

Article

# Carbonation of Natural Wollastonite at Non-Ambient Conditions Relevant for CCS—the Possible Use as Cementitious Material in Wellbores

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**Abstract:** The reaction of wollastonite with CO<sub>2</sub> accompanied by SO<sub>2</sub> and NO<sub>2</sub> in the presence of a chloride-rich brine (230 g/L NaCl, 15 g/L CaCl<sub>2</sub>, 5 g/L MgCl<sub>2</sub>) at temperatures relevant to injection conditions (333 K) in carbon capture and storage (CCS) were investigated within the joint BMWi (Federal Ministry for Economic Affairs and Energy) research project CLUSTER. The reaction which describes the formation of wollastonite during metamorphism is reversed and shows a strong temperature dependence. Wollastonite reacts in the presence of CO<sub>2</sub> ( $\bar{C}$ ) in aqueous conditions to form calcium carbonate and amorphous silicon oxide. At 333 K and 2 MPa the carbonation reaction of wollastonite ( $\bar{C}CS$ ) is fast (<24 h). To determine the conversion rate of the reaction quantitatively different methods were used and compared: Powder X-ray diffraction (PXRD) with the Rietveld method and differential scanning calorimetry with thermogravimetry, coupled with a mass spectrometer (DSC-TG/MS) for quantitative phase analysis and for determination of the carbonation. The carbonation (CO<sub>2</sub> accompanied by SO<sub>2</sub> and NO<sub>2</sub>) of natural wollastonite at 333 K in presence of chloride-rich brine was rather fast (almost complete after 24 h reaction time).

**Keywords:** carbonation; wollastonite; CCS; CLUSTER

## 1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) climate report, 2018 [1] concluded that reduction of CO<sub>2</sub> emissions was necessary, because the current CO<sub>2</sub> concentrations are still considerably rising and currently amount to 408 ppm [2]. Therefore, it is a mandatory challenge to reduce CO<sub>2</sub> emissions. One possible option being currently investigated and discussed [3] is carbon capture and storage (CCS). Using CCS, CO<sub>2</sub> emissions from different sources (energy production, steel, and cement industries) could be reduced by finding and exploring suitable deep geologic formations (e.g., sandstones) for CO<sub>2</sub> storage. The formations considered for injection could be on- or offshore which could be in part already exploited former gas fields [3]. During and after injection, the casing and sealing of boreholes at storage sites must feature high reliability, because CO<sub>2</sub> has an impact on the stability of conventional hydrated cements [4,5], i.e., it leads to degradation due to carbonation.

Therefore, the right choice of suitable sealing systems is challenging. The material has to resist the harsh conditions at the point of injection considering pressure, temperature, acidic environment, and the composition of aggressive fluids (chloride-rich brines, CO<sub>2</sub> accompanied by NO<sub>2</sub> and SO<sub>2</sub>). The high amount of CO<sub>2</sub> and fluids will impose massive impact on cement properties. The commonly

used ordinary Portland cements (OPC) are often limited due to their instability under these conditions for sealing wellbores.

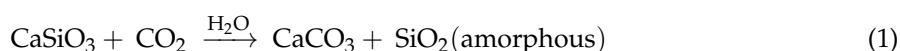
The current study is based on the investigation of carbonation as a hardening method to obtain carbonates as reaction products by using wollastonite. Although this reaction has been investigated [6–8], its use for CCS is still not widely evaluated.

Wollastonite has a Ca–Si ratio of 1:1 and, therefore, during industrial production, a better CO<sub>2</sub> balance than conventional cements with Ca–Si ratio 2:1 and 3:1 [6,9].

However, resources are limited. To overcome this bottleneck of wollastonite supply, it can be produced by adjusting a conventional cement rotary kiln production process. Additionally, CO<sub>2</sub> will be redeemed during this process and improve the CO<sub>2</sub> balance.

The present study considers the back reaction by carbonation of wollastonite forming CaCO<sub>3</sub> and SiO<sub>2</sub> as a base [10] within the joint BMWi (German Federal Ministry for Economic Affairs and Energy) research ([6–8,11,12] CLUSTER). The conditions, especially non-ambient ones, for the reaction of CaSiO<sub>3</sub> (CS) with CO<sub>2</sub> () were investigated.

The carbonation reaction of wollastonite is described as extremely slow in the absence of water at low temperatures [13]. However, at 333 K and ambient pressure, the  $\overline{\text{CCS}}$  (CO<sub>2</sub> + CaSiO<sub>3</sub>) reaction is accelerated (several hours up to one day) in the presence of H<sub>2</sub>O [6,7,13]. Microstructure development of the carbonation was investigated by Villani et al. [14] and Sahu and DeCristofaro [15]. Both studies showed a carbonation starting from the surface to the center of the wollastonite grains, analogous to the model of the shrinking core [16]. In the presence of CO<sub>2</sub> in aqueous conditions, CaSiO<sub>3</sub> is consumed and calcium carbonate is formed. Adding an internal standard of known weight to the mixture, it is possible to determine the amorphous silicon oxide formation through X-ray diffraction [6]:



The chosen temperature (333 K) and brine composition (230 g/L NaCl, 15 g/L CaCl<sub>2</sub>, 5 g/L MgCl<sub>2</sub>) defined within this joint project [11] simulated conditions in deep geological formations envisaged for CCS. According to Gartner and Hirao [13] and Longo et al. [17], the presence of water is crucial for the carbonation reaction. Our experiments were performed using chloride-rich brine as the carbonation media, because aqueous and chloride-rich solutions are expected to be present at the point of injection in wellbores.

