Synergistic Effects between Carbonation and Cracks in the Hardened Cement Paste

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Abstract: This paper investigates the synergistic interaction between carbonation and microcracks in hardened cement pastes. Ordinary Portland cement pastes with three different water/cement ratios of 0.4, 0.5 and 0.6, hydrated for 28 days with crack apertures ranging from 10 to 150 µm were subjected to accelerated carbonation in a climate chamber that controls the targeted relative humidity (65 and 75%), CO₂ concentration (0.3 vol.% and 1 vol.%) and temperature (20 °C). Mercury intrusion porosimetry, N₂-adsorption and thermogravimetry analysis were used to quantify the carbonation-induced changes in pore size distribution, porosity and phase assemblages. Additionally, the changes in crack apertures were followed during carbonation. The results indicated that cracks within the investigated range facilitate the carbonation along the crack surface due to a faster gas diffusion process. The cracks with apertures below 50 µm increase the carbonation depth at least by a factor of two for all studied w/c and environmental conditions. We observed a constant increase in crack openings during carbonation and its linear relationship with the amount of precipitated calcium carbonate. Due to depletion of CH and decalcification of C-S-H close to the sample surface, the crack aperture increase becomes limited. Therefore, the crack apertures do not increase further after the material around the crack is carbonated. It was also found that the densification of the carbonated cement matrix coexists with large capillary pores (>50 nm) or cracks, especially for the low w/c samples. The shift in pore size distribution from about 100 nm towards smaller pores (4.5–50 nm) and a decrease in gel pore fractions after 28 days of carbonation also indicate a simultaneous calcium carbonate precipitation in meso/capillary pores and decalcification of C-S-H at the nanoscale.

Keywords: carbonation; crack; cracked cement paste; C-S-H decalcification; carbonation depth; carbonation coefficient; pore size distribution

1. Introduction

As the most widely used building material globally, concrete plays a key role in infrastructure and construction. Although concrete has high durability, several degradation mechanisms can occur as a result of chemical changes in the material. Among them, carbonation is a common chemical process that can take place in concrete exposed to the atmosphere and CO₂-rich fluids and may impair the structural durability and serviceability of concrete structures due to carbonation-induced corrosion damage at the structural level [1,2]. Therefore, the investigation of the carbonation mechanism and its effect on cement material properties is relevant for an accurate service life assessment and is directly related to the crack resistance of concrete and material failure of cements, which was intensively studied in recent years [3–6].
Carbonation of concrete is a diffusion-driven process and its progress, in its most simple form, can be estimated based on Fick’s first diffusion law. This assumes that the carbonation depth $x_C$ (mm) is proportional to the square root of time $t$ (day) as:

$$x_C = k \cdot \sqrt{t},$$

where $k$ is a coefficient that represents the carbonation rate (mm/day$^{0.5}$) [7]. The coefficient reflects the diffusion of CO$_2$ and the amount of reactive material in the cement structure. It depends on the parameters related to the cement composition (e.g., the amount of reactive Ca-based constituents), curing duration and conditions, internal saturation degree, aggressivity of the environment (e.g., external relative humidity, CO$_2$ concentration and temperature) and pore structure [7–10]. The effect of environmental conditions such as CO$_2$ concentration and relative humidity on carbonation have been thoroughly investigated before [7,9,11,12] and is well known [13,14]. However, often it is described separately from other HCP properties, such as microstructure and hydrated phase composition, leaving coupled effects less investigated.

The hydrated phases and microstructure of cement pastes have a significant influence on the carbonation process [15–17]. For example, a higher amount of reactive minerals (e.g., calcium hydroxide and C-S-H) per unit of volume would increase the CO$_2$ uptake by concrete [8]. On the other hand, denser material with smaller pore sizes would decrease the CO$_2$ diffusivity through the structure. However, the presence or initiation of cracks during carbonation would facilitate the diffusion of CO$_2$ into the cement matrix. It has been shown that microcracks with an aperture size below 0.3 mm might increase the carbonation depth and decrease the carbonation resistance significantly [18–21]. Moreover, there is a direct relationship between the gas diffusion coefficient inside a crack and the crack width when the width is in the range of 0.1 to 0.4 mm [22]. Nevertheless, there is a lack of information on the effect of microcracks with apertures below 0.1 mm on the carbonation depth estimation and service life assessment of concrete structures [18,19,21,23].

An important consequence of carbonation is the alteration of the pore structure of the hydrated cement matrix. Calcium carbonate typically grows on the crystal surfaces of calcium hydroxide [24], which leads to a decrease in the porosity and eventually clogging of the pores. This slows down further carbonation by limiting the transport of water and CO$_2$. On the other hand, the carbonation of C-S-H, which is the most abundant calcium-bearing phase in hydrated cement paste, induces complex alterations in the pore structure depending on the carbonation duration and the CO$_2$ concentration. Initially, decalcification of C-S-H as a result of the removal of Ca from the interlayer space densifies the pore structure by calcite precipitation. Further carbonation at >3 vol.% of CO$_2$ results in a Ca/Si ratio of carbonated C-S-H below 1.3, which causes significant decalcification and shrinkage, implying coarsening of the pore structure [3,11,25,26]. Consequently, these phenomena facilitate CO$_2$ diffusion deeper in the structure [27,28] and increase carbonation depth. Moreover, simultaneous porosity decrease (pore clogging), and shrinkage cracking during carbonation may coexist in hardened cement pastes [27]. Therefore, it is often difficult to predict how the effective transport properties will change during carbonation. In addition, there is limited information on the effect of carbonation shrinkage on cement pore structure and crack evolution [29]. Furthermore, the mechanism of carbonation shrinkage is not fully investigated. It is assumed that carbonation shrinkage is related to the reorganization of the C-S-H layered microstructures or polymerization as a result of decalcification, which results in the decrease in total solid volume and densification (formation of sheet-like morphology) [25,26,30].

The mutual relation between carbonation depth and crack aperture results in a significant increase in both parameters, which is known as a synergistic effect. The aim of this study is to investigate the synergistic effects of microcrack aperture and carbonation at different environmental conditions and the pore structure of hydrated cement pastes under partially saturated conditions. Cement pastes with varying w/c ratios (0.4, 0.5 and 0.6) and crack apertures (ranging from 10 to 150 $\mu$m) were carbonated at 65% and
75% RH and 0.3 vol.% and 1 vol.% CO\textsubscript{2} concentrations. The changes in cement properties and crack apertures during carbonation were characterized, and the results are presented and discussed.

2. Experimental Program

In this section, the experimental program details are provided. First, the material and cracked sample preparation methods are described. Next, the accelerated carbonation procedure is explained. Finally, the details on characterization techniques used to analyze the samples before and after carbonation are provided.

