature of maximum conversion and the accompanying maximum conversion itself both increase with a higher CO₂ pressure (Figure 7.II). In other words, the reaction temperature and, thus the conversion, can be increased further at higher CO₂ pressures before the adverse effect of the reduced (bi)carbonate activity becomes dominant. A similar influence of the temperature and CO_2 pressure can be observed in the data on aqueous wollastonite carbonation presented by O'Connor et al. (2005), although the temperature effect in that study is less evident since the conversion approaches the theoretical maximum already at T = 100 °C mainly due to the smaller particle size used.

The conversion-temperature plot at 20 bar CO_2 for various particles sizes (Figure 7.VI) shows that the maximum conversion increases with decreasing particle size, but

that the shape of the curve and the optimum reaction temperature remain roughly the same. Apparently, the decreasing (bi)carbonate activity has a similar influence on the conversion for all particle sizes. The temperature-profiles can be plotted analogously to an Arrhenius-plot using $\frac{\zeta_{Ca}}{t}$ as a pseudo-reaction rate (Figure 7.IV). The resulting pseudo-activation energies (Ea) are 22, 20 and 16 kJ/mol for the <38, <106 and <500 µm batches, respectively, based on the carbonation results at 25-150 °C (*i.e.*, the conditions at which the (bi)carbonate activity is not influencing the conversion). The activation energies determined should only be used qualitatively, since no actual reaction rates were measured. Actual activation energies reported in the literature are significantly higher, *e.g.*, 72 kJ/mol as used by (Brady, 1991).

Based on the temperature profiles, two regimes of process conditions can be defined: regime I at a temperature below the optimum reaction temperature and regime II at higher temperatures. The reaction mechanisms in both regimes will be discussed in more detail below.

Regime I. In regime I, reaction steps involving CO_2 or (bi)carbonate are unlikely to be rate determining, since no dependency of the conversion on the CO_2 pressure was measured. In addition, increasing the specific surface area of wollastonite was found to result in a substantially higher carbonation rate. Therefore, it can be concluded that the leaching of Ca (eq. 2) is probably the rate-determining reaction step in regime I. The limited influence of the stirring rate on the conversion at the conditions typically applied in regime I suggests that the Ca-leaching rate is probably determined by the Ca-diffusion rate through the silicate rim, rather than by the boundary layer at the solid/liquid interface. **Regime II.** In regime II, where the conversion was found to depend on the CO_2 pressure, processes in which CO_2 or (bi)carbonate is involved are likely to dominate the carbonation rate. Four process steps in which CO_2 is (in)directly involved can be distinguished: (1) dissolution of CO_2 , (2) conversion of dissolved CO_2 to the (bi)carbonate-ion, (3) leaching of Ca, influenced by pH as controlled by the amount of dissolved CO_2 and (4) nucleation and growth of calcium carbonate.

Since the particle size has a similar influence on the conversion in regimes I and II (Figure 7.V), it is likely that the conversion in regime II is limited by process steps in which Ca is also involved (*i.e.*, process steps 3 or 4). The influence of a change in CO₂ solubility on pH and Ca-leaching could not be studied directly in the experimental set-up used, since it was not possible to adequately measure the pH *insitu*. Chemical equilibrium modelling (GWB) of 20 bar CO₂ saturated demineralised water (i.e., without wollastonite present) resulted in a pH of 4.0 and 4.1 at200 and 225 °C, respectively. A similar simulation with wollastonite present at L/S = 5 kg/kg resulted in a pH of 5.3 at both 200 and 225 °C. These simplified calculations suggest that the pH increase between 200 and 225 °C is small relative to the large decrease in conversion that is observed between these temperatures. Therefore, it seems more probable that nucleation and growth of CaCO₃ (*i.e.*, process step 4) limit the conversion in regime II, rather than (pH-dependent) leaching of Ca (*i.e.*, process step 3).