The use of a cementitious material, based on the carbonation of wollastonite (CS), seems very promising [18–20], because CO<sub>2</sub> has an impact on the stability of conventional hydrated OPCs and wellbore cements [4–6].

In previous studies, the carbonation of calcium silicates in general [21,22] and wollastonite in particular [6–8,13,17,23] in the presence of pure water and pure CO<sub>2</sub> was investigated.

In this study, carbonation of wollastonite in a chloride-rich brine (230 g/L NaCl, 15 g/L CaCl<sub>2</sub>, 5 g/L MgCl<sub>2</sub>) as aqueous solution with CO<sub>2</sub> accompanied by 70 ppm SO<sub>2</sub> and 70 ppm NO<sub>2</sub> at 333 K was investigated. The conditions were defined within the project CLUSTER as a realistic scenario during injection of CO<sub>2</sub> in a geologic formation in CCS.

## 2. Materials and Methods

A series of non-ambient experiments were performed and different analytic techniques were applied, to determine the reaction of wollastonite with carbon dioxide (CO<sub>2</sub>) in the presence of a chloride-rich brine. For the characterization of educts and products, powder X-ray diffraction (PXRD) and differential scanning calorimetry with thermogravimetry (DSC-TG) coupled with a mass spectrometer (MS) and an infrared spectrometer (IR) were applied.

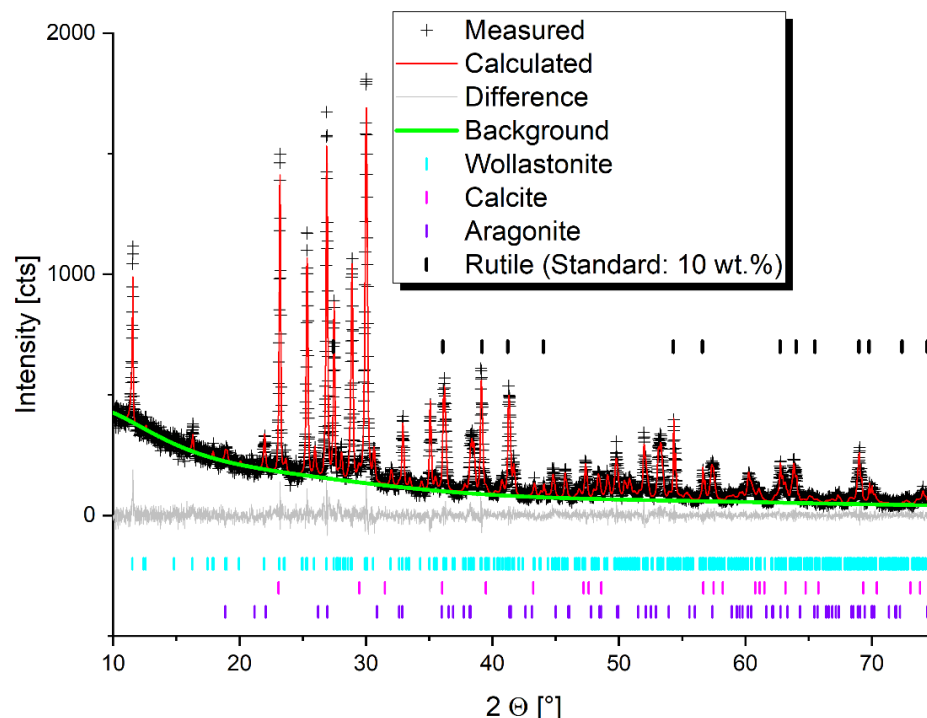
## 2.1. Materials

Steel vessels with Teflon liners from the company Büchi AG (capacity: 100 mL) were used. According to the experiments of Huijgen et al. [23] and Svensson et al. [6], the carbonation experiments were performed at 2 MPa. The temperature was chosen at 333 K. The composition of the used CO<sub>2</sub> (doped with ~70 ppm SO<sub>2</sub> and ~70 ppm NO<sub>2</sub>) and synthetic brine were identical to the studies of the authors [6–8,12]. The natural wollastonite, i.e., CaSiO<sub>3</sub> was supplied by Alfa Aesar (calcium silicate, meta, reagent grade, <20 µm powder). As described by Huijgen et al. (2006), the chosen grain size (20 µm) of the wollastonite raw material benefits the carbonation reaction. The chemical composition of the used raw material was determined by X-ray fluorescence spectroscopy (XRF) [6]. The main elements in the used natural CaSiO<sub>3</sub> were SiO (50.55 wt.%) and CaO (45.95 wt.%), while the impurities (Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, MnO, TiO<sub>2</sub>, K<sub>2</sub>O, SrO) were <1.5%. The loss of ignition was determined at 1323 K and accounted for 2.09 wt.%.