2.1. Cement Paste Mixing, Casting and Curing

The experiments were performed on hardened cement pastes (HCP) that were prepared by mixing the Portland cement type I (CEM I 52.5 N) and tap water. The oxide compositions of this cement measured by X-ray fluorescence are shown in Table 1. Three different w/c ratios (0.4, 0.5, 0.6) were used to obtain different microstructures to study their effects on the carbonation process. The cement paste was prepared using a 5 L laboratory mixer in order to obtain a homogeneous mixture [31]. Then it was vibrated to remove entrapped air and was cast in sealed cylindrical PVC molds with an inner diameter of 9.75 cm and height of 40 cm that prevented carbonation during curing for 28 days [17].

The samples were rotated during the first 24 h of curing using a rotation machine [32] to prevent segregation and then transferred to a fixed flat position for the remaining 27 days of curing in a controlled temperature room of 20 ± 2 °C (Figure 1a). After curing, HCP samples were demolded and cut into 2.5 ± 0.05 cm thick disk halves by a diamond saw (Figure 1b). The disk halves were then stored in saturated lime water (for 1 to 5 days before further sample preparation such as polishing and pre-conditioning) to avoid Ca leaching and carbonation.

Table 1. Cement CEM I 52.5N oxide compositions obtained by X-ray fluorescence (XRF).

| Component | wt.%  |
|-----------|-------|
| CaO       | 63.56 |
| SiO\textsubscript{2} | 19.86 |
| Al\textsubscript{2}O\textsubscript{3} | 4.87  |
| Fe\textsubscript{2}O\textsubscript{3} | 3.14  |
| SO\textsubscript{3} | 3.06  |
| MgO       | 1.81  |
| K\textsubscript{2}O | 0.49  |
| P\textsubscript{2}O\textsubscript{5} | 0.35  |
| Na\textsubscript{2}O | 0.31  |
| Loss of ignition | 1.4   |

2.2. Artificial Crack Preparation

The obtained HCP disk halves were polished (Figure 1c,d) and then attached together with an electric isolation tape that covered the lateral surface of the disk. This method is similar to the one used in [33] and allows obtaining an artificial crack with a predefined geometry and width (Figure 1e). The method was chosen in order to avoid the interlocking effect that is common for natural cracks [21] so that crack surface geometry does not influence the diffusive transport of CO\textsubscript{2} gas. The cross-section surfaces were polished with sandpaper (P180 ∼ 82 μm particle diameter) to reduce the surface irregularities and, therefore, the interlocking effect before attaching the half disks to obtain an artificial crack, as shown in Figure 2. Ethanol was used during polishing instead of water to avoid calcium leaching or carbonation during sample preparation. Different crack widths were obtained by placing 0–2 pieces of duct tape in between the two half disks. The obtained crack widths were measured with the digital microscope (Keyence VHX-6000, Osaka, Japan). Additional reference samples were monitored to check if crack width changes occurred during non-elevated conditions (fixed 65% RH and atmospheric CO\textsubscript{2}).
Figure 1. Preparation of the cracked samples: the cement pastes were cast in cylindrical molds and rotated for the first 24 h (a). Then molds were kept in a fixed flat position for the remaining 27 days. After curing, samples were cut into half-disks (b). Next, the samples were polished with ethanol by polishing machine (d) with a specially designed fixture (c). Finally, to make an artificial crack (e), the polished samples with 3 pieces of duct tape at the crack surface (f) were attached.
Figure 2. Crack aperture of 0.5 w/c sample measured with the digital microscope before carbonation (a) and increased crack aperture after 28 days of carbonation at RH 65% and CO\textsubscript{2} 1 vol.% (b). Note also the appearance of a “natural” crack after carbonation at a place where a narrow initial cracking already preexisted. The numbers in brackets in the figure are the measurement points numbering.

Three reference samples with 0.4, 0.5 and 0.6 w/c ratios were prepared similarly to carbonated samples but were kept in a desiccator with fixed RH and atmospheric CO\textsubscript{2}. Crack aperture increase was in the order of a few microns after 28 days, which is negligible in comparison to carbonated samples. Furthermore, in order to verify that this type of tape does not stretch during the experiment, 3 samples with 0.4, 0.5, 0.6 w/c embedded into epoxy resin were carbonated together with tape embedded samples. The crack aperture change was identical for both types of constraints. The samples with different crack apertures were grouped into 3 categories: (I) from 10 to 50 µm, (II) from 50 to 100 µm and (III) from 100 to 150 µm at the top and bottom. The aperture was not measured alongside the entire crack depth, but it can be assumed that its value is within the crack width range measured at the top and bottom of the disks (because of the flat polished surface of half disks). Crack width was monitored with a digital microscope before and after the carbonation test. In addition, the crack widths of a few samples were monitored during the carbonation test.

2.3. Sample Pre-Conditioning and Accelerated Carbonation Setup

Before carbonation, HCP samples were first equilibrated to reach the target relative humidity (RH) of 65% or 75%. To reduce the pre-conditioning duration, a two-step drying procedure was used [32]. In the first step, the samples were dried in an oven at 35 °C until the sample mass decreased enough to correspond to the target RH. The target mass change value was obtained from the van Genuchten saturation degree model [34,35] (see Appendix A). The gentle oven temperature was chosen to prevent the dehydration of cement hydrates and possible cracking due to drying shrinkage. After oven drying, the samples were placed into a desiccator with a saturated salt solution (NaCl or NaNO\textsubscript{2} that created a constant RH of 75% and 65%, respectively, at the temperature of 21 °C) until the sample mass reached a stable state (i.e., mass difference between 2 measurements within 24 h is less than 0.2%) of equilibration between the internal and external RH. The duration of pre-conditioning was typically 3–4 weeks, depending on the w/c ratio. After pre-conditioning, the samples were immediately placed into a customized climate chamber for carbonation tests under controlled CO\textsubscript{2} concentration, temperature and RH conditions.
(Table 2). The bottom surface and the lateral area of the disks were covered with tape in order to carbonate a single surface with a crack and avoid advective gas flow through the crack. In addition, the sample masses were recorded during the carbonation and pre-conditioning period (see Appendix C).

