Acta Polytechnica CTU Proceedings **53**:28–32, 2025
https://doi.org/10.14311/APP.2025.53.0028

Published by the Czech Technical University in Prague

CARBONIZABLE CALCIUM SILICATES BY CO_2 ATMOSPHERE IN A PRESSURE CHAMBER

Andrea Jančíková*, Michal Křištof, Karel Dvořák

Brno University of Technology, Faculty of Civil Engineering, Veveří 331/95, 602 00 Brno, Czech Republic

* corresponding author: andrea.jancikova@vut.cz

Abstract. The paper deals with the possibility of different calcium silicate minerals namely wollastonite (CS), belite (C_2S), and rankinite (C_3S_2) on their curing in CO_2 atmosphere. It describes the laboratory preparation of these individual minerals from p.a. pure chemical clean materials. For comparison a representative sample of natural mined wollastonite was chosen for carbonation as well. Following this, for setting basic parameters analyses determining the properties of the samples by XRD analysis and Rietveld evaluation, particle size characterization by laser granulometry and milling fineness by the Blaine method. It also addresses the issue of forming samples suitable for carbonation using a hydraulic press and the actual curing and conditions necessary for carbonation of the minerals in pressure chamber. It summarizes the measured results of compressive strengths, weight changes and mineralogical evaluation of the composition of the samples before and after carbonation. In the conclusion, together with a summary of the measured findings, it is pointed out what direction further research in this field should be aimed for.

Keywords: CO_2 carbon curing, calcium silicate minerals, belite (C_2S), wollastonite (CS), rankinite (C_3S_2).

1. Introduction

Belite cements, as a low-carbon material for concrete construction and components, are attracting increasing attention of the research world-wide. This is not only because of their relatively low energy consumption, but also because belite clinkers and cements with higher belite content offer higher resistance of the matrix to weather conditions, which can extend the service length. This ensures longer durability for the smaller concrete products such as concrete pavers and tiles compared to traditional Portland cement, which is responsible for 7–9 % of global man-made CO_2 emissions nowadays [1, 2].

Unlike conventional Portland clinker, which is the most widely used cement worldwide, belitic cement is made up of 40–60 % belite, replacing alite mineral. The industrial production of belitic clinkers requires the same raw materials as Portland cement, but in a different proportion, which contributes to sustainability. The ideal sintering temperature for belite clinkers is approximately 1 250–1 350 °C, which is about 100–200 °C lower than to produce Portland clinker. This lower firing temperature leads to a reduction in fuel consumption. The production of belite cement uses on average 15-20 % less energy than the production of Portland cement [1–4].

However, the energy savings are slightly compensated by the more difficult milling process, which consumes approximately 10 % more energy than Portland clinker. Overall, the total energy savings are in the range of 5–10 %. However, this energy saving is insufficient if the fact that belitic cement, without treatment, has very long and slow strength development and develops very low hydration heat [2–5].

This issue is currently being studied extensively and it can be partially avoided by various modifications to the final concrete component. To increase the early strengths of belitic cement, some methods are currently being studied. These are mainly ionic doping of clinker with foreign ions, implementation of nanomaterials into the matrix, curing of the material at higher temperature and humidity and carbonation curing of β and γ-C_2S cements in CO_2 atmosphere. Belite appears in several forms under atmospheric pressure: α (hexagonal), αH', αL' (orthorombic), β (monoclinic) and γ (orthorombic) [2, 3, 6].

These forms have a very similar arrangement of Ca^{2+} and SiO^{4-} ions, except for γ-C_2S, which has a different structure. The β form is the most common in industrial clinkers. As mentioned β-belite is very difficult to mill, but when β is transformed into γ-C_2S it expands by up to 13 %, leading to a phenomenon called "dusting" where the material spontaneously breaks down. This transformation can be prevented by rapid cooling or the use of stabilisers and is widely used today in Portland clinker where gamma γ-C_2S is unwanted [4, 7, 8].

On the other hand, it is a very desirable mineral for carbonation curing. Among calcium silicates, γ-dicalcium silicate (γ-C_2S) is theoretically relatively easy to sinter. The high-temperature α-C_2S can spontaneously turn into γ-C_2S powder during cooling, reducing the energy needed for milling. The reactivity of γ-C_2S with CO_2 has been explored as a potential low-carbon building material. Research showed that γ-C_2S, after carbonation for two hours at 0.2 MPa, can

absorb up to 18.3 % CO_2 and achieve a compressive strength of 36.4 MPa. Carbonation forms $CaCO_3$ as the main product, along with amorphous silicate structures identified through nuclear magnetic resonance (NMR) [8–10].