The composition of the used raw material is given in Table 1 and Figure 1. Besides wollastonite (90.7 wt.%), the calcium carbonates, calcite (1.9 wt.%) and aragonite (1.0 wt.%), could be determined as well. For the determination of the X-ray amorphous content rutile (TiO<sub>2</sub>) as internal standard was added. The amorphous part amounts to 6.4 wt.%.

**Table 1.** Phase composition of the wollastonite raw material (CaSiO<sub>3</sub>), qualitatively and quantitatively analyzed, using powder X-ray diffraction (PXRD) and the Rietveld method [24].

Phases	Content [wt.%]
Wollastonite	90.7 ± 0.8
Calcite	1.9 ± 0.2
Aragonite	1.0 ± 0.5
Amorphous	6.4 ± 0.5



**Figure 1.** Diffraction pattern with Rietveld plot [24] of natural wollastonite used for the experiments. Wollastonite (~91 wt.%), calcite (~2 wt.%) aragonite (~1 wt.%), and an X-ray amorphous content (~6 wt.%) could be observed and were determined by adding an internal TiO<sub>2</sub> standard (10 wt.%) of known weight.

An ISCO-pump (Teledyne ISCO, Model 500D Syringe pump) was used for supplying the gases and adjusting the pressure. CO<sub>2</sub> (purity 4.5; 99.995%), SO<sub>2</sub> (purity 3.0; 99.9%), and NO<sub>2</sub> (purity 1.8; 98%) were supplied by Westfalen AG. The chloride-rich brine (H<sub>2</sub>O with 230 g/L NaCl, 15 g/L CaCl<sub>2</sub>, 5 g/L MgCl<sub>2</sub>) was produced using NaCl (Carl Roth GmbH + Co. KG), CaCl<sub>2</sub> (AppliChem GmbH; Panreac Quimica SLU; ITW Companies), and MgCl<sub>2</sub> (Carl Roth GmbH + Co. KG).

## 2.2. Analytical Methods

Powder X-ray diffraction (PXRD) was used to analyze the educts. The parameters of the PXRD measurements were identical to the work of Svensson et al. [6] (PANalytical X'Pert<sup>3</sup> Powder with PIXcel 1D detector; 45 kV, 40 mA; apertures: 0.04 rad Soller and fixed slits (0.125° and 0.25°)). Diffractograms range from 10° to 75° 2 $\theta$  with 49.725 s per step and step size 0.013° 2 $\theta$  [6]. For qualitative phase analysis, the ICDD (International Centre for Diffraction Data) database [25] implemented within the HighScore Plus suite [26] and, for quantitative phase analysis, the Rietveld method [24] with the software package Profex-BGMN [27,28] were applied. The amorphous content was determined by adding crystalline TiO<sub>2</sub> (Kronos 2900–TiO<sub>2</sub>; rutile, supplied by KRONOS TITAN GmbH) of known weight (~10 wt.%).

The degree of carbonation of the samples was investigated depending on experimental time. The decrease of wollastonite accompanied by the increasing of calcium carbonate and amorphous contents had to be quantified. Different approaches were applied to identify and evaluate educts and products quantitatively. The weight fractions of wollastonite, calcite, aragonite, and X-ray amorphous material were determined with the Rietveld method [24]. To quantify the fraction of CaCO<sub>3</sub>, heat flow coupled with thermogravimetric analysis (DSC-TG; STA 449 F3 Jupiter NETZSCH) were carried out. The gas release during the heating regime was additionally recorded with MS (QMS 403D Aeolos NETZSCH). The atom mass units were counted from 1 to 100 u. The thermoanalytical measurements were carried out in the temperature interval from 296 K (23 °C) to 1273 K (1000 °C). The heating rate was 10 K per minute. Approximately 15–25 mg of sample material was used per measurement [6].

The products were milled before the PXRD and DSC-TG/MS measurements were carried out. An internal standard (rutile) was added for PXRD measurements.

The amount of X-ray amorphous content of CaCO<sub>3</sub> in the product could be analyzed as well with DSC-TG/IR/MS.

The content of carbonate (crystalline and amorphous) was determined by the loss of CO<sub>2</sub> which is given in Equation (2):

$$\text{CaCO}_3[\text{wt.}\%] = \frac{\text{mass loss CO}_2 [\text{wt.}\%]}{\left(\frac{\text{mass CO}_2 [\text{g/mol}]}{\text{mass CaCO}_3 [\text{g/mol}]}\right)} \quad (2)$$

