



Carbonation of natural pure and impure wollastonite

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Abstract

Wollastonite can be used as cementitious material, for example in carbon capture and storage (CCS application). The interaction of wollastonite (CS) and pure CO₂ in the presence of H₂O at temperature (333 K) relevant to injection conditions for CCS were investigated within the joint BMWi research project CLUSTER. The reaction which describes the formation of wollastonite during metamorphism, is reversed. Wollastonite reacts in the presence of CO₂-pressure under aqueous conditions to form calcium carbonate and amorphous silicon oxide. To determine the driving force for this reaction it is important to investigate the impact of CO₂ pressure (p) and temperature (T). The reaction kinetics of the carbonation reaction of wollastonite is strongly dependent to temperature. At 333 K and 2 MPa CO₂ the CCS reaction is fast (≤ 24 h). The chemical composition of wollastonite was analyzed by X-ray fluorescence. To determine the conversion rate of the reaction quantitatively powder X-ray diffraction with Rietveld method were applied. For further application, it is important to understand the specific reactions during the carbonation. Therefore, the influence of different treatments on wollastonite raw material (hydrochloric acid, acetic acid and temperature), before the carbonation experiments, on the carbonation reaction were investigated. The conversion of wollastonite, depending on temperature, was performed successfully. It could be proven, that aragonite acted as seed crystal for further aragonite formation. Furthermore, indications for the formation of aragonite out of amorphous CaCO₃ were observed.

Keywords CO₂ · CCS · Carbonation · Wollastonite

1 Introduction

To reduce the amount of CO₂ in the atmosphere (currently 408 ppm, [19]) several possibilities must be considered. One promising technology being investigated and discussed is carbon capture and storage (CCS). The goal of CCS is reducing CO₂ emissions from energy, cement and steel industry and burning of fossil fuel by storing considerable amounts in suitable deep geologic reservoirs. The reservoirs considered for injection could be on- or offshore formations which could be in part already former exploited gas fields [4, 12]. After injection, the sealing of wells in deep geologic formations being considered for CCS must be sustainable.

Therefore, the choice of a tight and durable cement, used for sealing, is critical. The material has to resist the extreme conditions at the point of injection considering pressure, temperature, pH, and the composition of aggressive fluids (chloride rich brines, supercritical (sc) CO₂ accompanied with NO₂ and SO₂). The high amount of CO₂ and the fluids will have a considerable impact on cement properties. Hence, the term carbonation is described in the literature as a post hydration reaction of cementitious materials [16, 30]. Ordinary Portland cements (OPC) cannot be used under these conditions for sealing wellbores due to their instability [16, 30].

The current study describes carbonation as a beneficial method to obtain carbonates as reaction products. Studies on the reaction of natural wollastonite with CO₂ as curing

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method under different pressures and temperatures were investigated and presented as literature review in the present study. One of the challenges of modern construction sites are CO₂ neutral building materials. Wollastonite has a Ca:Si ratio of 1:1 and therefore, during production, a better CO₂ balance than conventional cements with Ca:Si ratio 2:1 and 3:1 (Table 1) [20]. Additionally, the CO₂ will be consumed during the carbonation reaction, thereby improving the CO₂ balance by forming carbonates. To overcome the limited natural resources, wollastonite could be produced by adapting a conventional cement rotary kiln process (T 1100 °C). The use of a CaO reduced material for reaction forms thermodynamically stable products, which are also stable in the presence of CO₂.

The interaction of wollastonite and CO₂ [21] was investigated within the joint BMWi (German Federal Ministry for Economic Affairs and Energy) research project CLUSTER [7, 26–29].

In nature, wollastonite is formed during metamorphism. The present study considers the back reaction by carbonation of wollastonite forming CaCO₃ and SiO₂ [21]. The carbonation reaction of wollastonite is described as extremely slow in absence of water at low temperatures [11]. Yet, at 333 K and ambient pressure the $\bar{C}CS$ reaction (CaSiO₃ + CO₂) is fast (10 to 24 h) in presence of water [11, 27, 28]. Microstructural aspects of the carbonation were investigated by Vilani et al. [31] and Sahu and DeCristofaro [23]. Both studies showed a carbonation starting from the surface to the center of the wollastonite grains, similar to the shrinking core model [1]. Wollastonite reacts in the presence of CO₂ in aqueous conditions to calcium carbonate and amorphous silicon oxide:

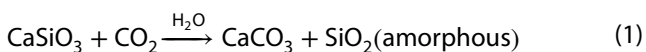


Table 1 Raw meal CO₂-output of selected cement clinker phases [20]

Phase	g of CO ₂ per g phase	Raw materials
C ₃ S (alite)	0.58	3 CaCO ₃ /SiO ₂ -OPC
C ₂ S (belite)	0.51	2 CaCO ₃ /SiO ₂
CS (wollastonite)	0.38	CaCO ₃ /SiO ₂
C ₃ A	0.49	CaCO ₃ /Al ₂ O ₃
CA	0.28	CaCO ₃ /Al ₂ O ₃
CA ₂	0.17	CaCO ₃ /Al ₂ O ₃
C ₂ F	0.32	CaCO ₃ /Fe ₂ O ₃
"C ₂ A"	0.41	CaCO ₃ /Al ₂ O ₃
C ₄ AF	0.36	CaCO ₃ /Al ₂ O ₃ /Fe ₂ O ₃
C ₃ A ₃ CS (calcium sulfoaluminate)	0.22	CaCO ₃ /Al ₂ O ₃ /CaSO ₄

The chosen temperature (333 K) was defined by the project CLUSTER (2018) and equates to the conditions in deep geological formations envisaged for CCS (1600 m). Gartner and Hirao [11] and Longo et al. [17] found, that the carbonation reaction strongly depends on the presence of water. These experiments were performed under aqueous conditions, because aqueous solutions are expected to be present at the point of injection in wellbores.

CO₂ has an impact on the stability of conventional hydrated cements [6, 16, 30]. The use of carbonation reactions instead of hydration reactions, or the combination of both, will consume CO₂ and therefore, improve the CO₂ balance. Additionally, the reactions products will be stable in CO₂-rich environments. Therefore, the use of a cementitious material, based on wollastonite (CS, CaSiO₃) curing in the presence of CO₂ (\bar{C}), seems very promising [14, 15, 25].

A literature review describing the reaction of wollastonite with CO₂ is presented. Min et al. [18] performed carbonation experiments of wollastonite at typical geological storage conditions (333 K and 10 MPa). They investigated the microstructure of the carbonated wollastonite and found, that after 20 h the reaction was controlled by the diffusion of water-bearing sCO₂ across the product layer on wollastonite surfaces. A layer of amorphous SiO₂ covered the surface of the wollastonite and functioned as a barrier.