Table 2. Experimental parameters and conditions for carbonation.

| Case A       | Case B             | Case C             |
|--------------|--------------------|--------------------|
| RH = 65%     | RH = 75%           | RH = 65%           |
| CO$_2$ = 1%  | CO$_2$ = 1%        | CO$_2$ = 0.3%      |
| w/c 0.4      | 1 and 4 weeks of   | 4, 8 and 14 weeks of |
| w/c 0.5      | carbonation        | carbonation        |
| w/c 0.6      | carbonation        | carbonation        |

The reference carbonation conditions were 1 vol.%, 20 ± 1 °C and 65% for selected CO$_2$ concentration, temperature and RH, respectively (case A, Table 2). Two other carbonation conditions were used to study the effect of RH and CO$_2$ concentration on the carbonation process: 75% RH and 1 vol.% CO$_2$ (case B, Table 2) and 65% RH and 0.3 vol.% CO$_2$ (case C, Table 2). The RH of 65% is often used in accelerated carbonation tests to fulfill the optimal range of 50–70%, which is the most ideal condition for CO$_2$ transport and hydration in porous media [15,27,36]. In this study, the RH of 75% was chosen, on the one hand, to study the effect of the increased moisture content on the carbonation rate but still to be close to the optimal RH range to observe carbonation in relatively short experimental periods of 7 and 28 days. The relatively low CO$_2$ concentrations of 1 vol.% and 0.3 vol.% were chosen to be sufficient to speed up carbonation but not too high to form a different microstructure or morphology of precipitate from the one under natural conditions. Typically, high CO$_2$ concentrations above 3 vol.% can lead to significant differences in microstructure and hydrated cement phase composition compared to natural carbonation, as indicated in the literature [9,11,15,37].

2.4. Phenolphthalein Tests

A standard phenolphthalein spraying test was performed to assess the carbonation depth for different experimental conditions, including the w/c ratio and the environmental conditions (i.e., CO$_2$ and RH). The number of measurements for each condition is indicated in Appendix B (Tables A1 and A2). In this study, we define two types of carbonation depths for the phenolphthalein test. First, the exposed carbonation depth is the depth of carbonation from the exposed surface far from the crack. The mean carbonation front is calculated as $x_C = \sum x_C^i / n$, where $x_C^i$ is the carbonation depth measured at the $i$-th point ($i \in [1, n]$, $n$ varies from 15 to 20) along the carbonation front, and $n$ is the total number of points distributed every 1 mm along the carbonation front detected by the phenolphthalein spraying test. The carbonation front values were extracted from two to five cross-section images taken from each sample after carbonation (Table 2). The crack carbonation depth is the carbonation depth inside the crack calculated as the maximum value of the carbonation front along the crack surface (schematically shown in Figure 3). The number of measured crack carbonation depths is limited from 2 to 8 due to the small number of sample pieces after breaking the carbonated samples.

2.5. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was applied to estimate the portlandite and calcium carbonate content along the exposed surface. Samples were taken from the carbonated surface by gently drilling a hole with a diameter of 7 mm and collecting the dust every 3 mm (Figure 3). Then the residual pore water was removed after one day of vacuum drying, and samples were stored in dry sealed conditions before the measurement to prevent further carbonation of the powders [38]. TGA was performed in a NETZSCH STA 409 PC
apparatus on samples with a mass of 30 ± 2 g. The temperature was increased under N2 atmosphere from 30 to 1010 °C, with a heating rate of 10 °C per minute.

Figure 3. Schematic 2D cross section of a cracked sample. The purple area is the uncarbonated zone indicated by the phenolphthalein test that is used to measure carbonation depth at the exposed surface and inside the crack. The vertical line with a hole at the top represents the location and depths of TGA sampling at a diameter of 7 mm.

Table 3 shows the properties of uncarbonated samples. The CH mass fractions calculated with the tangential method (see Appendix D.1) increase with the w/c ratio, which is also reported in the literature [39]. The obtained CH volume fraction indicates a minor increase with decreasing w/c. We can conclude from Table 3 that CH is present in an almost equal amount per unit of volume of HCP (cm³) for all studied w/c ratios.

Table 3. Uncarbonated cement paste characteristics obtained from TGA.

|                 | w/c 0.4 | w/c 0.5 | w/c 0.6 |
|-----------------|---------|---------|---------|
| CH content, wt. % | 15.06   | 16.96   | 18.94   |
| C content, wt. %  | 2.15    | 1.63    | 1.49    |
| CH volume fraction, vol. % | 11.54   | 11.33   | 10.87   |

2.6. MIP and N2-Adsorption Measurements

Mercury intrusion porosimetry (MIP) and N₂-adsorption techniques were used to characterize the pore structure of carbonated and uncarbonated HCP. Freeze-drying for 24 h under a pressure of 0.02 mbar was used for pore water removal [38]. Then the samples were stored in dry and sealed conditions until measurement. The porosimeter PASCAL 140/240 with combined low- and high-pressure modes up to 200 MPa was used to perform MIP. N₂-adsorption tests were conducted with the Micrometrics Tristar II apparatus. The pore size distribution was obtained with the apparatus software based on the cumulative intrusion volume and applied pressure [40].

3. Results and Discussion

3.1. Carbonation Depth Measured by Phenolphthalein Spraying

Figure 4 shows the mean of the exposed carbonation depths after 28 days of carbonation. The error bars in Figure 4 correspond to the standard deviation of the measured carbonation depths. The obtained carbonation depths follow the trends reported in the
literature [3,7,8,15] and depend on w/c and environmental conditions. Moreover, the environmental conditions and w/c ratio have roughly the same effect on mass uptake during carbonation Figure A5 as on carbonation depths. The carbonation depth increases with the increase in CO$_2$ concentration and decreases with the increase in RH from 65% to 75%. Additionally, a higher w/c leads to a larger carbonation depth because of larger porosity and average pore size (Table 3) and, therefore, larger CO$_2$ diffusivity [16]. On the other hand, the w/c is negatively correlated to the standard deviation that indicates the heterogeneous distribution of hydrated phases or possible microcracking in samples with w/c ratio of 0.4 (see further in Section 3.3).

![Figure 4](image)

**Figure 4.** Mean of exposed carbonation depths measured with the phenolphthalein test after 28 days of carbonation for different w/c (0.4, 0.5, 0.6) and environmental conditions. The error bar represents the standard deviation of the measured samples.

The crack carbonation depth increases with time as well as the exposed carbonation depths (see Figure A2 for exposed carbonation depth and Figure A3 for crack carbonation depth in Appendix B). As the process is diffusion-controlled, we calculate the crack carbonation coefficient $K$ (mm$^2$/day) as $\frac{s_{\text{max}}^2}{t}$ that equals $k^2$ according to Equation (1). The values of carbonation coefficients for the cracked and uncracked samples under different carbonation conditions are shown in Figure 5 (the exposed surface carbonation depths values are used for uncracked samples, while the crack carbonation depths are used for cracked samples). Despite a high variation of the measured crack carbonation depths (Figure A3), the results in Figure 5 indicate the dependency of $K$ on the crack size. These results indicate the relationship between crack size and carbonation depth and, therefore, the influence of CO$_2$ diffusivity on the carbonation process that is defined by the crack size [18–20]. The carbonation coefficient is more than twice as large as for crack apertures in the range of 10–50 µm compared to the samples without cracks due to larger CO$_2$ flux.