## 2.3. Experimental Setup

The reaction of wollastonite with CO<sub>2</sub> at conditions close to geological storage conditions (333 K, CO<sub>2</sub> accompanied by SO<sub>2</sub> and NO<sub>2</sub>, and chloride-rich brine) was investigated. In the experiments 5 mL chloride-rich brine (H<sub>2</sub>O with 230 g/L NaCl, 15 g/L CaCl<sub>2</sub>, 5 g/L MgCl<sub>2</sub>) was added to 1 g of sample material. The pH value of the brine was ~6. This mixture was put in steel autoclaves for further treatment, i.e., 25 mL CO<sub>2</sub> accompanied by SO<sub>2</sub> (2000 ppm, 0.1 MPa), 25 mL CO<sub>2</sub>, accompanied by NO<sub>2</sub> (2000 ppm, 0.1 MPa), and 25 mL CO<sub>2</sub> (5.5 MPa) were filled with an ISCO-pump into the reaction vessel. End pressure was adjusted to 2 MPa inside the reactor. For heating, the autoclaves were placed in a drying oven. A series of experiments were carried out by varying time intervals. The pressure (2 MPa) and temperature (333 K) remained constant. As preliminary tests, wollastonite raw material was carbonated in brine for 24 h using pure CO<sub>2</sub> (purity 4.5; 99.995%) and wollastonite raw material was carbonated in water for 24 h using pure CO<sub>2</sub> (purity 4.5; 99.995%) (Table 2).

After carbonation, the samples were washed with pure water to remove the salts and dried at 303 K (30 °C).

**Table 2.** Overview of performed series of experiments at constant pressure and temperature and varied time.

Temperature [K]	Carbonation Medium	Gas Composition	Pressure [MPa]	Reaction Time [h]
333	water	CO <sub>2</sub>	2	24
333	brine	CO <sub>2</sub>	2	24
333	brine	CO <sub>2</sub> + SO <sub>2</sub> + NO <sub>2</sub>	2	0, 3, 6, 12, 18, 24

### 3. Results

The carbonation of wollastonite in a chloride-rich brine (H<sub>2</sub>O with 230 g/L NaCl, 15 g/L CaCl<sub>2</sub>, 5 g/L MgCl<sub>2</sub>) with pure CO<sub>2</sub> and CO<sub>2</sub> accompanied by ~70 ppm SO<sub>2</sub> and ~70 ppm NO<sub>2</sub> was investigated.

After 24 h reaction time at the selected conditions, the experiments were terminated [6]. As carbonation products, Svensson et al. [6] observed calcite, aragonite, and amorphous content. In addition, small contents of wollastonite were observed, due to the reaction process, which can be described by the shrinking core model [17].

#### 3.1. PXRD Analysis

In Table S1, the phase composition of the carbonated samples (chloride-rich brine, 333 K, 2 MPa), determined by PXRD and Rietveld method [24], obtained in this study is presented.

Contrary to the results of the reference experiment (Table 3), no additional newly formed aragonite was observed. This was due to the chloride-rich brine, which contained high amounts of sodium chloride (NaCl). Sodium chloride is known to inhibit the formation of aragonite [29,30].

**Table 3.** Results of the differential scanning calorimetry with thermogravimetry (DSC-TG) measurements.

Reaction Time [h]	Gas Composition	Weight Loss [%]	CO <sub>2</sub> Content [wt.%]	Calculated Content of CaCO <sub>3</sub> [wt.%]
0	—	2.1	1.7	3.9
3	CO <sub>2</sub> + SO <sub>2</sub> + NO <sub>2</sub>	7.6	7.0	16.1
6	CO <sub>2</sub> + SO <sub>2</sub> + NO <sub>2</sub>	13.4	12.2	28.0
12	CO <sub>2</sub> + SO <sub>2</sub> + NO <sub>2</sub>	20.2	18.6	42.7
18	CO <sub>2</sub> + SO <sub>2</sub> + NO <sub>2</sub>	22.4	21.4	49.0
24	CO <sub>2</sub> + SO <sub>2</sub> + NO <sub>2</sub>	25.9	24.4	56.0
24	CO <sub>2</sub>	25.7	24.3	55.8

#### 3.2. DSC-TG/MS Measurements

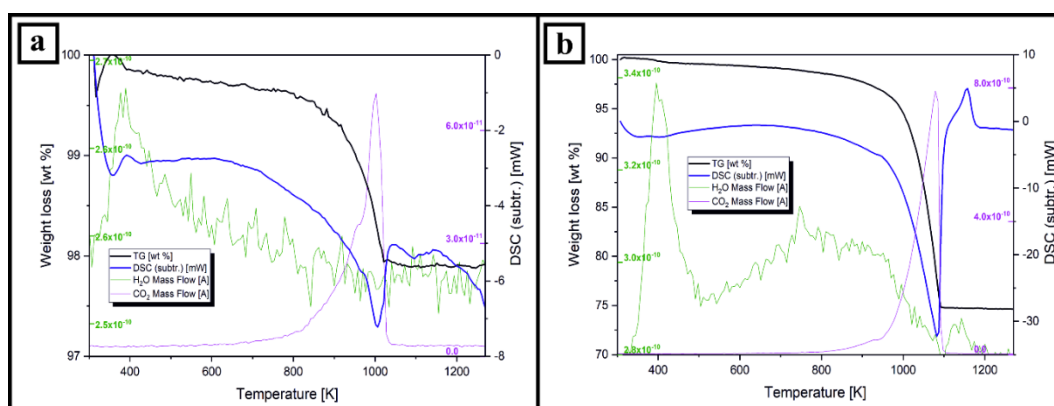
DSC-TG/MS measurements of the wollastonite raw material (educt) and the carbonated wollastonite (CO<sub>2</sub> + SO<sub>2</sub> + NO<sub>2</sub>, 333 K, 2 MPa) were carried out to determine the full content of water and carbonate (Table 3). This was necessary because X-ray amorphous carbonate could not be determined directly with PXRD, when additional phases (SiO<sub>2</sub>) contributed to the total amorphous content [6].