For CO_2 curing of belite and other calcium silicate-based minerals, crucial very specific properties of the curing environment must be achieved. These are mainly the amount of water required to prepare the sample (water coefficient), sample pressing pressure, cement particle size and specific surface area, relative humidity of the curing atmosphere, temperature and CO_2 concentration [1–4].

According to the carbonation mechanism, moisture acts as a solvent and is critical in carbonation reactions. The ratio of water to solid material (w/s) has a significant effect on the dissolution of Ca^+ ions and the diffusion of CO_2 because determines the thickness of the water coating adsorbed on the particle surface. On other hand low w/s ratio can retard Ca^+ ions dissolution and the diffusion of CO_2 in due to the very thin water coating on the mineral surface. On the other hand, high w/s ratio may slow down the penetration of ions and slower the rate of CO_2 diffusion into structure [3–5, 7].

Particle size is an internal parameter that significantly influences the rate and efficiency of carbonation. It is generally accepted that finer mineral particle size increases the surface area available for reaction with CO_2, promotes reaction and space for dissolution of Ca^+ ions on mineral particles and increases the rate of carbonation. However, ultrafine particles may reduce the speed of carbonation. Previous studies have suggested that ultrafine particle size significantly increases the degree of carbonation in the first moment due to the quick formation of carbonate precipitate, which later prevents the particles from encountering water and CO_2 needed for continuation of the process [5–7].

Like the water to solid ratio, relative humidity significantly influences the carbonation efficiency of calcium minerals by affecting water saturation in the pores and capillaries of the materials. The optimum relative humidity content is between 50 to 70 %, when the highest rate of carbonation is achieved [4–8].

All these special conditions need to be investigated individually, along with the question of which of the minerals is relatively easy to produce in the laboratory conditions. Then successfully carbonate it to achieve appropriate compressive strengths. This issue of the preparation of individual minerals and their carbonation under the same conditions is dealt with in this article.

2. Material and methods

2.1. Preparation of raw material powders

The mixtures for belite, wollastonite and rankinite samples were prepared from $CaCO_3$ and SiO_2. Calcium carbonate ($CaCO_3$, p.a. purity, Penta, Praha, Czech Republic), Silicon dioxide, (SiO_2, p.a. purity, Penta, Praha, Czech Republic). Raw powder materials were prepared according to the required CaO: SiO_2 stoichiometry ratio of 1:1 for wollastonite, 2:1 for belite and repetitively 3:2 for rankinite. Due to the requirement of high purity raw material to produce raw powder and proper solid-phase reaction, the loss on ignition (LOI) was carried out on SiO_2. The SiO_2 was milled at dry first in a FRITSCH PULVERISETTE 6 planetary mill in an agate 500 ml milling bowl with 25 agate milling balls. Mill was set at 350 rpm for 1 min. The firing itself was carried out at a temperature of 1 000 °C for 60 minutes. After firing, LOI of SiO_2 was measured to be 1.27 %.

The 160 g of those raw materials in the proper ratios were first dry mixed by hand in a laboratory porcelain bowls. Afterwards transferred to a 500 ml agate milling bowl with 25 grinding balls with a diameter of 20 mm. Wet milling was carried out in 180 ml of water in a planetary mill (FRITSCH PULVERISETTE 6). Mill was set at 350 rpm for 10 min. After milling, the suspension was poured back into a clean laboratory bowl and placed in a laboratory dryer (BINDER C 170) at 105 °C for 24 hours. During drying the nodules 10–15 mm in diameter were formed spontaneously.

2.2. Firing procedure

In the next step, a series of two-step firings were carried out in a superkhantal furnace (CLASSIC 2017 S). The samples were placed in platinum crucibles with different volumes ranging from 40 to 120 ml.

For belite, the first step firing was set to 900 °C for 60 min with a ramp of 8 °C min^{-1}. During this step calcination of $CaCO_3$, change in volume and increase in reactivity occurs. In the second step, the actual solid phase reaction between CaO and SiO_2 takes place at 1 450 °C for 60 min. During the production of gamma belite, the sample was left in the furnace and spontaneously cooled to 400 °C. The sample was heated to this temperature for 12 hours to ensure the conversion of beta belite to gamma belite. The samples were then slowly cooled to laboratory temperature.

For wollastonite, the first step was the same as for belite and in second step the temperature was set at 1 100 °C for 120 min. Samples were then spontaneously cooled in the furnace.

For rankinite, the first step was the same as for belite and in second step the temperature was set at 1 450 °C for 600 min. Samples were then spontaneously cooled in the furnace.