Ashraf et al. [2] compared a calcium silicate-based cement (CSC), OPCs and OPCs with 20% fly ash. They investigated the effects of high temperature (723–783 K) on (CSC), OPCs and OPCs with 20% fly ash. During the experiments, the OPCs showed a reduction of stiffness (60%), an increase of porosity (30%) and a loss of mass (13–15%) higher than the CSC (stiffness: 6%; porosity: 20%; mass loss: 3%). Asraf and Olek [3] compared the carbonation behaviors of hydraulic and non-hydraulic calcium silicate phases with regards to CO₂ sequestration. They found, with respect to the overall amount of CaCO₃ formed, all investigated calcium silicate phases (C₃S—tricalcium silicate, γ -C₂S— γ -dicalcium silicate, C₃S₂—rankinite, CS—wollastonite) had the same efficiency level for carbonation. Longo et al. [17] showed that water has a huge impact on the carbonation reaction of wollastonite. Without water the wollastonite sample carbonated on the surface rather fast, yet after a carbonate monolayer was formed, the reaction stopped. The presence of water completely changes the reaction and causes ongoing carbonation. Daval et al. [8] investigated the carbonation reactions of wollastonite at conditions relevant to geologic CO₂ sequestration in subsurface environments. They performed experiments in batch reactors at 363 K and 25 MPa. After carbonation, they found two reaction products: Calcite and amorphous silica. No other carbonate polymorph was observed.

Huijgen et al. [13] investigated the mechanisms of aqueous wollastonite carbonation, using three different grain sizes ($< 38 \mu\text{m}$, $< 106 \mu\text{m}$ and $< 500 \mu\text{m}$). At short time intervals (5–60 min), a temperature range from 298 to 498 K and a pressure variation up to 4 MPa was investigated. A maximum conversion of 70% in 15 min at 473 K, 2 MPa (CO_2) partial pressure and with a particle size of $< 38 \mu\text{m}$ was achieved. They were able to show, that the aqueous carbonation mechanisms of wollastonite, steel slag and olivine are generally similar, although they showed, that wollastonite carbonation was rapid, relative to the carbonation rate of Mg-silicates.

Svensson et al. [26–29] investigated the carbonation of wollastonite at conditions relevant for CCS technology. They observed differences in the carbonation reaction between treated (hydrochloric acid) and untreated raw material. While using the untreated raw material for carbonation showed an unexpected formation of aragonite. In the products of previously treated (HCl, 10%) raw material aragonite was not present. Natural aragonite is formed at conditions (333 K, 500 MPa, [24], which were not reached in the steel reactors by Svensson et al. [27], 333 K, 2 MPa).

Svensson et al. [26–29] assumed that a small content of aragonite functioned as seed crystal for further metastable aragonite formation. During purification the small amount of aragonite in the raw material was removed. For a successful application of wollastonite as cementitious material in the CCS technology, the carbonation reaction has to be investigated in depth. Therefore, the presence and absence of aragonite and the overall distribution of the calcium carbonate polymorphs in the reaction products of carbonated wollastonite was investigated. The wollastonite raw material was treated differently (HCl, CH_3COOH and temperature) and potential seed crystals from different sources (aragonite from

Castilla–La Manche, Spain; calcite from Bavaria, Germany; previously carbonated wollastonite) were added.

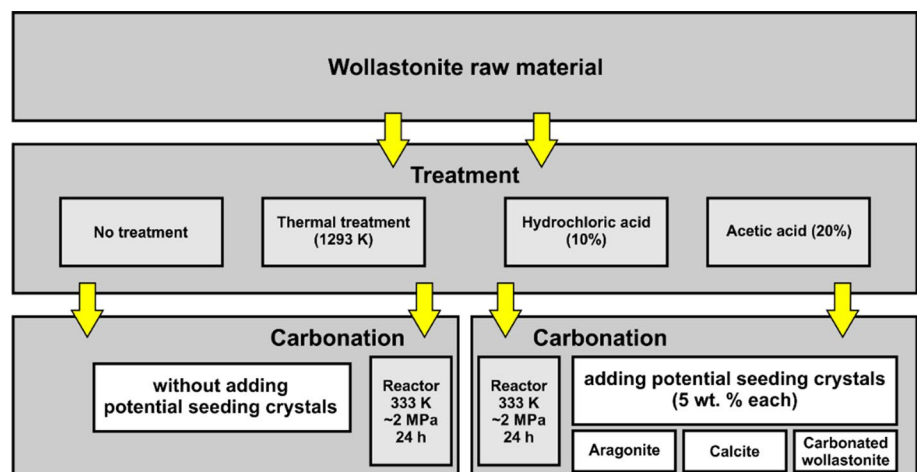
2 Materials and methods

To determine carbonation rates, several series of experiments were performed and different analytic techniques were applied. Educts and products were analyzed with powder X-ray diffraction (PXRD). The chemical composition of the educts was analyzed with wave length dispersive X-ray fluorescence (XRF). The used raw material was treated in different ways (hydrochloric acid, acetic acid, temperature) before the carbonation experiments took place. The used materials comply with the used materials of Svensson et al. [26–29] and so do the applied methods correspond with necessary adjustments (different treatments of the raw material, admixtures). Figure 1 illustrates the experimental workflow scheme of this study.

2.1 Methodology

The mineralogical composition of the raw materials was measured by PXRD (Panalytical X'PERT³ Powder with Pixel 1D detector). The PXRD measurements were carried out with 45 kV and 40 mA. As apertures 0.04 rad soller slit and fixed slits (0.125° and 0.25°) were used. Diffractograms were recorded from 10° to $70^\circ 2\theta$ with 49.725 s per step and stepsize: $0.013^\circ 2\theta$. For qualitative investigation the Highscore Plus Suite [9] and for quantitative phase analysis the Rietveld method [22] with Profex-BGMN [5, 10] was used. To determine the amorphous content, 10 wt% rutile (Kronos 2900– TiO_2 ; rutile, supplied by KRONOS TITAN GmbH) was added as internal standard. Chemical composition of the raw material was analyzed with wave length dispersive X-ray fluorescence (SRS 3000; Siemens; Rh-tube; vacuum: 200 mbar; measurement, 30 s for each line) by

Fig. 1 Experimental setup for the wollastonite raw material and treatment



Svensson et al. [27], using prepared molten discs with 1 g sample material and 8 g Di-Lithium Tetraborate (FX-X100-2, FLUXANA).

Different approaches were applied to identify and quantify educts and products to investigate the degree of carbonation depending on pressure (p) and temperature (T), the contents of wollastonite accompanied by the increase of calcium carbonate and increase of the amorphous phase contents. For quantitative phase analysis, PXRD with the Rietveld method [22] was used. On selected samples differential scanning calorimetry with thermogravimetry (DSC–TG; STA 449 F3 Jupiter Netzsch) coupled with mass spectrometer (MS; QMS 403D Aeolos Netzsch; atom mass units 1 to 100 u were recorded) were used. The thermoanalytical measurements were carried out from ambient temperature (296 K) to 1273 K (1000 °C) with a heating rate of 10 K per minute. For the DSC–TG measurements ~ 20 mg sample material per measurement were used. By applying DSC–TG/MS measurements, the amount of X-ray amorphous content of CaCO_3 in the product could be analyzed as well. The content of carbonate was calculated from the mass loss associated with CO_2 :

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

The experiments described, were performed on differently treated wollastonite before it was used for carbonation at 333 K and 2 MPa for 24 h (Fig. 1).