DSC-TG/MS measurements (Figure 2a) were carried out by Svensson et al. [6] with the raw material. Figure 2b represents the results of DSC-TG/MS measurements of carbonated wollastonite (24 h CO<sub>2</sub>, 333 K, 2 MPa). During the measurement of the raw material, the weight loss was 2.1%, from which 1.7 wt.% could be associated with CO<sub>2</sub>. Hence the original content amounts to 3.9 wt.% carbonate (CaCO<sub>3</sub>) in the sample (Figure 2a, Equation (2)). The Rietveld analysis (5 wt.%) and the DSC-TG (4 wt.%) measurements of the raw material for the CaCO<sub>3</sub> exhibited similar values [6].

DSC-TG/MS/IR analysis of the carbonated wollastonite (24 h CO<sub>2</sub>, 333 K, 2 MPa), shown in Figure 2b, was carried out. During heating, a weight loss of 24.4% was recorded. From which 23.9 wt.% could be attributed to CO<sub>2</sub>. According to Equation (2), the original content of carbonate was 54.8% (Figure 2b). The results of the Rietveld method and the DSC-TG measurements of the carbonated wollastonite for the content of carbonate showed again similar results (Rietveld: 50%; DSC-TG: 55%) [6].

Thermal (DSC-TG) and spectroscopic (MS) analyses on previously treated wollastonite with CO<sub>2</sub> and SO<sub>2</sub>/NO<sub>2</sub> (~70 ppm each) at 333 K and 2 MPa is shown exemplarily in Figure 3. During

heating, 25.9% of the weight was lost; 24.4% could be attributed to CO<sub>2</sub>, i.e., to 56 wt.% carbonate in the sample (Figure 3, Table 3, Equation (2)). The MS curve (green) detected a maxima of the mass flow of H<sub>2</sub>O (Figure 3) at approximately 400 K, which decreased distinctly at 500 K. From 500 to 700 K the release of H<sub>2</sub>O increased again and dropped afterwards until 1050 K. The MS curve of CO<sub>2</sub> (Figure 3, magenta line) remained at a constant level until 700 K and increased slightly until 900 K, then it increased more distinctly and held a plateau until 950 K. Afterwards, a maximum at 1100 K was reached. At temperatures beyond 1100 K, no significant release of CO<sub>2</sub> could be observed. The TG curve (weight loss, Figure 3, black line) decreased with a small rate until 900 K. The loss of CO<sub>2</sub> could be observed clearly in the curve between 900 and 1080 K. Beyond 1100 K, the release of CO<sub>2</sub> stopped. The DSC signal (Figure 3, blue line) showed a maximum (endothermic) amplitude at 1080 K and correlated with the detected MS maximum of CO<sub>2</sub>. At approximately 1150 K, a positive amplitude for the DSC signal could be observed and indicated the formation of Ca<sub>2</sub>SiO<sub>4</sub> (i.e., C<sub>2</sub>S, larnite), which was confirmed by PXRD of the TG sample. The formation of larnite was similar to the work published by Svensson et al. [6].



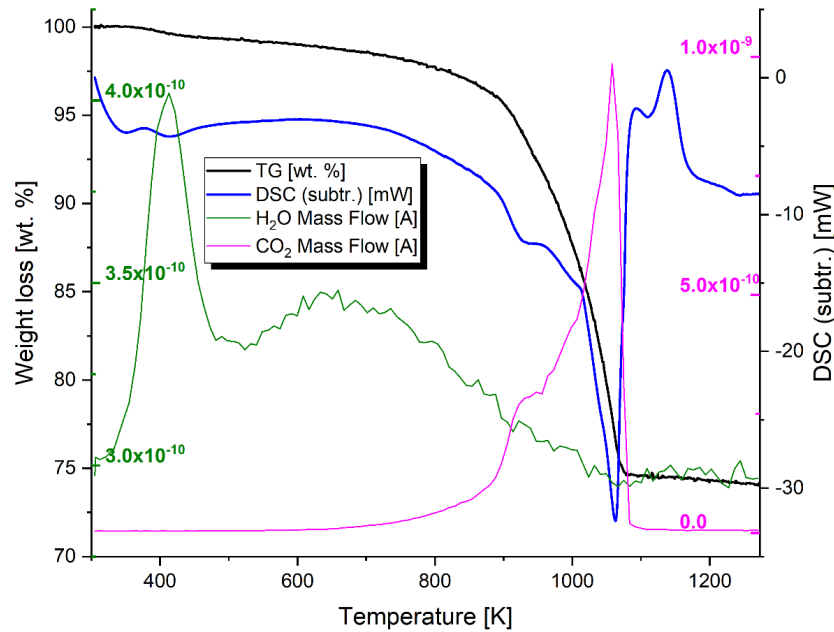
**Figure 2.** Results of differential scanning calorimetry with thermogravimetry, coupled with a mass spectrometer (DSC-TG/MS) measurements on (a) wollastonite raw material, initial weight 20.3 mg; and (b) carbonated wollastonite, initial weight 15.2 mg. Measurements were carried out from 296 to 1273 K with a heating rate of 10 K/min. The black lines represent weight loss (wt.%). The blue lines show the DSC signal (mW). The green lines refer to the mass flow (A) for H<sub>2</sub>O. The mass flow (A) for CO<sub>2</sub> is shown by magenta lines [6].