The samples were divided and prepared for the related analyses. Stored in labelled (PE) bags.

2.3. Sample preparation for XRD analysis

Samples selected for XRD analysis were milled in a vibratory disc mill (RS 200, Retsch, Haan, Germany)

at 1 100 rpm for 20 s. After that, 5 g of powder sample was milled to the required fineness for X-ray analysis in a mill (McCrone Micronising Mill, Glen Creston, London, UK) for 150 s in 15 ml of isopropanol.

The XRD analysis was performed using a multifunctional diffractometer (XRD, Empyrean, PANalytical B.V., Almelo, The Netherlands). The θ-θ reflection Bragg–Brentano para focusing geometry device is equipped with a Cu anode ($\lambda = 1.54184$ Å), programmable divergence slits, and a PIXcel3D detector (Empyrean, PANalytical B.V., Almelo, The Netherlands) The purity of the samples was verified via XRD using the Rietveld method. The ICSD database (released in 2012) was used to qualitatively analyse the diffraction patterns.

2.4. Particle size characterisation

Particle characterization was performed on untreated samples immediately after firing and cooling by a Malvern Mastersizer 2000 laser granulometry (Malvern Panalytical Ltd., Malvern, UK) with a hydro 2000 G fluid dispersion unit, using propan-2-ol as the dispersing agent was used for determining the granulometry. For natural wollastonite, the granulometry was checked both before and after milling of the sample.

2.5. Specific weight and specific surface area

The same samples as for particle characterization were also tested for specific weight by the AccuPyc II 1340 helium pycnometer and specific surface area by the Blaine method using the ZEB PC Blaine STAR automatic apparatus.

2.6. Preparation of carbonizable samples

The 80 g of sample and 8.8 g of water were hand-mixed in laboratory bowl and then inserted into a cylindrical mould adapted for hydraulic pressing. The filled cylinder was placed in a hydraulic press and loaded with 10 MPa pressure for 30 seconds. in the first step. In the second step the pressure was interrupted for 30 seconds. In the third step, the sample was again loaded with a pressure of 16 MPa for 120 seconds. The produced solid samples were weighed and placed in the carbonization chamber.

2.7. Carbonation and compressive strength test

The chamber was set to a pressure of 0.6 MPa, the humidity in the chamber was above 70 % and the CO_2 concentration was almost 100 %. The samples were left in these conditions for 24 hours. Due to the small amount of water in the samples, a wet sponge was also inserted into the chamber to increase the in the chamber.

After the carbonization process was completed, the samples were removed from the chamber, weighed and their diameter and height were measured using a calliper. These values were entered into a software that recorded the deformation of the solids during the application of the compressive force. The specimens were placed in a press and loaded at a constant rate until failure. The software automatically converted the maximum loading force to deformation.

The fractured specimens after the compressive strength test were ground in a rotary disc mill for XRD and DTA analysis.

3. Results and discussion

To compare the different powder materials, natural mined wollastonite was added to the laboratory created belite, wollastonite and rankinite samples prepared according to previous chapter material and methods. For the carbonation, the aim was to achieve the most similar properties of the samples by milling, both in terms of granulometry and fineness of milling, to be able to clearly compare the different minerals and their ability to carbonate under the same conditions. Table 1 summarizes the granulometry measurement of minimum d(0.1), mean d(0.5) and maximum d(0.9) particle size of the suspension. Measured by the wet method in propan-2-ol.

n	Label	d(0.1)	d(0.5)	d(0.9)
1	Belite	1.771	14.275	68.622
2	Lab. Wollastonite	1.539	6.618	16.439
3	Nat. Wollastonite	2.273	11.586	39.512
4	Rankinite	3.183	9.333	27.523

Table 1. Results of particle characterisation by laser granulometry.

The fineness of the belite has been considered as a reference because it is determined by the process of converting beta belite to gamma belite during firing and cooling. The other minerals produced, and the natural wollastonite were treated by grinding and their resulting granulometry was slightly finer.

The specific weight and milling fineness of the individual samples are given in Table 2. From the measured values it can be concluded that the samples had very similar specific weights, which differed between the highest and lowest values only by approx. 6 %. Determination of the specific surface area was necessary to perform any additional milling of the samples and to achieve a specific surface area as similar as possible for all samples.

n	Label	ρ [g cm^{-3}]	[cm^{-2} g]
1	Belite	2.9954	4 600
2	Lab. Wollastonite	3.0827	5 300
3	Nat. Wollastonite	3.0451	5 500
4	Rankinite	3.0829	4 100

Table 2. Results of specific weight and milling fineness (specific surface area).