For the carbonation 5 wt% of potential seed crystals (calcite, aragonite, previously carbonated wollastonite) were added to the differently treated raw material [untreated: CaSiO_3 -AA (AA = Alfa Aeser); temperature (1293 K): CaSiO_3 -1293 K; hydrochloric acid (10%): CaSiO_3 -HCl; acetic acid (20%): CaSiO_3 - CH_3COOH] and several experiments were performed (Table 2). The hydrochloric acid had a molarity of 2.87 mol/L and the acetic acid a molarity of 3.26 mol/L. Hydrochloric acid is aggressive and attacks the wollastonite as well, therefore a second, less aggressive acid (i.e. acetic acid) was chosen. As carbonates are not stable at high temperatures, temperature as third treatment for purification was chosen. The chosen temperature (1293 K) decomposed the carbonates (i.e. calcite and aragonite) but did not alter the wollastonite.

Two carbonation experiments at lower temperatures (303 K and 313 K) and longer reaction time (120 h at 303 K and 42 h at 313 K) were performed to verify and complete the conversion diagram of wollastonite (Fig. 11).

As starting conditions 1 g sample material was mixed with 5 mL H_2O in the steel reactors. The pH was neutral. 20 mL CO_2 (5.5 MPa) were pumped by the ISCO-pump into the steel reactor, to obtain a pressure of 2 MPa inside the

Table 2 Overview of performed experiments with different admixtures and raw material treated differently

Raw material (1 g)	Admixture (5 wt%)	Reaction time (h)
CaSiO_3 -AA	–	24
CaSiO_3 -AA	Aragonite	24
CaSiO_3 -AA	Calcite	24
CaSiO_3 -AA	CaSiO_3 -AA-carb.	24
CaSiO_3 -1293 K	–	24
CaSiO_3 -1293 K	Aragonite	24
CaSiO_3 -1293 K	Calcite	24
CaSiO_3 -1293 K	CaSiO_3 -AA-carb.	24
CaSiO_3 -1293 K	CaSiO_3 -AA-carb.	48
CaSiO_3 -1293 K	CaSiO_3 -AA-carb.	72
CaSiO_3 -HCl	–	24
CaSiO_3 -HCl	Aragonite	24
CaSiO_3 -HCl	Calcite	24
CaSiO_3 -HCl	CaSiO_3 -AA-carb.	24
CaSiO_3 -HCl	CaSiO_3 -AA-carb.	48
CaSiO_3 -HCl	CaSiO_3 -AA-carb.	72
CaSiO_3 - CH_3COOH	–	24
CaSiO_3 - CH_3COOH	Aragonite	24
CaSiO_3 - CH_3COOH	Calcite	24
CaSiO_3 - CH_3COOH	CaSiO_3 -AA-carb.	24
CaSiO_3 - CH_3COOH	CaSiO_3 -AA-carb.	48
CaSiO_3 - CH_3COOH	CaSiO_3 -AA-carb.	72

Temperature (333 K) and pressure (~ 2 MPa) were constant

reactor. The temperature in steel reactors was adjusted by placing them in a drying chamber.

To determine carbonation and reactions rates educts and products were analyzed by PXRD and DSC–TG/MS.

2.2 Used materials

For the experiments, steel reactors with Teflon liners from Büchi AG were used. The used raw material (natural CaSiO_3 , calcium silicate, meta, reagent grade, < 20 μm powder) was supplied by Alfa Aeser (CaSiO_3 -AA). The chemical composition of the used raw material is given in Table 3 and an exemplary SEM image of the raw material is shown in Fig. 2.

The wollastonite raw material was treated before carbonation. Exemplary SEM images of the treated raw materials are given in Fig. 3a–c.

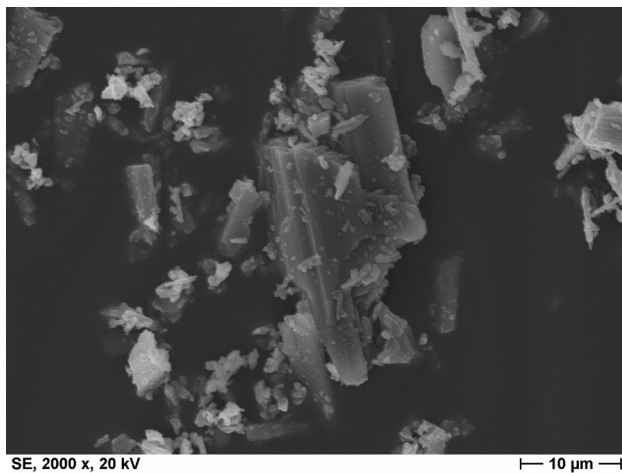
The pressure in the reactors was adjusted using an ISCO-pump (Teledyne ISCO, Model 500D Syring pump). CO_2 was supplied by Westfalen AG and had a purity of 4.5 (99.995%).

To investigate the influence of potential seed crystals on the carbonation reaction of wollastonite, three different

Table 3 Chemical composition of the used raw material determined by XRF (Siemens SRS 3000) [27]

Element (oxides)	Content (wt%; normalized)
SiO ₂	50.55
CaO	45.95
Fe ₂ O ₃	0.52
Al ₂ O ₃	0.52
MgO	0.17
MnO	0.13
TiO ₂	0.05
K ₂ O	0.03
SrO	0.01
LOI ^a	2.09
Total	100.02

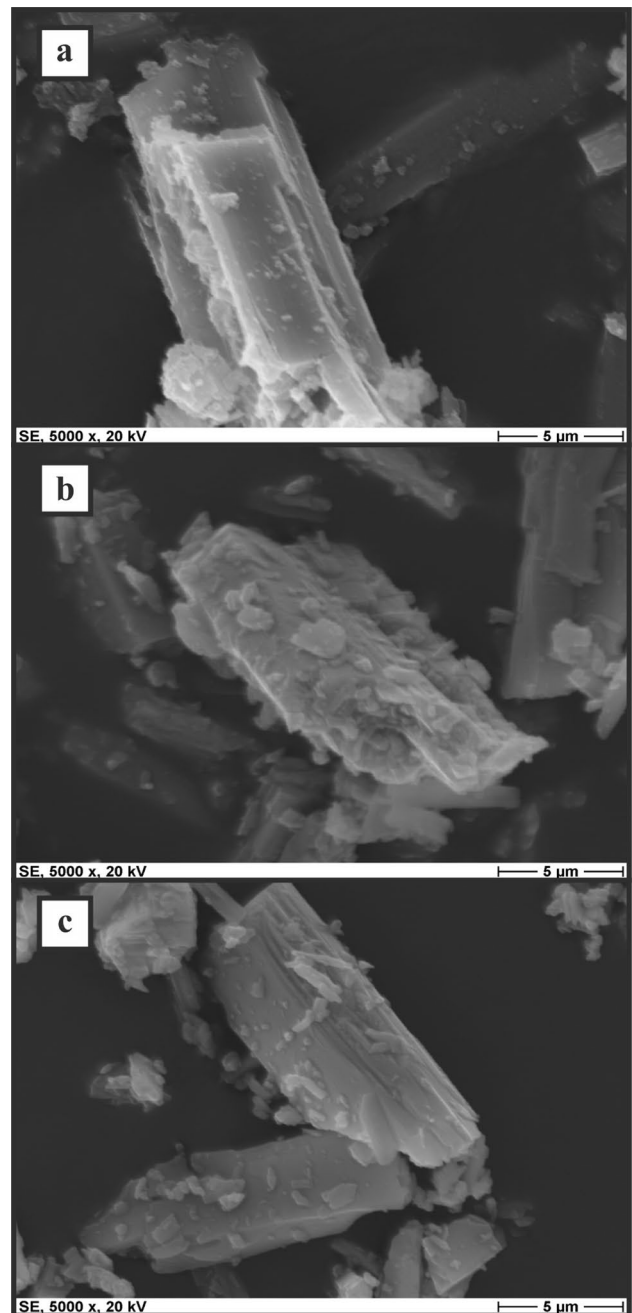
^aLOI: loss of ignition at 1323 K

**Fig. 2** Exemplary SEM image of the untreated wollastonite raw material (CaSiO₃-AA)

materials were used as admixtures in this study (Table 4 and Figs. 4, 5, 6, 7, 8, 9).