The quantitative PXRD and the DSC-TG analysis of the carbonated wollastonite (CO<sub>2</sub> + SO<sub>2</sub> + NO<sub>2</sub>, 333 K, 2 MPa) for the content of carbonate were of similar magnitude (Rietveld: 58.4 ± 0.5 wt.%; DSC-TG: 56 ± 2.8 wt.%).

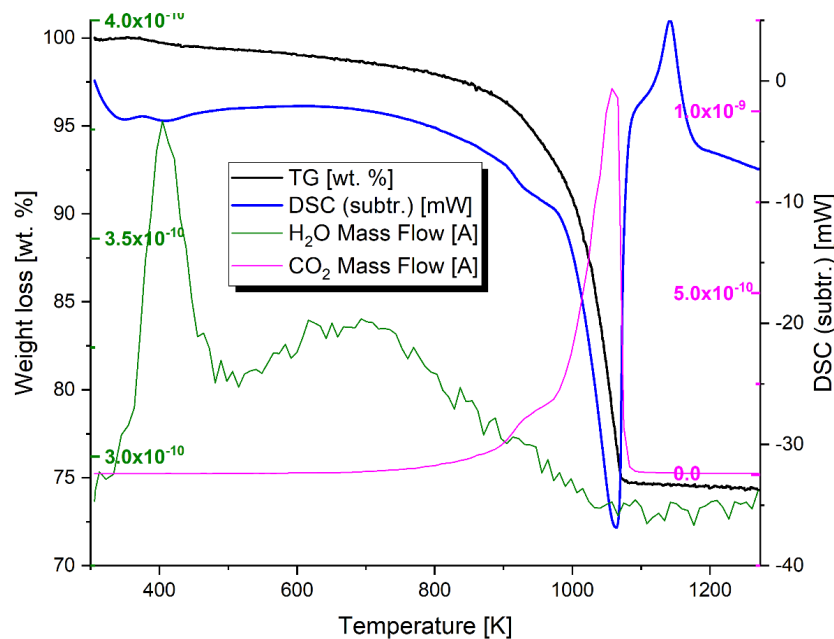
Thermal (DSC-TG) and spectroscopic (MS) analyses on previously treated wollastonite with CO<sub>2</sub> at 333 K and 2 MPa is shown exemplarily in Figure 4. During heating, 25.7% of the weight was lost; 24.3% could be attributed to CO<sub>2</sub>, i.e., to 55.8 wt.% carbonate in the sample (Figure 4, Table 3, Equation (2)). The MS curve (green) detected a maxima of the mass flow of H<sub>2</sub>O (Figure 4) at approximately 400 K, which decreased distinctly at 500 K. From 550 to 650 K the release of H<sub>2</sub>O increased again and dropped afterwards until 1050 K. The MS curve of CO<sub>2</sub> (Figure 4, magenta line) remained at a constant level until 700 K and increased slightly until 900 K, then it increased more distinctly and held a plateau until 950 K. Afterwards, a maximum at 1080 K was reached. At temperatures beyond 1080 K, no significant release of CO<sub>2</sub> could be observed. The TG curve (weight loss, Figure 4, black line) decreased with a small rate until 900 K. The loss of CO<sub>2</sub> could be observed clearly in the curve between 900 and 1080 K. Beyond 1100 K, the release of CO<sub>2</sub> stopped. The DSC signal (Figure 4, blue line) showed a maximum (endothermic) amplitude at 1080 K and correlated with the detected MS maximum of CO<sub>2</sub>. At approximately 1150 K, a positive amplitude for the DSC signal could be observed and indicated

the formation of  $\text{Ca}_2\text{SiO}_4$  (i.e.,  $\text{C}_2\text{S}$ , larnite), which was confirmed by PXRD of the TG sample. The formation of larnite was similar to the work published by Svensson et al. [6].

The quantitative PXRD and the DSC-TG analysis of the carbonated wollastonite ( $\text{CO}_2 + \text{SO}_2 + \text{NO}_2$ , 333 K, 2 MPa) for the content of carbonate were of similar magnitude (Rietveld:  $58.4 \pm 0.5 \text{ wt.}\%$ ; DSC-TG:  $56 \pm 2.8 \text{ wt.}\%$ ).