The environmental conditions also play an important role in fractured cement pastes, as well as in the case of uncracked cement surfaces. The effect of CO$_2$ concentrations and RH on the crack carbonation depth is similar to uncracked cement for 0.4 and 0.5 w/c, but, in the case of 0.6 w/c, the difference between $K$ coefficients is less significant. This indicates a fast CO$_2$ diffusion in the highly porous structure of the 0.6 w/c sample [41,42]. Furthermore, the results for low w/c indicate a high variation of crack carbonation depths (Figure A3). The w/c effect is not as pronounced for the crack carbonation depths as for exposed carbonation depths shown in Figure 4. However, in the case of 0.4 w/c, the carbonation coefficient is the largest for 1 vol.% CO$_2$ concentration and crack aperture between 100 and 150 µm in comparison to 0.5 and 0.6 w/c, as shown in Figure 5. Furthermore, due to the low gas diffusivity of 0.4 w/c HCP, in total, less CO$_2$ would react with cement phases compared to 0.5
and 0.6 w/c for the same time period. Therefore, more CO$_2$ can diffuse into the crack for low w/c HCP, which leads to higher crack carbonation and lower exposed carbonation depth.

**Figure 5.** Range of carbonation coefficients $K$ (mm$^2$/day) for different environmental conditions, w/c and crack sizes based on estimates of the exposed and crack carbonation depths. The crack width types are labeled as follows: (−) is a sample without crack, (I) is a crack with the initial aperture of 10–50 µm, (II) is a crack with the initial aperture of 50–100 µm and (III) is a crack with the initial aperture of 100–150 µm. The error bar represents the minimum and maximum K values estimated from the exposed and crack carbonation depths.

### 3.2. Portlandite and Calcium Carbonate Phase Changes

The phenolphthalein spraying method indicates only the areas with a pH below 9 and does not reflect the extent to which CH and C-S-H phases have been partially converted into CCO [10,15,43]. Our results confirm that the pH 9 boundary visualized by phenolphthalein spraying is closer to the surface compared to the extent of the partially carbonated zone in which some residual CH remains. This can be observed in Figure 6 near the border between the pink and grey zones. Results in Figure 6 also indicate that the precipitated CCO originated from the carbonation of other cement phases along with CH because the total mass fractions CCO are higher than the mass fractions of CCO originated from CH. For example, for w/c 0.6 (last column in Figure 6), the CH phase is completely carbonated next to the surface and the fraction of reacted Ca from other phases is slightly higher than for lower w/c. The fraction of calcium carbonate formed from CH and C-S-H is the lowest in the case of 75% RH and 0.4 w/c (subfigures (g) and (j) in Figure 6) because of low CO$_2$ diffusivity through a denser pore structure with a higher saturation degree.
Figure 6. Mass fractions of calcium carbonate (C\textsubscript{C}) (total and formed from CH and C-S-H) and portlandite obtained from TGA measurements after 7 and 28 days of carbonation at depths between 0 and 18 mm for cases A (RH 65%, CO\textsubscript{2} 1 vol.%) (a–f), B (RH 75%, CO\textsubscript{2} 1 vol.%) (g–l) and C (RH 65%, CO\textsubscript{2} 0.3 vol.%) (m–o). Grey and pink zones represent the average carbonated and uncarbonated domains defined with the phenolphthalein test where pH is lower or higher than 9, respectively (Figure 3).

Comparison of locations at a given distance from the surface after 7 and 28 days of carbonation reveals that the carbonation reaction of CH continued after 7 days. Evidence in the literature indicates that precipitated C\textsubscript{C} grows on the surface of portlandite crystal faces and forms a protective layer around portlandite, which decreases the dissolution-precipitation reaction rates with time [24,44,45]. The precipitate decreases the consumption of CO\textsubscript{2} so that it is transported further into the cement matrix. The protective C\textsubscript{C} layer can explain the fast CH dissolution rate at the beginning of the reaction (before 7 days) and the decrease in the CH carbonation rate with time. In addition, the decrease in carbonation rate with time leads to a decrease in total mass uptake during carbonation (Figure A5).

The increase in the environmental RH leads to slower reaction kinetics due to a decrease in the effective diffusivity through a pore structure with a higher saturation degree. For example, for a w/c of 0.5 (Figure 6b,k), the mass fraction of carbonated phases near the surface is similar, but less carbonation occurred at 75% RH between 3 and 6 mm even though the phenolphthalein test showed similar carbonation depths. Figure 6 also shows that a lower CO\textsubscript{2} concentration results in lower amounts of carbonated cement phases. Comparison of subplots (f) and (o) in Figure 6 clearly shows that C\textsubscript{C} in the carbonated area for case A is slightly higher than for case C.

The increase in CO\textsubscript{2} concentration from 0.3 vol.% to 1 vol.% (e.g., acceleration under laboratory conditions) slightly promotes C-S-H carbonation, which supports the findings
Moreover, a higher CO$_2$ concentration leads to a larger total amount of carbonated phases (both CH and C-S-H) due to larger carbonation depth. For example, in Figure 6 for w/c 0.4 (subplot (d)), CH at a 1.5 mm depth was completely carbonated at 1 vol.% CO$_2$ after 28 days of carbonation but is still present at 0.3 vol.% CO$_2$ (subplot (m)). In addition, the amount of reacted C-S-H is lower for 0.3 vol.% CO$_2$ (subplot (m), 0–3 mm) than for 1 vol.% CO$_2$ (subplot (d), 3–6 mm) even for the same amount of residual CH phase.

### 3.3. Effect of Carbonation on the Pore Structure

As reported by several studies, carbonation in HCP causes a decrease in the total porosity due to the densification of the pore structure as a result of precipitation from both C-S-H and CH carbonation [3,3,46]. MIP and N$_2$-adsorption measurements of samples before carbonation indicate an increase in the pore volume and BET surface area and a decrease in bulk densities with the increase in the w/c ratio (Tables 4 and 5). MIP bulk density values could be slightly underestimated (even though they correspond with the literature values [46]) since part of the gel pore volume is not taken into account due to the limitations of the technique [38], and therefore, we combine the measurement with the N$_2$-adsorption technique, which covers the gel pore radius range. However, MIP still provides important information about the changes in the pore structure with respect to w/c and carbonation duration. Additionally, the calculated critical and threshold pore radii (obtained as described in [47], see also Figure A7) increase with increasing w/c ratio (Table 4).

