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Savija, Branko; Luković, Mladena

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Carbonation of cement paste: understanding, challenges, and opportunities

Branko Šavija^{a*} and Mladena Luković^{b#}

^a Microlab, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1, 2628 CN Delft, the Netherlands. e-mail: b.savija@tudelft.nl

^bConcrete Structures Group, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1, 2628 CN Delft, the Netherlands. e-mail: m.lukovic@tudelft.nl

[#]Formerly at the Microlab, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1, 2628 CN Delft, the Netherlands.

* Corresponding author

Tel: +31(0)15 27 88986

Fax: +31(0)15 27 86383

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Abstract

Cement paste is known to react with atmospheric carbon dioxide. Carbonation of cement paste has long been recognized as one of the causes of reinforcement corrosion. On the other hand, carbonation causes numerous chemomechanical changes in the cement paste, most notably changes in strength, porosity, pore size distribution, and chemistry. Furthermore, it can cause shrinkage and cracking of the cementitious matrix. The present review summarises the state of the art regarding the understanding and consequences of carbonation of cement paste. Apart from the passive process of reaction of atmospheric CO₂ with cement paste, carbonation is sometimes used on purpose in order to improve certain properties of cementitious materials. This review further summarises recent efforts regarding active use of carbonation as a tool for manipulating certain properties of cement based materials.

Possible fields of application include accelerated curing, improvement of fibre reinforced cementitious composites, concrete recycling, and waste immobilization.

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1. Introduction and background

Carbon dioxide from the atmosphere can react with hydrated cement in presence of moisture [1]. This reaction affects both the cement microstructure and durability of (reinforced) concrete. Although the aim of this paper is to systematically review the former, the latter is first briefly discussed.

In the past, a lot of research has been devoted to studying effects of carbonation on durability of reinforced concrete. In concrete, reinforcing steel is protected from active corrosion by a passive film of ferrous oxide which forms on its surface in the highly alkaline concrete pore solution [2, 3]. This alkalinity, corresponding to a pH value above 12.5, is provided by dissolution of solid CH (calcium hydroxide, i.e. portlandite) in the pore solution. Carbonation of hydrated Portland cement paste reduces the pH of the pore solution to values lower than 9 (as low as 8.3) [4]. This is lower than the depassivation threshold of reinforcing steel, which is around 9.5 [5, 6]. Thus, if the front of low pH reaches the surface of reinforcing steel, the protective oxide film on its surface breaks down. Corrosion then initiates, provided that moisture and oxygen are present [7]. It is generally acknowledged that carbonation results in generalized corrosion, with uniform pressure being exerted on the surrounding concrete and resulting in cracking of the concrete cover [8-12]. Corrosion of reinforcing steel is well recognized as a problem, and is not a focus of this review.

Reaction of carbon dioxide with calcium bearing phases in the cement paste can also cause chemo-mechanical changes in the microstructure. It is commonly assumed that the carbon dioxide diffuses through the concrete cover following a square root of time relation, resulting in a carbonation front [13-15]. However, some studies show that the paste does not become completely carbonated on one side of a sharp reaction front but rather that a zone of partially

carbonated material can exist to a depth substantially greater than the depth of full carbonation (i.e. that indicated by phenolphthalein spraying) [16-18]. On the contrary, SEM observations showed (under supercritical carbonation exposure, as explained later) a series of carbonation and dissolution fronts, which progressively translate with time from the outside towards the inside of the sample [17]. They suggested that the affected HCP consists of a carbonated zone, a carbonation front, a dissolution front, and the inner part of the sample (Figure 1). With increasing exposure, this geometry moves inwards, and relicts of these fronts are observed backwards in the carbonated zone.