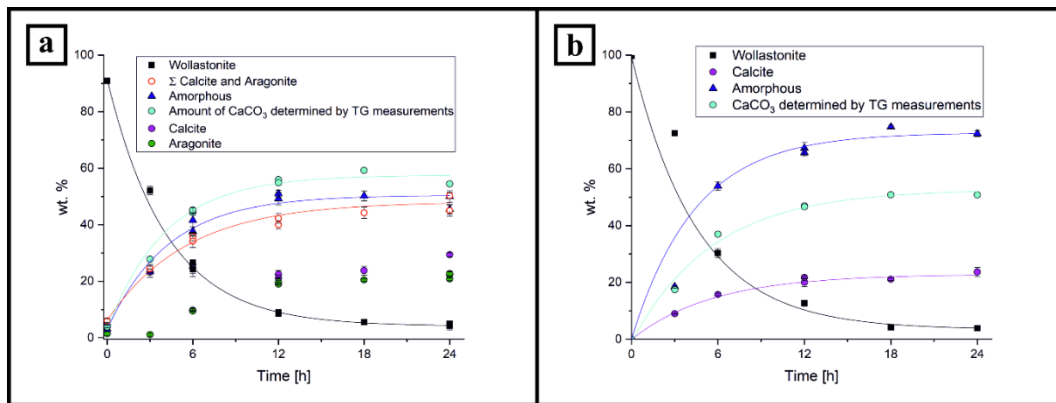
**Figure 3.** Result of the DSC-TG/MS measurement of carbonated (at 2 MPa  $\text{CO}_2 + \text{SO}_2 + \text{NO}_2$  and 333 K for 24 h in brine) wollastonite (initial weight 21.7 mg). Measurement from 296 to 1273 K with a heating rate of 10 K/min. The weight loss (wt.%) is represented by the black line, the DSC signal (mW) by the blue line. The green line shows the mass flow (A) for  $\text{H}_2\text{O}$ , and the magenta line the mass flow (A) for  $\text{CO}_2$ .



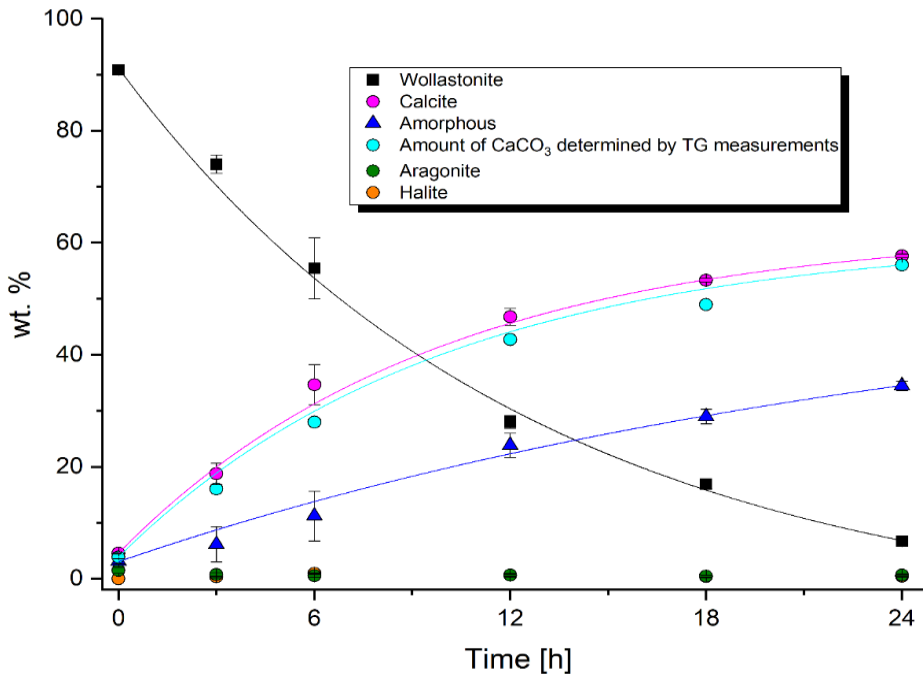
**Figure 4.** Result of the DSC-TG/MS measurement of carbonated (at 2 MPa pure  $\text{CO}_2$  and 333 K for 24 h in brine) wollastonite (initial weight 20.4 mg). Measurement from 296 to 1273 K with heating rate of 10 K/min. The weight loss (wt.%) is represented by the black line, the DSC signal (mW) by the blue line. The green line shows the mass flow (A) for  $\text{H}_2\text{O}$ , and the magenta line the mass flow (A) for  $\text{CO}_2$ .

### 4. Discussion

The overall carbonation reaction at 333 K, 2 MPa CO<sub>2</sub> pressure (accompanied by 70 ppm SO<sub>2</sub> and 70 ppm NO<sub>2</sub>), and in brine were in good agreement with the results of Svensson et al. [6,7] (Figure 5, 333 K, 2 MPa pure CO<sub>2</sub> pressure, in water; Figure 6).



**Figure 5.** Carbonation of untreated (a) and purified (b) wollastonite at 333 K (60 °C), 2 MPa (pure CO<sub>2</sub>), and aqueous condition (H<sub>2</sub>O). The quantity of the phases wollastonite (black squares), amorphous (blue triangles), calcite (magenta circles), and aragonite (green circles) were determined by the Rietveld method. The red circles symbolize the sum of calcite and aragonite and, therefore, the content of carbonate in the sample detected by PXRD. The amount of CaCO<sub>3</sub> determined by TG measurements is symbolized by cyan circles [6,7]. Figure 5b was adapted from [7]. Permission for using Figure 5b was granted by the International Cement Microscopy Association (ICMA).