It can be stated that the achieved specific surface area of the samples, apart from the natural wollastonite, did not need to be modified. The original specific surface of natural wollastonite was $3\,500\,cm^2\,g^{-1}$. This sample was milled to a finer specific surface of $5\,500\,cm^2\,g^{-1}$. Table 3 shows the mineral content of each sample before the carbonation process, measured by XRD Rietveld analysis in software HighScore plus 4.1.

Label	**1**	**2**	**3**	**4**
γ-C_2S	62.3	-	-	39.1
β-C_2S	35.9	69.8	0.0	25.2
C_3S	1.8	-	-	-
Wollastonite	-	25.7	21.0	0.0
Pseudo-wollastonite	-	-	-	18.0
Cristobalite	-	1.2	-	-
Free Lime	-	3.3	-	-
Calcite	-	-	29.5	-
Quartz	-	-	9.1	-
Grossular	-	-	16.9	-
Diopside	-	-	9.9	-
Albite	-	-	10.4	-
Clinochlore	-	-	1.4	-
Muscovite	-	-	1.2	-
Rankinite	-	-	-	14.4
Gehlenite	-	-	-	3.3
Sum [%]	100.0	100.0	100.0	100.0

TABLE 3. Results of XRD analysis according to Rietveld refinement before carbonation in %.

It is evident that the production of rankinite and wollastonite was not very successful, as the resulting samples contained only 14.4 % and 25.7 % of the required mineral. Nevertheless, the samples contained enough minerals that could be carbonated.

Weight changes after 24 hours of carbonation in the carbonation chamber indicate the formation of carbonates. Therefore, a large increase in these carbonated phases is predicted for belite, laboratory wollastonite and rankinite. Compressive strength is critical property for carbonizable clicker like powder materials. The results of the increase in weight and compressive strength are given in the Table 4. The measured values from Table 4 are shown graphically in Figure 1.

n	**Label**	**Δm [%]**	σ **[MPa]**
1	Belite	15.12	56.18
2	Lab. Wollastonite	15.54	14.41
3	Nat. Wollastonite	0.42	0.94
4	Rankinite	12.06	24.47

TABLE 4. Results of changes in weights and resulting compressive strengths.

The results of XRD analysis after carbonation show the conversion of minerals to carbonates (mainly calcite, aragonite and vaterite). Results are shown in Table 5. below.

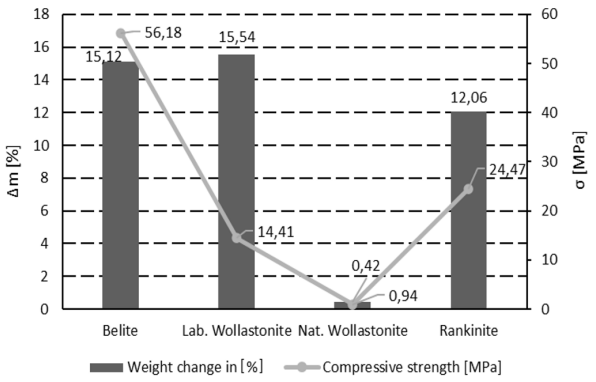

FIGURE 1. Graphical representation of the results from the Table 4.

The analysis showed the formation of carbonation products that were not present in the samples prior to the carbonation process. Calcite is the most abundant carbonate, except in the rankinite sample, where mainly aragonite was formed as a carbonation product. The DTA confirmed the results of the XRD analysis and the assumptions that natural wollastonite forms a minimal amount of carbonation products.

Label	**1**	**2**	**3**	**4**
γ-C_2S	13.5	-	-	3.2
β-C_2S	39.8	25.9	-	31.1
C_3S	2.5	-	-	-
Wollastonite	-	17	13.6	-
Cristobalite	-	1.0	-	-
Rankinite	-	-	-	-
Calcite	33.5	41.9	24.0	3.0
Vaterite	8.9	13.1	-	12.6
Aragonite	1.8	1.1	-	21.2
Quartz	-	-	7.4	-
Other minerals		17.0	55.0	28.9
Sum [%]	100.0	100.0	100.0	100.0

TABLE 5. Results of XRD analysis according to Rietveld refinement after carbonation.

However, the resulting sample contained the highest amount of calcite, 45.1 %. the higher values for all samples can be explained by the fact that the amorphous phase, which affects the absolute amount, was not calculated. Nonetheless, it is evident that γ-C_2S carbonates the most of all the minerals of which the samples were prepared. DTA and XRD analysis also revealed several newly formed carbonates. These were very similar for the belite, laboratory wollastonite and rankinite. Natural wollastonite was confirmed to already contain some carbonates before carbonation process and after carbonation only very small amounts of new carbonates were formed.