3.2. Comparison to other carbonation feedstock

As stated in the introduction, the use of a Ca-silicate for the mineral carbonation experiments enables the direct comparison of the carbonation mechanisms to that of steel slag as reported earlier (Huijgen et al., 2005b). Figure 8 shows the influence of the reaction temperature on the conversion of the Ca-silicates wollastonite and steel slag. The shape of the curve and the optimum temperature are similar for both materials. Steel slag, however, shows a higher conversion, especially at low temperatures, which confirms the tendency of alkaline thermal residues to be more susceptible for weathering due to their (geo)chemical instability, as suggested by Huijgen et al. (2005b). The carbonation of wollastonite, on the other hand, shows a stronger temperature dependency, *i.e.*, pseudo-Ea \approx 20 *vs.* 4 kJ/mol for steel slag (Huijgen et al., 2005b). As a result, the amount of CO₂ reacted with wollastonite at higher temperatures approaches that of steel slag.

The mechanisms for the aqueous carbonation of the Ca-silicates wollastonite (this study and O'Connor et al., 2005) and steel slag (Huijgen et al, 2005b) are generally similar to those reported for the Mg-silicate olivine (e.g. O'Connor et al., 2002, 2005). The influence of the reaction temperature and the optimum temperature for the Ca-silicates correspond roughly with those reported for the Mg-silicate olivine (185 °C, O'Connor et al., 2005). The formation of a SiO₂-rim was also observed for the aqueous carbonation of olivine by O'Connor et al. (2002) and Chizmeshya et al. (2004). A possible difference in the mechanisms reported, which warrants further investigation, is the location of carbonate formation (see also IEA GHG, 2005). In our experiments on steel slag carbonation, the calcite precipitates on the particle surfaces (Huijgen et al, 2005b), whereas O'Connor et al. (2002, 2005) reported that magnesite forms as separate particles. For wollastonite, we have observed both situations for the

precipitation of calcium carbonate (Figure 6.IV). Finally, comparison of both ores (*i.e.*, wollastonite and olivine) shows that the CO_2 pressure required to carbonate wollastonite via the aqueous carbonation route, without the use of additives or pretreatment steps other than conventional grinding, is significantly lower than for Mg-silicates, *i.e.*, typically 10-40 bar *vs.* > 100 bar for olivine, as was also observed by O'Connor et al. (2005).

3.3. Process improvement

The maximum conversion that was obtained within the ranges of process conditions applied is 72% by combining each process parameter's optimum value (d < 38 μ m, T = 200 °C, p_{CO2} = 40 bar, t = 60 min, L/S = 10 kg/kg and n = 500 rpm). Studies aiming at a further increase of the wollastonite carbonation rate, which might be required for cost-effective CO₂ sequestration, should focus on surmounting the factors limiting the reaction rate, as identified in this paper. Application of reaction conditions outside the ranges studied (*e.g.*, further grinding or higher temperature in combination with a higher pressure) could enhance the carbonation rate, but the energy consumption and sequestration costs do then also increase. An alternative might be the use of an extraction agent such as acetic acid (Kakizawa et al., 2001) or additives to enhance the calcium leaching (e.g., NaCl and NaHCO₃ (O'Connor et al., 2005) or NaNO₃ (Geerlings et al., 2002)).

4. Conclusions

The aqueous carbonation of wollastonite for mineral CO_2 sequestration occurs in two subsequent steps via the aqueous phase (*i.e.*, Ca-leaching and CaCO₃ precipitation). A key process variable is the specific surface area of the wollastonite particles. The applied CO_2 pressure determines the optimum reaction temperature at which maximum conversion is reached. At temperatures below the optimum, the overall reaction rate is probably limited by the leaching of Ca from wollastonite into the water phase, which is suggested to be controlled by diffusion of Ca through a Cadepleted silicate rim formed by incongruent leaching. At higher temperatures, a reduction of the bi(carbonate) activity probably causes the nucleation and growth of calcium carbonate to limit the conversion.

The aqueous carbonation mechanisms of wollastonite, olivine and steel slag were shown to be generally similar. Wollastonite carbonates rapidly compared to Mg-silicates, with a maximum conversion in 15 min of 70% at relatively mild conditions (d<38 μ m, T = 200 °C and p_{CO2} = 20 bar). However, resources of wollastonite are limited, relative to those of Mg-silicates. The process conditions required to sequester CO₂ by the aqueous carbonation of wollastonite seem technically feasible. However, the energy consumption and costs associated particularly with the grinding to a small particle size (e.g. <38 μ m or D[3,2] = 8 μ m) are likely to be substantial. Therefore, an essential step in the further development of this process is an assessment of the energetic and economic feasibility of aqueous wollastonite carbonation as a possible CO₂ sequestration process.