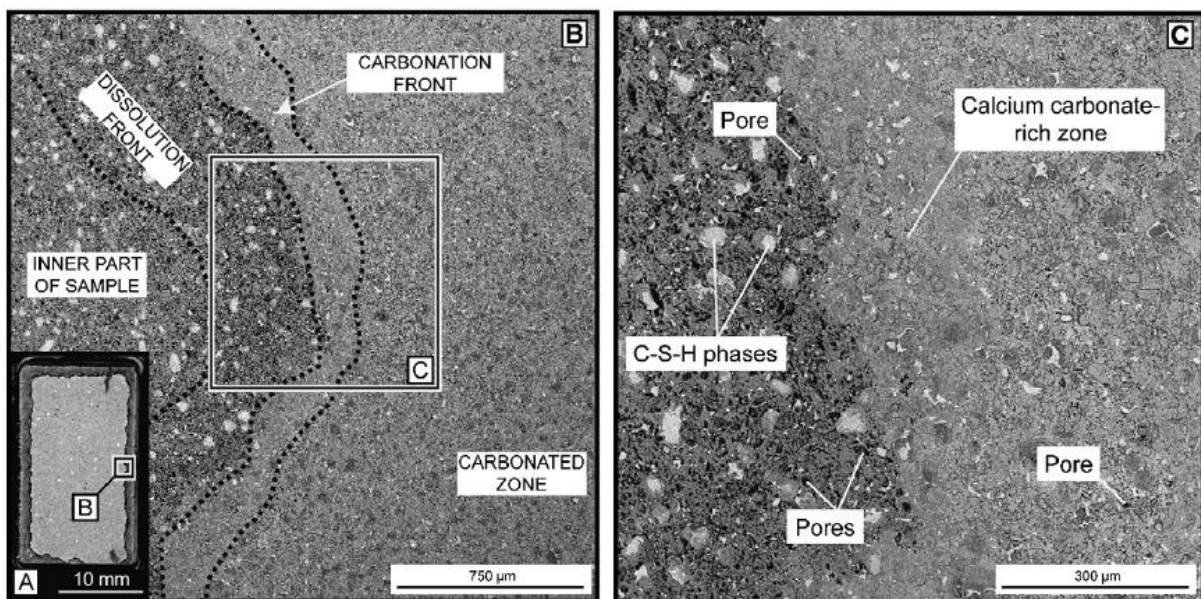


Figure 1. An SEM micrograph of a Portland cement paste carbonated in CO₂-saturated water for 2 days at 280 bars and 90 °C [17]. Different zones in the affected paste are marked by dashed lines on the left.

Apart from causing the pH drop, most notable changes are changes in porosity, (micro)mechanical properties, and appearance of cracks [19]. These changes can be

considered *passive*, because they occur spontaneously when cement paste reacts with carbon dioxide. Therefore, they are commonly considered as deterioration (or ageing) effects, even though some properties of certain cement pastes can be actually improved, as discussed later. On the other hand, there has been a number of recent advances aiming at utilizing the ability of cement paste to react with carbon dioxide to achieve certain economical or environmental benefits (or both). This can be considered as an *active* decision to take advantage of this reactivity.

In short, a passive carbonation process is when carbonation causes unwanted and unplanned changes in the surface layer of a concrete structure or an element when exposed to the environment. Even though passive carbonation can sometimes even result in improvement of certain properties (as elaborated later), it is generally considered as an ageing mechanism. A majority of studies leading to fundamental understanding of chemomechanical mechanisms of carbonation in cementitious materials are based on studying passive carbonation (e.g. using accelerated carbonation experiments with elevated concentrations of CO₂), and are thoroughly reviewed in sections 2-4. On the other hand, an active carbonation process results from a procedure designed to intentionally take advantage of the ability of calcium bearing phases of cement paste to react with CO₂ for different applications. Active carbonation assumes controlled exposure of cementitious materials to elevated CO₂ concentrations for certain periods of time, resulting in benefits in terms of mechanical performance or environmental impact of the material. Different procedures which use active carbonation are reviewed in section 5. Passive and active effects of carbonation are summarized in Figure 2, and discussed further in detail.