### Table 4. Pore size properties of uncracked HCP samples measured by MIP before and after carbonation (at RH 65% and CO$_2$ 1 vol.%).

| Carbonation Duration | w/c 0.4 | w/c 0.5 | w/c 0.6 |
|----------------------|---------|---------|---------|
| Accessible pore volume, % |         |         |         |
| 7 days               | 15.03   | 25.05   | 32.89   |
| 28 days              | 18.26   | 20.42   | 29.68   |
| Bulk density, g/cm$^3$ |         |         |         |
| 7 days               | 1.71    | 1.48    | 1.28    |
| 28 days              | 1.83    | 1.71    | 1.59    |
| Threshold pore size, µm |        |         |         |
| 7 days               | 0.048   | 0.386   | 0.409   |
| 28 days              | 0.281   | 0.668   | 0.512   |
| Critical pore size, µm |         |         |         |
| 7 days               | 0.046   | 0.017   | 0.017   |
| 28 days              | 0.055   | 0.041   | 0.057   |

### Table 5. Pore properties measured with N$_2$-adsorption before and after carbonation.

| Carbonation Duration | w/c 0.4 | w/c 0.5 | w/c 0.6 |
|----------------------|---------|---------|---------|
| Accessible pore volume, % |         |         |         |
| 7 days               | 14.62   | 19.08   | 20.81   |
| 28 days              | 10.58   | 12.04   | 16.23   |
| Bulk density, g/cm$^3$ |         |         |         |
| 7 days               | 7.06    | 7.71    | 15.2    |
| BET surface area, (m$^2$/g) |         |         |         |
| 7 days               | 67.32   | 85.81   | 110.54  |
| 28 days              | 12.31   | 21.02   | 29.95   |

The pore size distributions obtained from cumulative pore volumes (Figure A6 in Appendix D.2) are shown in Figure 7. The pore ranges are typically classified as gel micropores (<4.5 nm), mesopores (4.5–50 nm), middle capillary pores (50–100 nm) and large capillary pores (>100 nm) [46,47]. The results of this classification (based on the pore size distribution) are shown in Figure 8 for MIP and N$_2$-adsorption. A decrease in the
open porosity and BET surface area after carbonation is observed with the N$_2$-adsorption technique (Table 5), which is related to the amount of precipitated C$_{C}$ [48]. However, MIP measurements first show an increase in porosity for w/c 0.4 after 7 days of carbonation (which is a consequence of carbonation cracking at the micro-scale) and then a decrease after 28 days of carbonation (Table 4). Furthermore, the discrepancy between porosity measured by two techniques is probably related to the covered pore size range, and MIP better captures changes at larger scales [32]. Figure 7b indicates that the densification of the cement matrix due to carbonation occurs in the pore size range between 2 and 40 nm.

Figure 7. MIP (a) and N$_2$-adsorption (b) pore size distribution before and after carbonation at RH 65% and CO$_2$ 1 vol.% obtained from cumulative pore volumes (Figure A6). The line colors correspond to different samples: not carbonated (red), carbonated for 7 days (blue), carbonated 28 days (green). The colored areas also denoted with numbers corresponding to (1) gel micropores below 4.5 nm, (2) meso-pores below 50 nm and above 4.5 nm, (3) middle capillary pores below 100 nm and above 50 nm and (4) large capillary pores above 100 nm [46,47]. The pore volume fractions corresponding to these areas are shown in Figure 8.

In Figure 7, peaks of the pore size distribution of 0.5 and 0.6 w/c shifted towards smaller pore sizes (mesopores and small capillary pores in Figure 8) after carbonation. However, for w/c 0.4, the most frequent pore sizes (the highest peak in Figure 7) shifted towards larger pore sizes after 7 days of carbonation. This implies an increase in the middle capillary pores fraction in the range between 50 and 100 nm. After 28 days of carbonation,
the most frequent pore size shifts back to smaller pores, and therefore, the fraction of capillary pores decreases. However, a similar shift in the pore sizes was also observed in [49] for w/c 0.45 OPC paste exposed to 50 vol.% CO$_2$ after 14 days of carbonation. This increase in the porosity and capillary pores fraction for w/c 0.4 after 7 days of carbonation can be related to the changes in the capillary pores and/or microcracking caused by carbonation shrinkage [25,30,50]. We suppose that the high standard deviation of the carbonated front for 0.4 w/c in Figure 4 is also caused by microcracking during carbonation shrinkage and not by drying shrinkage because samples were always kept at stable RH conditions.

![Pore volume fractions (%) obtained from MIP](a) and N$_2$-adsorption, (b) pore size distribution (Figure 7) before and after carbonation at RH 65% and CO$_2$ 1 vol.%.](b)

**Figure 8.** Pore volume fractions (%) obtained from MIP (a) and N$_2$-adsorption, (b) pore size distribution (Figure 7) before and after carbonation at RH 65% and CO$_2$ 1 vol.%. The distribution of pore sizes after 7 days of carbonation for the 0.6 and 0.5 w/c samples is close to that of the 0.4 w/c sample, even though the initial pore size distribution
is different. There is no increase in the large capillary pores fraction for 0.6 or 0.5 w/c samples, but the fraction of middle capillary pores increases first and then decreases in a similar way to the 0.4 w/c sample. The pore size distribution in Figure 7 indicates that carbonation shrinkage causes microcracking with aperture size greater than 50 nm for all studied w/c, but it is more noticeable at low w/c since it has a lower fraction of capillary pores. Threshold pore size also increases after 7 days and decreases after 28 days of carbonation. MIP indicates that a longer carbonation duration leads to the filling of pores with pore sizes greater than 10 nm (Figure 7). At 0.5 and 0.6 w/c, the shift in the pore size distributions towards the smaller pores occurred during the 7 days of carbonation and continued until 28 days of carbonation, which is shown in Figure 7a).

Complementary to MIP, \( N_2 \)-adsorption indicates a decrease in gel pore fractions (below 4.5 nm) for all w/c during carbonation. \( N_2 \)-adsorption covers a smaller range of pore sizes compared to MIP and, therefore, provides a proper estimation of pore structure changes at the nanoscale. A change in the gel pore distribution is mostly related to carbonation of the C-S-H that involves the first step of a gradual decalcification of the C-S-H followed by the formation of an amorphous silica phase \[3,51\]. This initially leads to the densification of microstructure by precipitation and then to the coarsening of the pore structure due to the porous structure of silica gel and microcracks induced by a decalcification shrinkage below Ca/Si ratio of about 1.3. The change in the critical pore size after 7 days of carbonation (Table 4) suggests that carbonation together with C-S-H decalcification leads to the occurrence of pores with sizes greater than 40–50 nm. Longer carbonation duration causes a decrease in the critical pore size. Therefore, the peak growth at 30 nm in Figure 7b (w/c 0.6, 28 days carbonation) can be related to the clogging of both mesopores and capillary pores (>30 nm). The pore size distributions do not provide evidence of how exactly the pore volume fractions are affected by carbonation, i.e., whether the change in the pore volumes is a result of \( \text{C}_2 \) precipitation from C-S-H and CH and/or C-S-H decalcification. Precipitation in the range from mesopores to capillary pores is usually attributed to CH carbonation resulting in the decrease in capillary pore volumes \[52\]. The decrease in the gel micropores is mostly attributed to \( \text{C}_2 \) precipitation from C-S-H carbonation leading to pore clogging. Our \( N_2 \)-adsorption results also indicate that the fractions of gel micropores and mesopores below 10 nm decrease with carbonation (Figure 7b).