Notation

А

Pre-exponential factor Arrhenius equation, %/min

Ca _{total}	Total calcium content fresh wollastonite, kg/kg
CO ₂	Carbonate content, expressed in terms of CO_2 , wt%
D	Diameter of stirrer, m
d	Particle size, µm
D[3,2]	Surface area-based mean diameter, µm
D[4,3]	Volume-based mean diameter, µm
Ea	Activation energy, kJ/mol
L/S	Liquid to solid ratio, kg/kg
m _{105°C}	Dry weight of TGA sample, kg
MW	Molar weight, kg/mol
n	Stirring rate, rpm
N _p	Power number, -
р	Pressure, bar
t	Reaction time, min
Т	Temperature, °C

Greek characters

ΔH_r	Reaction enthalpy, kJ/mol
Δm _{105-1000°C}	Weight loss TGA between 105 and 1000 °C, kg
ζ	Conversion, %

Superscripts and subscripts

Ca Calcium

CO₂ Carbon dioxide

0 Fresh wollastonite

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Figure captions

Figure 1. Particle size distribution of original (<7000 μ m) and ground wollastonite samples with size class, D[3,2] (surface area-based mean diameter) and D[4,3] (volume-based mean diameter) (suspensions in water, not vibrated).

Figure 2. XRD spectra for both fresh and 35% carbonated wollastonite (reference case) with peak identifications.

Figure 3. Ca- and Si-leaching from fresh and carbonated ($\zeta_{Ca} = 45\%$) wollastonite in nanopure-demineralised water (pH_{stat}, L/S = 10 kg/kg, 48 h) and geochemical modelling of solubility control by specific minerals (CaSiO₃ = wollastonite, SiO₂ = amorphous silica, CaCO₃ = calcite). An open symbol indicates the native pH of the sample.

Figure 4. Reactor temperature, total pressure and CO₂ partial pressure during an example carbonation experiment (reference case).

Figure 5. TGA-MS curve of 35% carbonated wollastonite (reference case). Weight of sample (----), temperature (----) and MS-signals (-----) as a function of the measurement time.

Figure 6. Scanning electron micrographs. I: 35% carbonated wollastonite (reference case). II: 72% carbonated wollastonite (maximum conversion obtained). III: calcite

crystal. IV: backscatter electron (BSE) micrograph of polished cross section of 72% carbonated wollastonite embedded in resin with EDX spot analyses results.

Figure 7. Influence of various process variables on the Ca-conversion (ζ_{Ca}) and carbonate content (CO₂) of wollastonite. Data series including the reference case experiment (\blacklozenge). (I) Reaction time. (II) Temperature at various CO₂ pressures. (III) CO₂ pressure at various temperatures. (IV) Arrhenius-plot for various particles sizes. Activation energy is based on data points with T \leq 150 °C. (V) Volume-based mean diameter at various temperatures. (VI) Temperature at various particle sizes. (VII) Agitation power determined by the stirring rate. (VIII) Liquid to solid ratio.

Figure 8. Influence of reaction temperature on calcium carbonate content, expressed in terms of CO₂ of carbonated wollastonite (\blacktriangle) (t = 15 min, L/S = 5 kg/kg) (Figure 3) and steel slag (\blacksquare) (t = 30 min, L/S = 10 kg/kg) (Huijgen et al., 2005b).

Tables

Component	Content [%]
CaSiO ₃	84.3
SiO ₂	12.3
MgSiO ₃	2.5
CaCO ₃	1.8
CaO	0.3
Other (e.g., Mn, Fe)	0.9

Table 1. Wollastonite composition based on XRD, TGA-MS and $\rm pH_{stat}$ analysis of solid and ICP-AES analysis after total digestion.

Figure 1



















Figure 6







Figure 8