4. Conclusion

In the first step of the experiment, the raw material powders of belite, rankinite and wollastonite were produced, to which sample of natural wollastonite from the Bludov mine was added for comparison. Initial XRD, DTA, milling fineness and particle size characterization by laser granulometry were performed on the samples. In the second step, the solid samples were used for a carbonation process. The results obtained in terms of changes in weights, compressive strengths, XRD analysis and differential thermal analysis show the suitability for carbonation in CO_2 atmosphere of the individual minerals. From the results of the materials tested, it can be stated that the gamma belite is the most suitable for carbonation. Laboratory produced rankinite and wollastonite also show similar values of carbonate formation, but their compressive strengths are lower, which may be a consequence of particle sizes of belite. The complete suitability and comparison of each mineral cannot therefore be accurately determined as the same input conditions were not followed. On the other hand, natural wollastonite can be practically excluded as a mineral suitable for the carbonation process. The formation of new carbonates is minimal, as is its strength.

As recommendation for further research from the results obtained are:

- Focus on carbonation conditions – temperature, moisture, granulometry, porosity.
- Carbonation process of the same mineral with different water coefficient.
- Evaluation of porosity on the rate of carbonation.
- Measurement of crystallography of carbonated minerals.
- Measurement of the properties of individual carbonates – mainly calcite, vaterite and aragonite.

Acknowledgements

We acknowledge the financial support to projects, (CEITEC VUT/FAST-J-23-8309) Mechanical behaviour of calcium phosphate cements wet with liquids of different polarity and, (GA23-05122S) The role combination of fluxes and mineralizers on properties of low-energy clinker.

References

[1] E. Gartner, T. Sui. Alternative cement clinkers. *Cement and Concrete Research* **114**:27–39, 2018. Report of UNEP SBCI working group on low-CO_2 eco-efficient cement-based materials. https://doi.org/10.1016/j.cemconres.2017.02.002

[2] A. Smigelskyte, R. Siauciunas, H. Hilbig, et al. Carbonated rankinite binder: Effect of curing parameters on microstructure, strength development and durability performance. *Scientific Reports* **10**(1):14462, 2020. https://doi.org/10.1038/s41598-020-71270-w

[3] S. Gupta. Carbon sequestration in cementitious matrix containing pyrogenic carbon from waste biomass: A comparison of external and internal carbonation approach. *Journal of Building Engineering* **43**:102910, 2021. https://doi.org/10.1016/j.jobe.2021.102910

[4] M. Zajac, J. Skocek, M. Ben Haha, J. Deja. CO_2 mineralization methods in cement and concrete industry. *Energies* **15**(10):3597, 2022. https://doi.org/10.3390/en15103597

[5] X. Wang, M.-Z. Guo, T.-C. Ling. Review on CO_2 curing of non-hydraulic calcium silicates cements: Mechanism, carbonation and performance. *Cement and Concrete Composites* **133**:104641, 2022. https://doi.org/10.1016/j.cemconcomp.2022.104641

[6] E. Gartner, H. Hirao. A review of alternative approaches to the reduction of CO_2 emissions associated with the manufacture of the binder phase in concrete. *Cement and Concrete Research* **78**:126–142, 2015. Keynote papers from 14th International Congress on the Chemistry of Cement (ICCC 2015). https://doi.org/10.1016/j.cemconres.2015.04.012

[7] L. C. Lange, C. D. Hills, A. B. Poole. The influence of mix parameters and binder choice on the carbonation of cement solidified wastes. *Waste Management* **16**(8):749–756, 1996. https://doi.org/10.1016/S0956-053X(97)00021-4

[8] A. Sanna, M. Uibu, G. Caramanna, et al. A review of mineral carbonation technologies to sequester CO_2. *Chemical Society Reviews* **43**(23):8049–8080, 2014. https://doi.org/10.1039/C4CS00035H

[9] W. Ding, H. Yang, J. Ouyang, H. Long. Modified wollastonite sequestrating CO_2 and exploratory application of the carbonation products. *RSC Advances* **6**(81):78090–78099, 2016. https://doi.org/10.1039/C6RA13908F

[10] W. Ashraf. Carbonation of cement-based materials: Challenges and opportunities. *Construction and Building Materials* **120**:558–570, 2016. https://doi.org/10.1016/j.conbuildmat.2016.05.080