### 3.4. Effect of Carbonation on Crack Evolution

Monitoring crack apertures during several carbonation experiments showed an increase in crack size after carbonation for all samples. Moreover, a crack network already developed at the initial stages of the carbonation experiment, which was also reported in the literature \[27\]. In our study, we noticed that these cracks preferentially developed from the existing microcracks, probably resulting from drying shrinkage. An example of such a crack is shown in Figure 2a, and its size increases from \(~1\) to \(11\ \mu \text{m}\) during carbonation (Figure 2b). We did not observe any significant crack aperture size increase in the samples that were kept at the same conditions (RH 65% and \(20 \pm 2 \degree \text{C}\) temperature) but not subjected to \( \text{CO}_2 \). Therefore, we conclude that the increase in crack aperture sizes was caused by carbonation shrinkage in accordance with the previous research works \[27,53\].

Figure 9 shows the aperture increase with time for the initial crack width in the range of 50–100 \(\mu \text{m}\) during carbonation at RH 65% and \( \text{CO}_2 \) 1 vol.% The crack width increase is larger for the highest w/c of 0.6 (+96 \(\mu \text{m}\)) compared to the growth in 0.5 w/c (+63 \(\mu \text{m}\)) and 0.4 w/c (+34 \(\mu \text{m}\)), which can be explained by different degrees of carbonation for samples with different w/c ratios. The results indicate that crack aperture increases faster in the early period of carbonation up to 14 days. After this period, there was only a slight increase in crack aperture that is related to \( \text{C}_2 \) precipitation since after some time there is no significant increase in its content (see Figure 6 (subplot (c) and (f) at 0–3 mm depth)). It was also reported in the study \[28\] that carbonation shrinkage is proportional to the carbonation depth. Our findings suggest that the crack aperture growth is affected by the
degree of carbonation (carbonation depth) that is defined by the environmental conditions (Figure 10), w/c ratio and carbonation duration.

![Figure 9](image1.png)

**Figure 9.** Crack width increase versus time at w/c in the range 0.4–0.6 throughout 28 days of carbonation at RH 65% and \( \text{CO}_2\) 1 vol.%. Scatter plot represents the measurements along the crack. Line colors (red, blue, green) correspond to different w/c ratios of 0.4, 0.5, 0.6, respectively.

![Figure 10](image2.png)

**Figure 10.** Crack width increase for different environmental conditions and w/c after 28 days of carbonation. Compared cases are A (RH 65%, \( \text{CO}_2\) 1 vol.%), B (RH 75%, \( \text{CO}_2\) 1 vol.%) and C (RH 65%, \( \text{CO}_2\) 0.3 vol.%). The average is taken for all ranges of the initial crack sizes from 10 to 150 µm.

Crack apertures grow regardless of the initial crack aperture size. In order to verify the origin of the crack aperture increase and carbonation shrinkage, we estimate the total amount of carbonated Ca in C-S-H based on the TGA results (Figure 6). Mass fraction of Ca per 100 (g) sample originated from C-S-H is transformed to the mass fraction of reacted CaO as follows:

\[
\frac{m_{\text{CaO}}}{m_{\text{CC}}} = \frac{M_{\text{CaO}}}{M_{\text{CC}}} \cdot \frac{M_{\text{C}_3}}{M_{\text{C}_3}}
\]

where \( M_{\text{CaO}} \) and \( M_{\text{CC}} \) are the molar masses of CaO and CaCO\( _3\), respectively [54]. Afterward, the resulting mass fraction \( m_{\text{CaO}} \) is integrated along 18 mm in all cases, which is the maximum depth of TGA measurements in Figure 6. The obtained value represents a mass fraction per 100 g of the sample at a depth of 18 mm (a depth larger than 18 mm can also be chosen but it would result in a smaller \( M_{\text{CC}} \) mass fraction).

![Figure 11](image3.png)

**Figure 11** shows a linear relationship between changes in crack width and the mass fraction of carbonated Ca from both CH and C-S-H phases. This suggests that the crack aperture change within the studied range is directly related to the carbonation degree. A closer look into the results in Figure 11 suggests that with higher RH (case B indicated with...
green color in Figure 11), the carbonation of both CH and C-S-H is less sensitive to the crack aperture than in the case of lower RH. On the other hand, for lower CO\textsubscript{2} concentration (case C indicated with blue color in Figure 11), the crack aperture is more sensitive, especially to the C-S-H carbonation rate. A possible reason is that with lower CO\textsubscript{2} concentration, there is less carbon available for reaction. Furthermore, since CH is more reactive, more CO\textsubscript{2} is consumed during the carbonation reaction with CH compared to C-S-H. Therefore, CO\textsubscript{2} becomes less available for the C-S-H carbonation and makes the latter more sensitive to the crack aperture change. However, to explore these relationships in more depth, more data points are required, which we recommend for future research. Moreover, since both CH and C-S-H phases are subjected to carbonation, the characterization techniques used in this work do not allow us to investigate the origin of the crack evolution. Most likely, the increase in the crack opening is related to the decalcification of C-S-H [25,26] and the consequent carbonation shrinkage [27]. Even if the C-S-H phase is possibly the main reason for carbonation shrinkage, while CH carbonation does not cause it, CH becomes carbonated continuously as long as CO\textsubscript{2} penetrates HCP. Therefore, there is a relationship between carbonated CH and crack aperture increase in Figure 11a. In addition, longer carbonation will not necessarily lead to a further increase in crack opening (see the crack size for w/c 0.6 between 14 and 28 days in Figure 9) but will cause changes at the inner parts of a crack since there are less residual unreacted phases close to the surface. Hence, the reaction front would move deeper into the cement matrix where unreacted CH and C-S-H are still present.

![Figure 11](image_url)

**Figure 11.** Relationship between crack aperture increase and carbonated CH (a) and CaO in the C-S-H phase, (b) mass fractions per 100 g of sample integrated along 18 mm length (as shown in Figure 3) after 28 days of carbonation. Compared cases are A (RH 65%, CO\textsubscript{2} 1 vol.%), B (RH 75%, CO\textsubscript{2} 1 vol.%) and C (RH 65%, CO\textsubscript{2} 0.3 vol.%). Dashed colored lines are the fitted linear models with cases A, B and C.