The first material, which functioned as potential seed crystals was a natural aragonite from Castilla-La Manche, Spain. PXRD-measurements with Rietveld analysis [22] showed only aragonite as crystalline phase (~65 wt%) and an amorphous content of ~35 wt% (Table 4 and Fig. 4). DSC-TG/MS measurements showed a CaCO₃ content of 98.9 wt%. Selected aragonite grains, used as potential seed crystals, are given in Fig. 5.

The second material, which functioned as potential seed crystals was a natural calcite from Bavaria, Germany. PXRD-measurements with Rietveld analysis [22] showed only calcite as crystalline phase (~84 wt%) and an amorphous content of ~17 wt% (Table 4 and Fig. 6). DSC-TG/MS

**Fig. 3** Exemplary SEM image of the wollastonite raw material. **a** treated with hydrochloric acid (CaSiO₃-HCl); **b** treated with acetic acid (CaSiO₃-CH₃COOH); **c** treated with temperature (CaSiO₃-1293 K)

measurements showed a CaCO₃ content of 100 wt%. An exemplary SEM image of the calcite grains, used as potential seed crystals is given in Fig. 7.

The third material, which functioned as potential seed crystals was a previously carbonated natural wollastonite (CaSiO₃-AA-carb; 24 h CO₂, 333 K). The raw material was supplied by Alfa Aeser. PXRD-measurements with

Table 4 Composition of the used admixtures determined using the Rietveld method [22] ($R_{wp} \sim 9\%$) and DSC–TG/MS measurements

Admixture	Calcite (wt%)	Aragonite (wt%)	Wollastonite (wt%)	Amorphous (wt%)	CaCO ₃ -TG (wt%)
Aragonite	–	64.9 ± 0.6	–	35.1 ± 0.6	98.9 ± 0.2
Calcite	83.5 ± 3.5	–	–	16.6 ± 3.5	100.0 ± 0.5
CaSiO ₃ -AA-carb.	23.5 ± 0.4	30.4 ± 0.2	3.0 ± 0.2	43.4 ± 0.2	54.6 ± 0.2

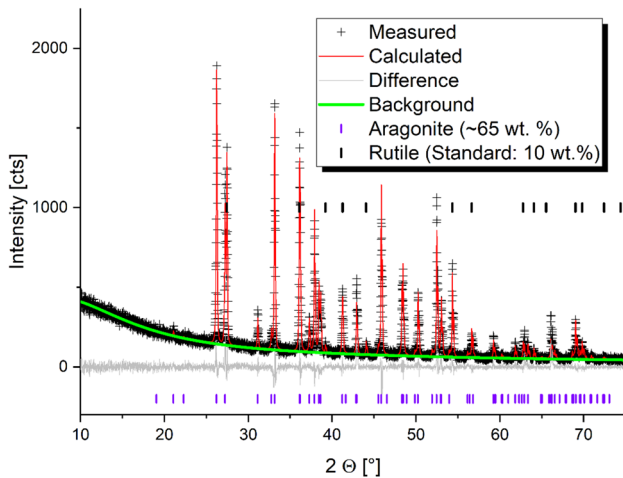


Fig. 4 PXRD with Rietveld analysis [22] of aragonite which was used as potential seed crystals

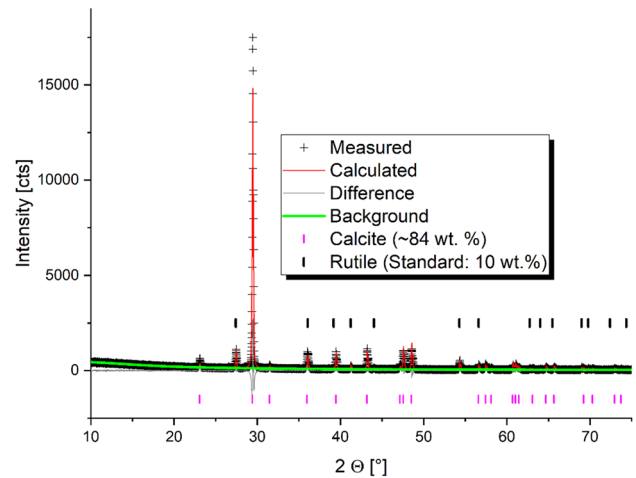


Fig. 6 PXRD with Rietveld analysis [22] of calcite which was used as potential seed crystal

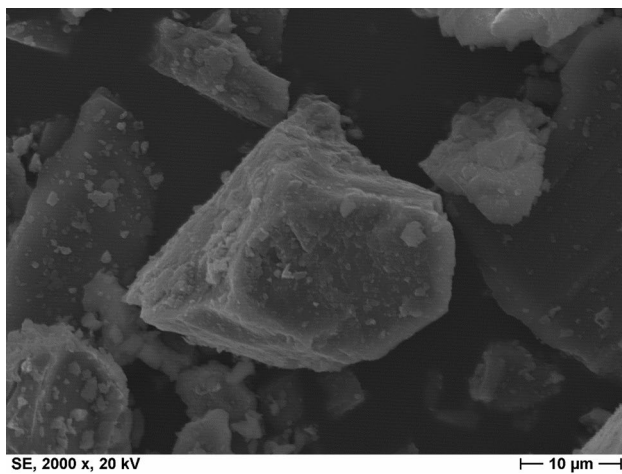


Fig. 5 SEM image of aragonite grains, used as potential seed crystals

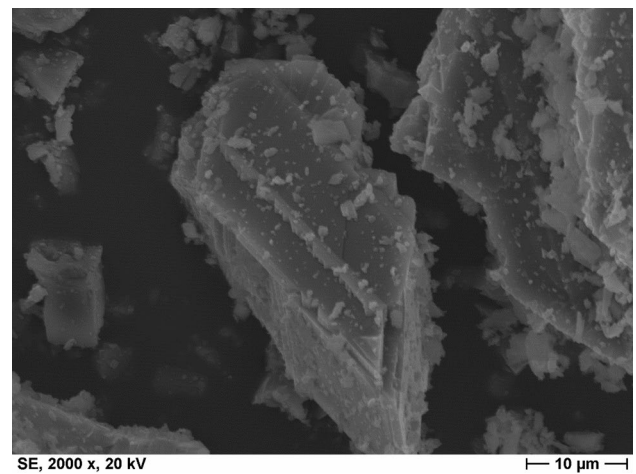


Fig. 7 Exemplary SEM image of calcite grains, used as potential seed crystals with apparent morphology