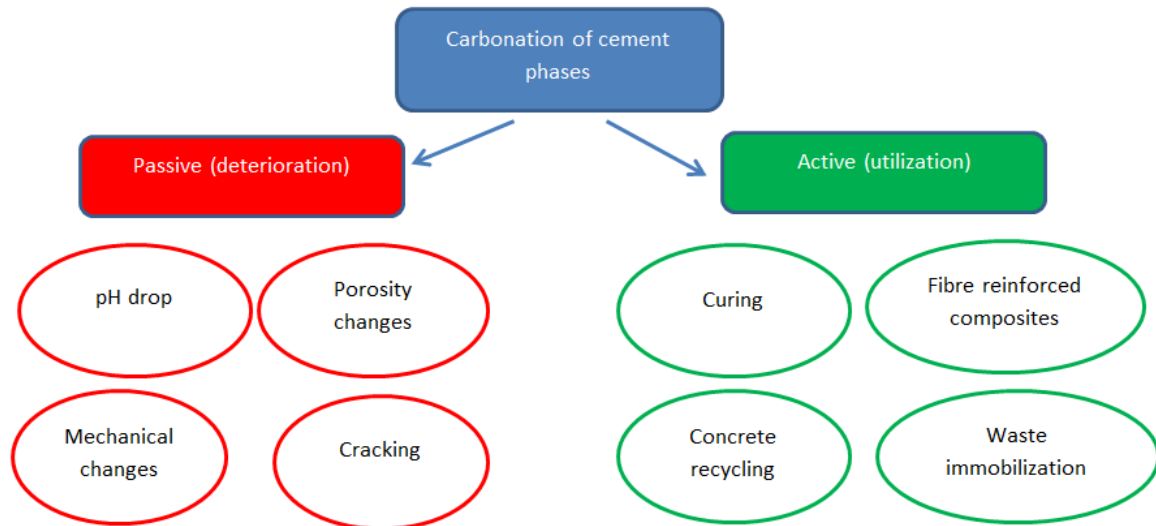


Figure 2. Carbonation of cement paste can be an active or a passive process, with different effects.

In order to understand the passive and (possible) active effects of carbonation on cement paste, it is important to understand the way that CO_2 reacts with main phases in the cement paste and the factors which influence this process. This is discussed in the following section.

2. Carbonation processes of main cement phases

2.1. Portlandite carbonation

It is commonly assumed that calcium hydroxide (CH, i.e. portlandite) is the hydration product which reacts most readily with CO_2 [1, 18]. Carbon dioxide can react with dissolved calcium hydroxide, resulting in precipitation of sparingly soluble calcium carbonate in the pore space [15, 20, 21]:



Carbonation of CH involves three main steps [20]: (1) dissolution of CH; (2) absorption of carbon dioxide and formation of carbonate ions; and (3) chemical reaction and precipitation.

Chemical reaction of CO_2 with $\text{Ca}(\text{OH})_2$ starts instantly and leads to formation of calcium carbonate [22]. In the early stage of carbonation, CO_2 diffusion through the already carbonated layer (step 2) is the rate-controlling step for carbonation of CH [15, 23]. Even though CO_2 diffusivity is significantly higher in gas filled pores, compared to water filled pores, the presence of moisture is necessary for gaseous CO_2 to react with CH [24]. The limiting step changes at later stages of the carbonation process as the rate of CH carbonation decreases due to the formation of a thin layer of calcium carbonate on the surface of CH crystals [16, 18, 22, 25-27]. Calcium carbonate crystals form at the CH surface apparently at random (Figure 3), but probably originating at dislocations (Figure 4). Eventually the surface becomes covered as the nucleation sites grow and coalesce [25]. This is facilitated by the relatively small surface areas of portlandite crystals in comparison with calcium-silicate-hydrates [28].

Which calcium carbonate polymorph will form as a result of eq. (1) will depend on which of two kinds of factors are dominant: kinetic or thermodynamic factors. If kinetic factors predominate, CaCO_3 will precipitate as aragonite or as vaterite, both of these polymorphs will convert finally into calcite, the more stable polymorph [29]. If thermodynamic factor predominates CaCO_3 will precipitate as calcite.

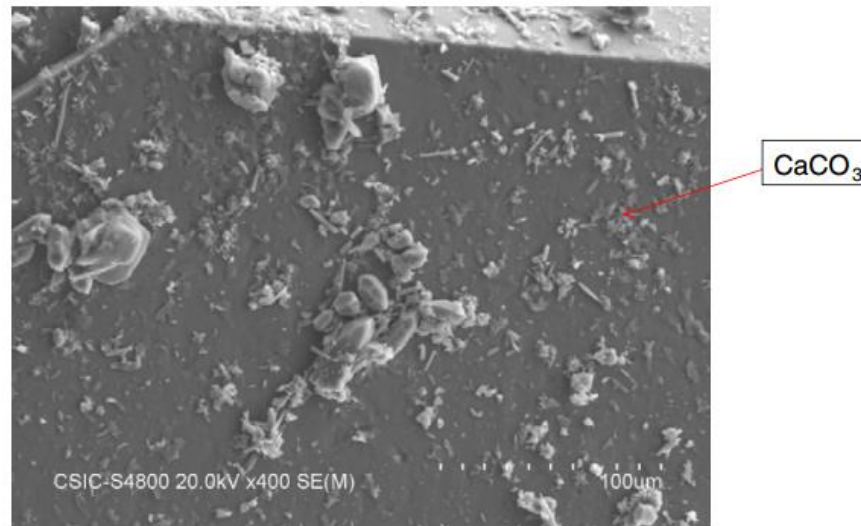


Figure 3. SEM micrograph of a lightly carbonated CH surface, showing nucleation of CaCO₃ with angular morphology [25]