4. Conclusions

In this study, the carbonation mechanism in cracked HCP was investigated in terms of alteration in the pore structure and cement hydration phases (CH and C-S-H). The results of this work deliver the following conclusions:

1. Carbonation leads to a decrease in total pore volume (due to precipitation and consequent densification of HCP) and formation of new mesopores and capillary pores and (micro)cracking due to the carbonation of CH and C-S-H phases. Additionally, a decrease in the gel pores (<4.5 nm) fraction was observed for all studied w/c (0.4, 0.5, 0.6) after carbonation at RH 65 and CO\textsubscript{2} 1%. The decrease in the gel pores is likely related to C-S-H carbonation leading to Ca precipitation, while further C-S-H decalcification increases the mesopore (>4.5 nm and < 50 nm) fractions. The fraction
of capillary pores with sizes greater than 50 nm, which formed after 7 days of carbonation, decreased after 28 days of carbonation. The increase in mesopore fraction (<50 nm) and the decrease in capillary pores (>50 nm) also suggest that precipitation preferentially occurs in larger pores.

2. The depth of carbonation is highly sensitive to the crack size within the studied range, which increased several times with larger crack openings due to faster CO$_2$ gas diffusion. Within the range of crack apertures in this study (10–150 µm), the carbonation along the crack surface increased with larger crack openings complementing the previous studies [21,22]. The cracks with apertures below 50 µm increase the carbonation depth at least by a factor of two. This observation was valid for all studied w/c and environmental conditions.

3. The crack monitoring showed that the crack openings at the surface grow during carbonation. The results indicate a synergistic relationship between the crack aperture increase and the degree of carbonation due to the mutual effect of these parameters on each other. Moreover, crack apertures reach a certain value and do not increase further due to the depletion of CH and decalcification of C-S-H close to the surface. We observed a linear relationship between both carbonated phases and the crack aperture increase. According to previous works [25,55], C-S-H carbonation is a primary reason for carbonation shrinkage and eventual cracking.

4. MIP pore size distributions suggest the formation of new large pores or microcracks in HCP with low w/c at the initial stages of carbonation and further clogging of these pores due to C-C precipitation. A higher fraction of newly formed large pores for 0.4 w/c would facilitate carbonation deeper into the structure and may increase the carbonation front variance. In addition, low diffusivity of the dense cement matrix of 0.4 w/c would restrict carbonation through the cement matrix and increase the carbonation depth along the microcracks.

The main contribution of this study is the identification of the possible mutual relationship between cracks and the carbonation process when crack openings become wider and facilitate carbonation even more. Our findings are based on the three groups of environmental conditions and material properties controlled by w/c ratios. However, to draw a strong conclusion on the interaction between investigated factors on the carbonation process, an extension of the range of environmental conditions (e.g., RH, CO$_2$ concentration, temperature), crack sizes and material types (e.g., w/c, supplementary cementitious materials) is suggested for future research, which can be achieved with an appropriate experimental design [36,57]. In such a way, more extensive conclusions on the synergistic relationship between cracks and carbonation could be made. We also suggest further investigating the crack geometry evolution (for example, how the crack depth and inner geometry are changing during carbonation) and its effect on CO$_2$ diffusion. Since this research was performed under accelerated carbonation conditions (increased CO$_2$ concentration and stable RH), it should be further investigated as to whether there is a similar relationship between crack opening evolution and the carbonation degree under natural atmospheric conditions. Furthermore, there is still missing knowledge on C-S-H structure evolution during carbonation in HCP. Further studies on these aspects will help to better explain the carbonation shrinkage process and the role of microcracks in the service life estimation of concrete materials.

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Abbreviations
The following abbreviations are used in this manuscript:

- **HCP**: Hardened Cement Paste
- **OPC**: Ordinary Portland Cement
- **CH**: Portlandite
- **C-S-H**: Calcium Silicate Hydrate
- **CC**: Calcium Carbonate
- **MIP**: Mercury Intrusion Porosimetry
- **TGA**: Thermogravimetric Analysis

Appendix A. Van Genuchten Model of Saturation Degree

In this study, we estimate the mass of pore water at a certain internal RH from the Van Genuchten saturation degree model [34]:

\[ S = \left(1 + (-\alpha \cdot \log(RH))^{1/\beta}\right)^{-\beta} \]  

(A1)

where \( S \) is the saturation degree fraction, \( RH \) is the relative humidity, \( \alpha \) and \( \beta \) are the fitting coefficients that were chosen as 5.72 and 0.444, respectively, obtained from [58] for OPC pastes with a similar \( w/c \) ratio of 0.45. Therefore, in order to reach a particular internal relative humidity, we have to obtain the saturation degree based on Equation (A1).

Assuming that we need to reach a certain \( RH \), we need to reach the sample mass \((m_{\text{sample}})\) during the pre-conditioning in a desiccator based on the following calculations:

\[ m_{\text{sample}} = m_{\text{sample} \ 95\%\ RH} - \Delta m_{H_2O} \]  

(A2)

\[ \Delta m_{H_2O} = \left(V_{H_2O \ 95\%\ RH} - V_{H_2O \ 100\%\ RH}\right) \cdot \rho_{H_2O} \]  

(A3)

\[ V_{H_2O \ 100\%\ RH} = V_{\text{sample}} \cdot \Theta \]  

(A4)

\[ V_{H_2O \ 95\%\ RH} = V_{\text{sample}} \cdot \Theta \]  

(A5)

where \( V_{H_2O} \) is the volume of water in the sample at a certain RH (cm³), \( \rho_{H_2O} \) is the density of water (g/cm³) and \( \Theta \) is the capillary porosity of HCP. We assume that the HCP sample has 95% RH at the initial stage of the pre-conditioning. Then, we estimate how much water should be evaporated in order to reach a particular saturation degree assuming that the sample has the approximate capillary porosity \( \Theta \) of 22%, 28% and 35% for 0.4, 0.5 and 0.6 \( w/c \), respectively (Equation (A5)).

Appendix B. Carbonation Depth Measurements

The phenolphthalein pH indicator is the most used technique for carbonation front measurement in cementitious materials because of its effectiveness and fast method of obtaining results [17,19,20]. Typical phenolphthalein depths of samples with different \( w/c \) ratios are shown in Figure A1. The number of measurements to determine the carbonation depths in bulk materials and along the cracks are reported in Tables A1 and A2, respectively.
Table A1. Number of measurements on the carbonated area to determine the bulk (exposed) 28-day carbonation depth.

| w/c | Case A (RH 65%, CO₂ 1 vol.% | Case B (RH 75%, CO₂ 1 vol.% | Case C (RH 65%, CO₂ 0.3 vol.%) |
|-----|-----------------------------|-----------------------------|-------------------------------|
| 0.4 | 7                           | 10                          | 18                           |
| 0.5 | 13                          | 9                           | 13                           |
| 0.6 | 15                          | 15                          | 19                           |

Figure A1. Examples of carbonation depths determined by phenolphthalein spraying methods of samples with w/c ratios of 0.4, 0.5 and 0.6 and artificial crack sizes ((I) from 10 to 50 µm, (II) from 50 to 100 µm and (III) from 100 to 150 µm at the top and bottom).