Rietveld analysis [22] showed three crystalline phases (calcite, ~ 24 wt%; aragonite, ~ 30 wt%; wollastonite, 3 wt%) and an amorphous content of ~ 43 wt% (Table 4 and Fig. 8). DSC–TG/MS measurements showed a CaCO₃

content of 54.6 wt%. The raw material was carbonated analogue to the experimental setup in this study and the work of Svensson et al. (333 K, 2 MPa, 24 h reaction time,

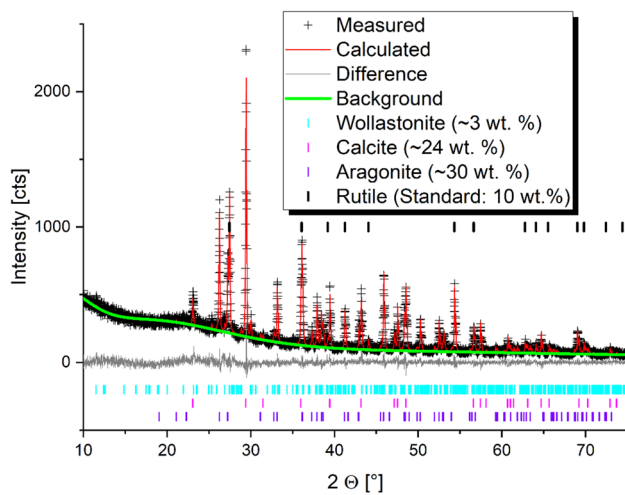


Fig. 8 PXRD with Rietveld analysis [22] of carbonated wollastonite (carbonated at 333 K, 2 MPa, with 24 h reaction time) which was used as potential seed crystal

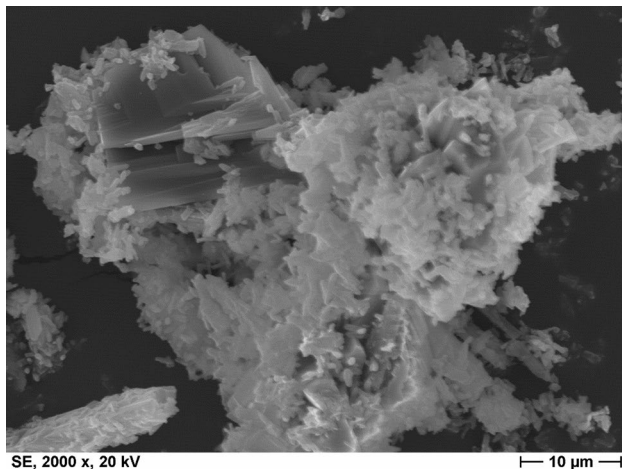


Fig. 9 Exemplary SEM image of carbonated wollastonite, used as potential seed crystals

[26–29]. An exemplary SEM image of the potential seed crystals is given in Fig. 9.

3 Results and discussion

The reaction kinetics of the carbonation of wollastonite depends on the temperature. Several carbonation experiments at different temperatures (296 K, 303 K, 313 K, 323 K, 333 K) were performed, to investigate the reaction kinetics of the carbonation reaction of wollastonite.

To investigate the influence of seed crystals on the carbonation reaction of wollastonite, several experiments

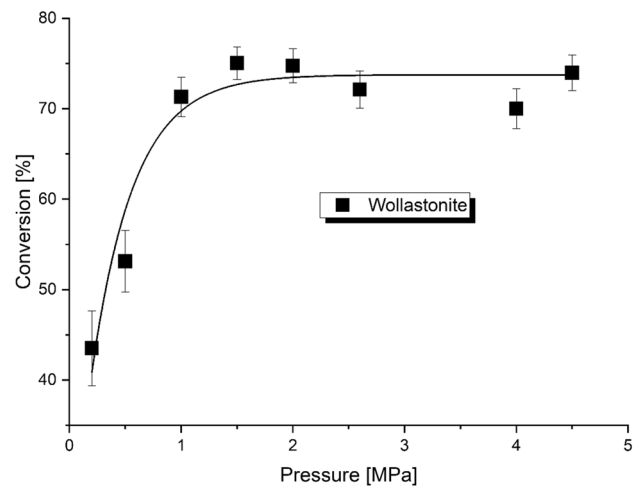


Fig. 10 Conversion of wollastonite dependent on pressure [27]

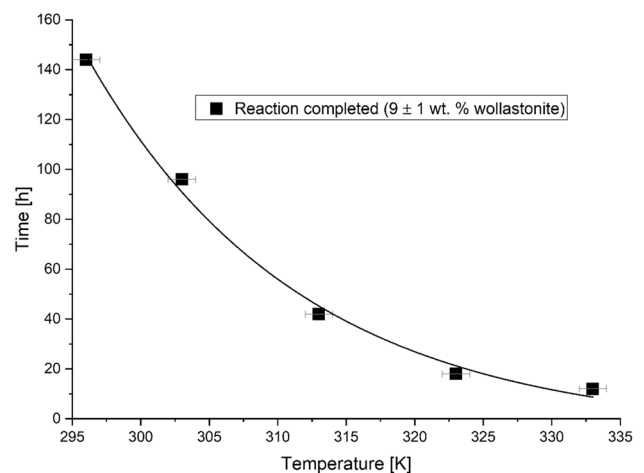


Fig. 11 Temperature-dependency of wollastonite conversion. The reaction time, until 9 ± 1 wt.% of wollastonite was reached, was 144 h at 296 K, 96 h at 303 K, 42 h at 313 K, 24 h at 323 K and 18 h at 333 K

with aragonite, calcite and previously carbonated wollastonite were performed (Fig. 1 and Table 2).

3.1 Reaction kinetics of the carbonation of wollastonite

The reaction kinetics of the carbonation of wollastonite depends on the temperature. The impact of pressure was less pronounced, considering CCS application pressure (Figs. 6, 10).

With increasing temperature, the reaction time decreased and the conversion of wollastonite fits an exponential curve (Fig. 11). Following the shrinking core model [1] and the results of Svensson et al. [27], a full conversion of wollastonite cannot be reached within the observed

experimental period. A fix point of wollastonite content (~ 10 wt%) had to be chosen to compare the different reaction times at different temperatures.

3.2 Carbonation of differently treated wollastonite with admixtures

The raw material was treated differently before carbonation (untreated: CaSiO₃-AA; temperature (1293 K):

CaSiO₃-1293 K; hydrochloric acid: CaSiO₃-HCl; acetic acid: CaSiO₃-CH₃COOH). Table 5 summarizes the results of the carbonation of wollastonite (treated and untreated) using Rietveld analysis.

In Table 6 the newly formed calcite and the newly formed aragonite, measured by the Rietveld method [22], is presented. The newly formed content of calcite and aragonite was calculated subtracting the initial content from the content in the product.