**Figure 6.** Carbonation of wollastonite at 333 K (60 °C), 2 MPa (CO<sub>2</sub> accompanied by 70 ppm SO<sub>2</sub> and 70 ppm NO<sub>2</sub>), and chloride-rich brine (H<sub>2</sub>O with 230 g/L NaCl, 15 g/L CaCl<sub>2</sub>, 5 g/L MgCl<sub>2</sub>). The quantity of the phases wollastonite (black squares), amorphous (blue triangles), calcite (magenta circles), and aragonite (green circles) were determined by the Rietveld method. Halite, as a remnant of the chloride-rich brine is represented by orange circles. The cyan circles symbolize the amount of CaCO<sub>3</sub> determined by TG measurements.



The re untreated wollastonite raw material at 333 K was more or less fully converted after 18 h (Figure 5a) [6]. The content of wollastonite (black squares) decreased exponentially, while the amounts of the products (calcite, aragonite, total amount of  $\text{CaCO}_3$ , and X-ray amorphous content) increased exponentially. The “full” (~95%) conversion of purified (HCl, 10%) wollastonite at 333 K was already achieved after 18 h (Figure 5b) [7]. The quantities of wollastonite, calcite, the total amount of  $\text{CaCO}_3$ , and the X-ray amorphous content developed in a similar manner compared to the untreated wollastonite raw material (Figure 5). However, in the products of the previously purified wollastonite raw material, no aragonite was observed.

The conversion of wollastonite under conditions expected at injection sites for CCS ( $\text{CO}_2$  accompanied by 70 ppm  $\text{SO}_2$  and 70 ppm  $\text{NO}_2$ , 333 K, chloride-rich brine) was practically fully completed after 24 h (Figure 6). The amount of calcite (magenta circles) and the total amount of  $\text{CaCO}_3$  measured by thermogravimetry (cyan circles) and the amorphous content (blue triangles) increased exponentially, whereas the vice versa amount of wollastonite (black squares) decreased exponentially. The content of aragonite was constant during the series of experiments and no newly formed aragonite was observed. The content of halite was less than 1 wt.% which functioned as a monitoring of the successful washing procedure after the carbonation reaction.

Compared to the work of Svensson et al. [6–9] (Figure 5), higher amounts of calcite and lower amounts of X-ray amorphous content were observed. This was possibly due to the washing process, which was necessary to remove the salts ( $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$ ) from the samples. No additional aragonite formation was observed, which was expected due to previous work [6,8,13]. According to the work of Kitano [29] and Kitano et al. [30], the chloride-rich brine, containing high amounts of sodium chloride (230 g/L), inhibited the aragonite formation.

## 5. Conclusions

Carbonation of wollastonite in chloride-rich brine using pure  $\text{CO}_2$  and  $\text{CO}_2$  accompanied by 70 ppm  $\text{SO}_2$  and 70 ppm  $\text{NO}_2$  was investigated. According to previous studies [6,8,13], the formation of aragonite was expected. However, no additional aragonite formation was observed, which was, according to the work of Kitano [29] and Kitano et al. [30], inhibited by the high amounts of sodium chloride in the brine.

The carbonation of wollastonite, depending on the reaction time (Table 3 and Figure 6), was in a good agreement with the work of Svensson et al. [6,7] (Figure 5). Higher amounts of calcite and lower amounts of X-ray amorphous content were observed. This was possibly due to the washing process, which was necessary to remove the salts ( $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$ ) from the samples.

The performed experiments showed that the carbonation reaction of wollastonite under conditions relevant for CCS (333 K, chloride-rich brine,  $\text{CO}_2$  accompanied by 70 ppm  $\text{SO}_2$  and 70 ppm  $\text{NO}_2$ ) was rather fast (24 h). The use of wollastonite as a CS-Cement in CCS seems possible. Even the aggressive fluid ( $\text{H}_2\text{O}$  with 230 g/L  $\text{NaCl}$ , 15 g/L  $\text{CaCl}_2$ , 5 g/L  $\text{MgCl}_2$ ) had no negative impact on the conversion of wollastonite.

The long-term stability is still under investigation and has to be evaluated in depth. As assumed and reported by Svensson et al. [6], the most likely use of wollastonite as a cementitious material in CCS application would be in finishing operations for sealing the borehole after the injection of  $\text{CO}_2$  in the reservoir is completed. Further concrete technology considerations will be the next step towards sustainable mixtures, which will be poured into the borehole.

**Supplementary Materials:** Supplementary materials can be found at <http://www.mdpi.com/2076-3417/9/6/1259/s1>. Table S1: Phase composition of the carbonated samples (chloride rich brine, 333 K, 2 MPa), determined by powder X-ray diffraction (PXRD) and Rietveld refinement [24] ( $R_{\text{wp}}$ : ~9 %).

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