Table A2. Number of measurements on the carbonated area to determine the 28-day carbonation depth along the cracks.

| w/c | Crack | Case A (RH 65%, CO₂ 1 vol.% | Case B (RH 75%, CO₂ 1 vol.% | Case C (RH 65%, CO₂ 0.3 vol.%) |
|-----|-------|-----------------------------|-----------------------------|-------------------------------|
| 0.4 | I     | 2                           | 5                           | 6                             |
|     | II    | 3                           | 3                           | 6                             |
|     | III   | 2                           | 2                           | 6                             |
|     | I     | 3                           | 3                           | 5                             |
| 0.5 | II    | 4                           | 3                           | 5                             |
|     | III   | 6                           | 3                           | 3                             |
|     | I     | 6                           | 6                           | 8                             |
| 0.6 | II    | 5                           | 6                           | 5                             |
|     | III   | 4                           | 3                           | 6                             |
Figure A2. Mean of phenolphthalein exposed carbonation depths (mm) after carbonation for different w/c, RH and CO₂ concentration. Error bars represent minimum and maximum value of measured carbonation depth.

Figure A3. Crack carbonation depth as a function of the square root of time.
Figure A4. Crack carbonation depths measured with the phenolphthalein test after 28 days of carbonation for different w/c (0.4, 0.5, 0.6) and environmental conditions. The error bar represents the minimum and maximum crack carbonation depths for the measured samples.

Appendix C. Mass Change

The mass increase in Figure A5 was calculated as the mass change of an entire sample divided by exposed surface area (without crack surface). The mass increase indicates changes that correspond to the carbonation depths measured with the phenolphthalein test (Figure A3). Both mass increase and carbonation depths are affected by changes in RH and CO₂ concentration. The mass of HCP during carbonation depends on how much CO₂ is reacted and how much water was released during the reaction with CH and C-S-H. Since both processes are diffusion-controlled, the carbonation reaction would be a function of the square root of time (Equation (1)). Interestingly, the mass gain for sample carbonated at 75% RH does not follow the square root of time law in comparison to 65% RH case (Figure A5). Higher external RH would lead to higher internal RH and, therefore, saturation degree. The released water during the reaction remains inside the cement microstructure, and more pores are filled with water; therefore, CO₂ gas cannot diffuse deeper into the cement matrix. In this case, carbonation will be driven mainly by liquid diffusive transport of dissolved CO₂ than by CO₂ gas diffusion.
Appendix D. Pore Structure and Phase Changes

Appendix D.1. Thermogravimetric Analysis Details

Portlandite (CH) and calcium carbonate (CaCO$_3$) mass profiles perpendicular to the surface were calculated from weight loss at temperature ranges 400–500 °C and 600–800 °C, respectively [54]. The measured CH mass fraction is obtained with the “tangential” method as described in [54], which is calculated as the integration of the DTG peak area:

$$CH_{tangential} = \left( WL_{400–500°C} - (DTG_{400°C} + DTG_{500°C}) \cdot \frac{\Delta T}{2} \right) \cdot \frac{M_{CH}}{M_{H_2O}}$$  \hspace{1cm} (A6)

where $WL$ is weight loss corresponding to portlandite, $M_{CH}$ is the molecular mass of portlandite (74 g/mol), and $M_{H_2O}$ is the molecular mass of water (18 g/mol), DTG is the temperature derivative value, and $\Delta T$ is the temperature range equal to 100 °C. The tangential method is more precise than the stepwise method because the weight of water from C-S-H and other phases is subtracted from CH. The measured CaCO$_3$ content is calculated with the “stepwise” method of Equation (A7)) because all water is gone before 600 °C, and the mass decreases due to CO$_2$ only at high temperatures:

$$CaCO_3_{measured} = WL_{600–800°C} \cdot \frac{M_{CaCO_3}}{M_{CO_2}}$$  \hspace{1cm} (A7)

where $M_{CaCO_3}$ is the molecular mass of calcium carbonate (100 g/mol), and $M_{CO_2}$ is the molecular mass of CO$_2$ (44 g/mol).

Additionally, mass fractions of carbonated CH and Ca in C-S-H were calculated based on the initial and residual CH fractions. CH is generally the first phase to be carbonated because of its higher solubility compared to solubility of C-S-H (and other minor phases). At first, the carbonated CH content is calculated as follows:

$$CH_{carbonated} = CH_{tangential}^{BC} - CH_{tangential}^{AC}$$  \hspace{1cm} (A8)

where $CH_{tangential}^{BC}$ is the CH amount of the reference sample (before carbonation) and $CH_{tangential}^{AC}$ is the CH amount after carbonation calculated according to Equation (A6). Then the carbonated CH content is converted to CaCO$_3$ as follows:

$$CaCO_3_{CH} = CH_{carbonated} \cdot \frac{M_{CaCO_3}}{M_{CH}}$$  \hspace{1cm} (A9)

The mass fraction of CaCO$_3$ originated from C-S-H is found as the difference between total CaCO$_3$ and CaCO$_3$ originated from CH:

$$CaCO_3_{CSH} = CaCO_3_{measured} - CaCO_3_{CH}$$  \hspace{1cm} (A10)
The CH mass fractions calculated with the tangential method increase with the w/c ratio, which is also reported in the literature [39]. The CH volume fraction $\phi_{CH}$, which is found as the mass fraction multiplied by the bulk density $\rho_{bulk}$ obtained with MIP (Table 4) and divided by CH density $\rho_{CH}$ of 2.23 g/cm$^3$, is as follows:

$$
\phi_{CH} = \frac{V_{CH}}{V_{HCP}} = \frac{m_{CH}/\rho_{CH}}{m_{HCP}/\rho_{bulk}} = CH_{tangential} \cdot \frac{\rho_{bulk}}{\rho_{CH}}
$$

where $m_{CH}$ is the mass of CH in HCP (g). The obtained CH volume fraction indicates a minor increase with decreasing w/c. We can conclude from Table 3 that CH is present in almost equal amounts per unit of volume of HCP (cm$^3$) for all studied w/c ratios.

Appendix D.2. Pore Size Distribution Details
Cumulative pore volumes are shown in Figure A6.

Figure A6. MIP (a) and $N_2$-adsorption (b) cumulative volume before and after carbonation at RH 65% and CO$_2$ 1 vol.%.

Critical and threshold pore sizes are illustrated in Figure A7.
Figure A7. An example (w/c 0.5 sample before carbonation) of determination of critical and threshold pore sizes and pore size classification.

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