Table 5 PXRD results of the performed carbonation experiments (24 h reaction time, 333 K, ~ 2 MPa CO₂ pressure, aqueous conditions)

Raw material	Admixture (5 wt%)	Calcite (wt%)	Aragonite (wt%)	Wollastonite (wt%)	Amorphous (wt%)
CaSiO ₃ -AA	–	27.4 ± 1.5	23.8 ± 0.6	3.9 ± 0.9	45.7 ± 2.2
CaSiO ₃ -AA	Aragonite	23.2 ± 1.2	26.9 ± 2.7	2.8 ± 0.3	47.1 ± 2.4
CaSiO ₃ -AA	Calcite	27.4 ± 0.8	21.0 ± 1.3	2.8 ± 0.1	49.0 ± 2.1
CaSiO ₃ -AA	CaSiO ₃ -AA-carb.	28.1 ± 1.0	20.1 ± 0.7	2.7 ± 0.1	49.1 ± 1.0
CaSiO ₃ -1293 K	–	25.1 ± 3.8	0.5 ± 0.2	9.2 ± 0.2	65.1 ± 3.8
CaSiO ₃ -1293 K	Aragonite	22.8 ± 3.6	2.0 ± 0.5	8.5 ± 0.7	66.4 ± 3.6
CaSiO ₃ -1293 K	Calcite	21.6 ± 1.3	0.3 ± 0.1	8.2 ± 0.6	69.8 ± 1.7
CaSiO ₃ -1293 K	CaSiO ₃ -AA-carb.	24.7 ± 1.2	1.9 ± 0.3	7.9 ± 0.5	65.6 ± 1.1
CaSiO ₃ -HCl	–	22.9 ± 2.4	0.3 ± 0.2	2.2 ± 0.6	74.5 ± 1.8
CaSiO ₃ -HCl	Aragonite	17.2 ± 1.7	6.3 ± 0.8	2.1 ± 0.5	74.4 ± 2.5
CaSiO ₃ -HCl	Calcite	22.4 ± 2.9	0.6 ± 0.1	2.1 ± 1.2	74.9 ± 3.0
CaSiO ₃ -HCl	CaSiO ₃ -AA-carb.	17.1 ± 3.0	9.0 ± 0.5	2.2 ± 0.6	69.7 ± 3.4
CaSiO ₃ -CH ₃ COOH	–	28.8 ± 2.6	0.5 ± 0.2	6.2 ± 0.5	64.5 ± 2.9
CaSiO ₃ -CH ₃ COOH	Aragonite	18.3 ± 0.5	5.1 ± 0.6	4.8 ± 0.8	71.7 ± 1.0
CaSiO ₃ -CH ₃ COOH	Calcite	21.2 ± 1.4	0.5 ± 0.1	4.9 ± 0.6	73.4 ± 2.0
CaSiO ₃ -CH ₃ COOH	CaSiO ₃ -AA-carb.	19.0 ± 2.8	7.1 ± 0.9	2.8 ± 1.3	71.1 ± 4.9

Composition determined using the Rietveld method [22] (R_{wp} ~ 9%)

Table 6 Newly formed calcite and aragonite for each raw material and admixture

Raw material	Admixture (5 wt%)	Initial content		Newly formed calcite (wt%)	Newly formed aragonite (wt%)
		Calcite (wt%)	Aragonite (wt%)		
CaSiO ₃ -AA	–	1.9 ± 0.2	1.0 ± 0.5	25.6 ± 1.7	22.8 ± 1.1
CaSiO ₃ -AA	Aragonite	1.9 ± 0.2	6.4 ± 0.2	21.4 ± 1.3	20.5 ± 2.9
CaSiO ₃ -AA	Calcite	7.1 ± 0.2	1.0 ± 0.2	20.3 ± 1.0	20.0 ± 1.5
CaSiO ₃ -AA	CaSiO ₃ -AA-carb.	3.3 ± 0.2	2.3 ± 0.2	24.8 ± 1.2	17.8 ± 0.9
CaSiO ₃ -1293 K	–	0.7 ± 0.2	0	24.4 ± 4.0	0.5 ± 0.2
CaSiO ₃ -1293 K	Aragonite	0.7 ± 0.2	5.5 ± 0.2	22.1 ± 3.7	-3.3 ± 0.7
CaSiO ₃ -1293 K	Calcite	5.8 ± 0.2	0	15.8 ± 1.5	0.3 ± 0.1
CaSiO ₃ -1293 K	CaSiO ₃ -AA-carb.	2.1 ± 0.2	1.2 ± 0.2	22.6 ± 1.4	0.7 ± 0.5
CaSiO ₃ -HCl	–	0.5 ± 0.1	0.4 ± 0.1	28.3 ± 2.7	0.1 ± 0.3
CaSiO ₃ -HCl	Aragonite	0.5 ± 0.1	5.5 ± 0.2	16.7 ± 1.8	0.8 ± 1.0
CaSiO ₃ -HCl	Calcite	5.9 ± 0.2	0.4 ± 0.1	16.5 ± 3.1	0.2 ± 0.2
CaSiO ₃ -HCl	CaSiO ₃ -AA-carb.	2.0 ± 0.2	1.7 ± 0.2	15.1 ± 3.2	7.3 ± 0.7
CaSiO ₃ -CH ₃ COOH	–	0.6 ± 0.1	0.2 ± 0.3	22.3 ± 2.5	0.2 ± 0.5
CaSiO ₃ -CH ₃ COOH	Aragonite	0.6 ± 0.1	5.5 ± 0.2	17.7 ± 0.6	-0.4 ± 0.8
CaSiO ₃ -CH ₃ COOH	Calcite	5.7 ± 0.2	0.2 ± 0.3	15.5 ± 1.6	0.4 ± 0.4
CaSiO ₃ -CH ₃ COOH	CaSiO ₃ -AA-carb.	2.0 ± 0.2	1.4 ± 0.2	17.0 ± 3.0	5.7 ± 1.1

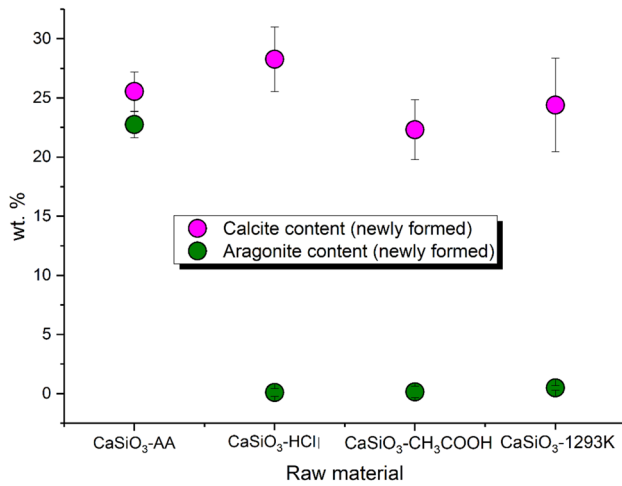


Fig. 12 Newly formed aragonite (green) and calcite (magenta) during the carbonation of wollastonite

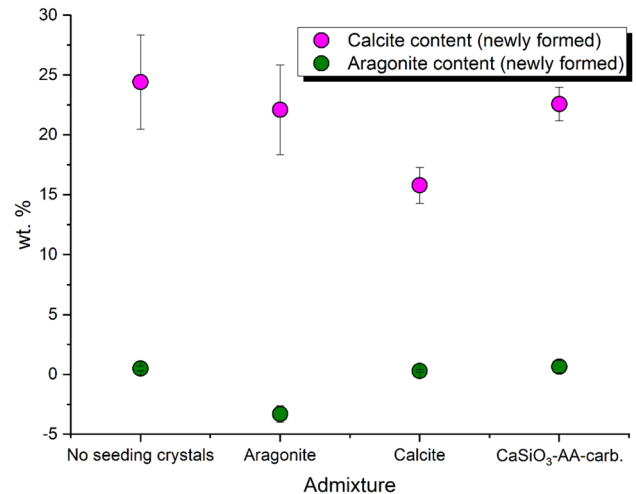


Fig. 14 Newly formed aragonite (green) and calcite (magenta) during the carbonation of thermally treated (1293 K) wollastonite

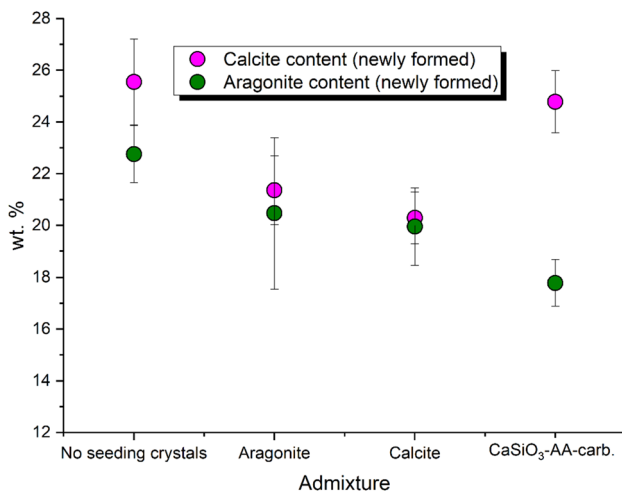


Fig. 13 Newly formed aragonite (green) and calcite (magenta) during the carbonation of untreated wollastonite

As described by Svensson et al. [26–29] the purified wollastonite (acetic acid: CaSiO₃-CH₃COOH; hydrochloric acid: CaSiO₃-HCl; temperature: CaSiO₃-1293 K) showed no newly formed aragonite after carbonation (Table 6). The reference experiment, where untreated wollastonite raw material (CaSiO₃-AA) was used for carbonation, showed aragonite formation (Table 6 and Fig. 12).

In the first set of experiments (cf. Figure 1 and Tables 2, 5) the carbonation of untreated raw material was investigated. In Fig. 13 the amount of newly formed calcite and aragonite is presented. Using potential seed crystals, newly formed aragonite was observed (Fig. 13). The highest amounts of calcite and aragonite formations were observed, using untreated wollastonite raw material (CaSiO₃-AA) with no seed crystals.

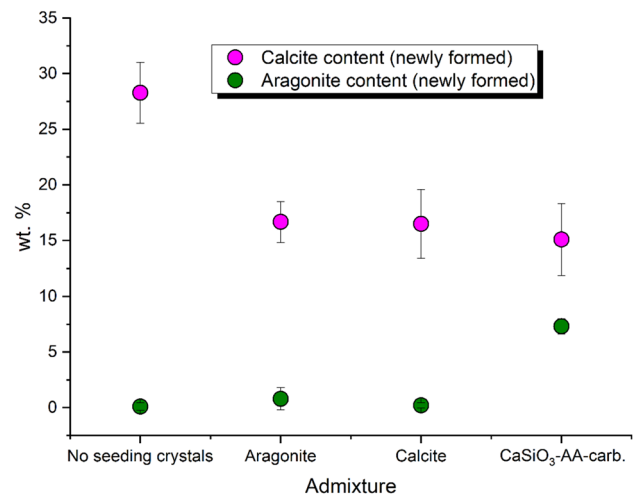


Fig. 15 Newly formed aragonite (green) and calcite (magenta) during the carbonation of wollastonite, treated with hydrochloric acid (HCl, 10%)

In the second set of experiments (cf. Figure 1 and Tables 2, 5) the carbonation of thermally treated (1293 K) wollastonite as raw material was investigated. Using potential seed crystals showed no newly formed aragonite (Fig. 14).

In the third set of experiments (cf. Figure 1 and Tables 2, 5) the carbonation of wollastonite treated with hydrochloric acid as raw material was investigated. Using natural aragonite (Castilla–La Manche, Spain) and natural calcite (Bavaria, Germany) as potential seed crystals showed no newly formed aragonite (Fig. 15). However, adding previously carbonated wollastonite (24 h-CO₂, 333 K, 2 MPa) as potential seed crystals showed newly formed aragonite (7.3 ± 0.7 wt%).

In the fourth set of experiments (cf. Figure 1 and Tables 2, 5) the carbonation of wollastonite, treated with acetic acid as raw material was investigated. Using natural aragonite (Castilla-La Manche, Spain) and natural calcite (Bavaria, Germany) as seed crystals, no newly formed aragonite (Fig. 16) was found. However, adding previously carbonated wollastonite (24 h-CO₂, 333 K, 2 MPa) as potential seed crystals showed newly formed aragonite (5.7 ± 1.1 wt%).

Carbonation experiments on differently treated wollastonite raw material (temperature, hydrochloric acid, acetic acid) and different reaction times (24 h, 48 h, 72 h) were performed (Tables 2, 7 and Fig. 17).

To each treated raw material, 5 wt% of potential seed crystals of previously carbonated wollastonite was added before carbonation.

With increased reaction time the content of newly formed aragonite increased (Fig. 17, magenta), while the

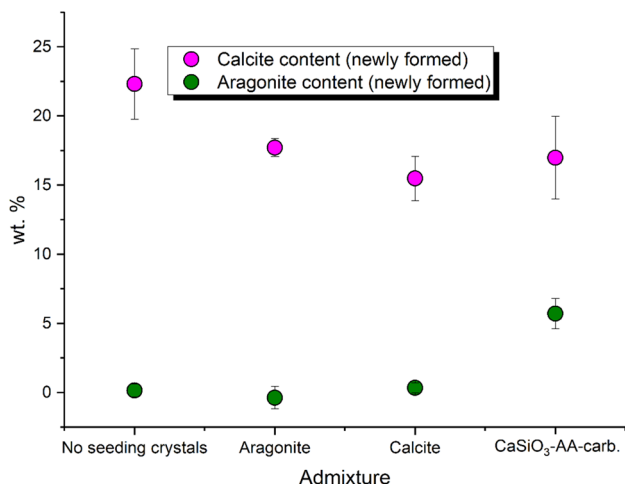


Fig. 16 Newly formed aragonite (green) and calcite (magenta) during the carbonation of wollastonite (treated with CH₃COOH, 20%)

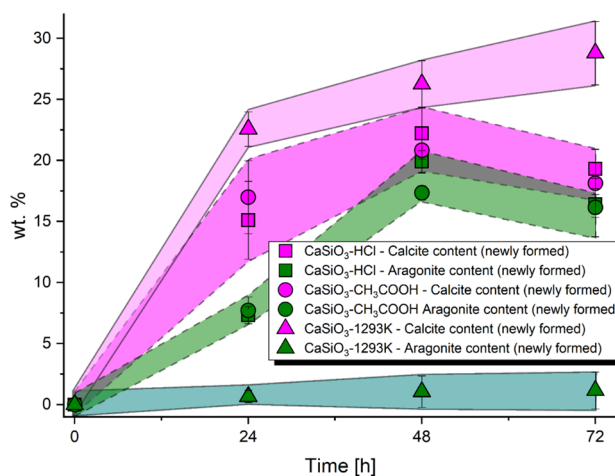


Fig. 17 Newly formed aragonite (green) and calcite (magenta) after carbonation of three differently treated wollastonite raw materials. Treatment 1: HCl, 10%—squares; Treatment 2: CH₃COOH, 20%—circles; Treatment 3: temperature, 1293 K—triangles

amorphous content decreased (Table 7 and Fig. 18). A different behavior could be observed by the raw material treated with temperature (1293 K) before adding seed crystals and before carbonation. Even after 72 h reaction time, no significant formation of aragonite was observed (Table 7 and Fig. 17, green triangles).

In Fig. 18 the amount of CaCO₃ (determined by TG measurements, cyan) is compared with the sum of calcite and aragonite (Rietveld analysis, red) and the amorphous content (Rietveld analysis, black). The amount of CaCO₃ measured by TG stayed more or less constant with increasing reaction time (Fig. 18, cyan). The sum of calcite and aragonite, determined by Rietveld analysis, increased with increasing reaction time (Fig. 18, red). The amount of measured X-ray amorphous content, determined by Rietveld analysis, decreased with increasing reaction time (Fig. 18, black).

Table 7 Results of the performed carbonation experiments (333 K, ~ 2 MPa CO₂ pressure, aqueous conditions) using different raw materials and reaction times

Raw material with CaSiO ₃ -carb.	Reaction time (h)	Calcite (wt%)	Aragonite (wt%)	Wollastonite (wt%)	Amorphous (wt%)
CaSiO ₃ -1293 K	24	24.7 ± 1.2	1.9 ± 0.3	7.9 ± 0.5	65.6 ± 1.1
CaSiO ₃ -1293 K	48	28.4 ± 1.7	2.3 ± 1.1	6.9 ± 0.3	62.5 ± 2.5
CaSiO ₃ -1293 K	72	30.9 ± 2.4	2.4 ± 1.3	7.3 ± 0.6	59.4 ± 3.0
CaSiO ₃ -HCl	24	17.1 ± 3.0	9.0 ± 0.5	4.2 ± 0.4	69.7 ± 3.4
CaSiO ₃ -HCl	48	24.1 ± 1.9	21.5 ± 0.7	3.1 ± 1.7	51.3 ± 3.3
CaSiO ₃ -HCl	72	21.2 ± 1.4	18.0 ± 0.6	2.9 ± 0.8	57.9 ± 1.7
CaSiO ₃ -CH ₃ COOH	24	19.0 ± 2.8	7.1 ± 0.9	2.8 ± 1.3	71.1 ± 4.9
CaSiO ₃ -CH ₃ COOH	48	22.8 ± 1.7	18.7 ± 0.4	2.4 ± 0.4	56.1 ± 2.2
CaSiO ₃ -CH ₃ COOH	72	20.1 ± 2.6	17.5 ± 2.2	3.0 ± 0.6	59.3 ± 3.3

Composition determined using the Rietveld method [22] (R_{wp} ~ 9%)

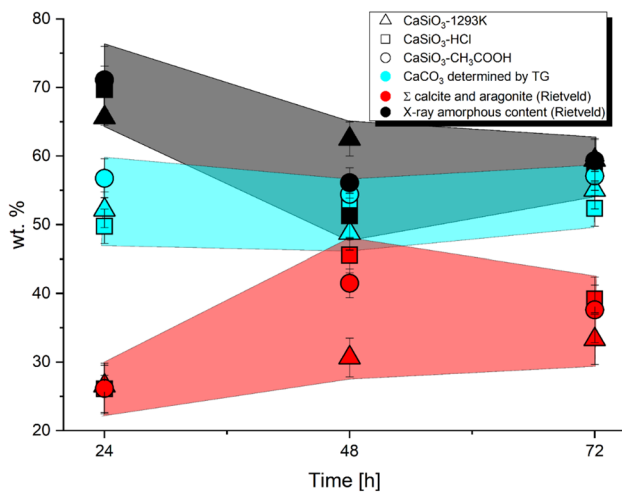


Fig. 18 Comparison of formation of calcite and aragonite (Rietveld method, red) and the general formation of CaCO₃ (determined by TG measurements, cyan) after carbonation of three differently treated raw materials. Treatment 1: HCl, 10%—squares; Treatment 2: CH₃COOH, 20%—circles; Treatment 3: temperature, 1293 K—triangles

4 Conclusions

This study showed the possible use of wollastonite as cementitious material in sealing boreholes in CO₂-rich environments. For example, the material will be pumped directly into the borehole, where the carbonation reaction will cause the sealing of the borehole. Currently a cementitious materials based on wollastonite and rankinite is used to produce precast modules [14, 15, 23, 25]. The reaction products will be stable in CO₂-rich environments and the cementitious material, based on wollastonite, will be one of the needed environmental green products, which are CO₂ neutral. The production of wollastonite will, compared to the production of C₃S and C₂S, produce less CO₂ (Table 1) [20] and during the carbonation reaction, additional CO₂ will be consumed.

The conversion-diagram of wollastonite dependent on temperature was completed (Fig. 11) [27]. At temperatures below 303 K the carbonation reaction of wollastonite was rather slow (96 h to 144 h). Above 313 K the reaction rate increased strongly and the reaction time was reduced drastically (42 h to 12 h). The conversion of wollastonite follows an exponential curve.

If wollastonite will be used as cementitious material, the carbonation reactions have to be understand and investigated. Therefore, the carbonation reactions of previously treated wollastonite with and without potential seed crystals were analyzed. The use of natural aragonite as potential seed crystal did not increase the content of aragonite (Table 6 and Figs. 13, 14, 15, 16). However, using previously

carbonated wollastonite as potential seed crystal led to newly formed aragonite in wollastonite raw material, treated with hydrochloric acid and acetic acid (Table 6 and Figs. 13, 14, 15, 16). Therefore, the assumption, that aragonite functioned as seed crystal could be confirmed in this study.

However, natural formed aragonite does not lead to further aragonite formation. A possible explanation for this behavior might be the conditions aragonite is formed in nature. The natural aragonite was formed at conditions (333 K, 500 MPa) [24], which did not reflect the experimental conditions in the steel reactors (333 K, 2 MPa). The aragonite formed in the reactors probably was metastable and formed only because of the presence of metastable aragonite as well. Conditions at which aragonite will form naturally were not established during the experiments. Therefore, it was assumed that, if a material should function as seed crystal, it is necessary to meet the conditions of formation. Otherwise the used material will not form new phases.

Carbonation experiments with carbonated wollastonite as admixture, different purification methods (Temperature, acetic acid and hydrochloric acid) and varied reaction times (24 h, 48 h and 72 h) showed the formation of aragonite out of the amorphous content with increasing reaction time (Table 7 and Figs. 17, 18).

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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