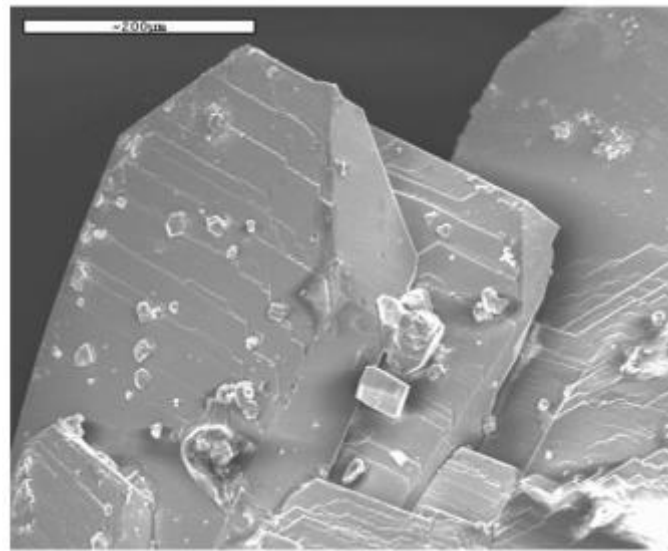


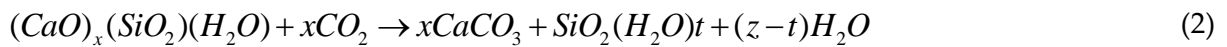
Figure 4. SEM micrograph of a CH crystal showing dislocations, imperfections, and CaCO₃ crystals [25]

2.2. Calcium-silicate-hydrate carbonation

In a study by Groves et al. [28], in which C₃S paste was used in order to allow for the degree of reaction of CH and C-S-H to be determined separately, it was shown that, although CH initially reacted more rapidly, its rate of reaction decreased with time, and was overtaken by the rate of reaction of C-S-H. This was attributed to the formation of a relatively dense microcrystalline calcium carbonate layers at the surfaces of reacting CH crystals (described in

the previous section). It is, therefore, of vital interest to also understand carbonation process of the calcium-silicate-hydrate phase.

Carbonation of C–S–H gel consists of the removal of calcium ions from the gel leading to the formation of an amorphous silica gel and various polymorphs of calcium carbonate [30-32]. Chemical reaction of C-S-H with carbon dioxide results in formation of calcium carbonate and amorphous silica gel, and can be written as follows [21, 30, 33]:



The type and extent of C-S-H gel carbonation depend strongly on the initial Ca/Si ratio of the gel [28, 34, 35]. It is known that when C-S-H carbonates, its Ca/Si ratio drops and it becomes highly porous, approaching amorphous silica [16, 29]. The rate of C-S-H decomposition, as a result of carbonation reactions, increases with decreasing Ca/Si ratio of the C–S–H [36], while the quantity of CaCO₃ formed by carbonation of C-S-H decreases [34]. Studies by NMR spectroscopy indicate that decomposition of C–S–H caused by carbonation involves two steps [36]: (1) a gradual decalcification of the C–S–H, where calcium is removed from the interlayer and defect sites in the silicate chains until Ca/Si = 0.67 is reached, ideally corresponding to infinite silicate chains; (2) calcium from the principal layers is consumed, resulting in the final decomposition of the C–S–H and the formation of an amorphous silica phase.

It is well established that C-S-H forms as one of two types, high- or low-density C-S-H (or inner and outer products) [37-40] (see Figure 5). While the Ca/Si ratio of C-S-H in neat Portland cement pastes varies from ~1.2 to ~2.3 with a mean of ~1.75 [41], small but significant differences were observed between the inner (Ca/Si=1.58±0.06) and the outer

product (1.89 ± 0.12) in TEM by Groves et al. [28]. Figures 5 and 6 show TEM micrographs of C-S-H before and after carbonation [42]. These TEM micrographs show a change in morphology after carbonation, and carbonated C-S-H sample was described as a multitude of carbonate microcrystals dispersed in a disordered matrix [42]. Calcite layers covering large areas of the residual C-S-H are observed as well. Such layers of calcium carbonate covering the C-S-H structure could eventually prevent the high-density C-S-H from being fully carbonated (sort of a passivation layer), or at least slow down the process (similar to the passivation of CH described previously). Low-density C-S-H carbonated more easily and completely disappeared, whereas some inner product remained, likely aided by the passivation effect [42]. Groves et al. [28] also found, in their study, that the outer product C-S-H has been completely carbonated, with inner product becoming inhomogeneous with some regions (presumably those least accessible to gas-filled pores in the outer product) having become silica-rich gel. The porosity of the outer product was found to be substantially reduced by the deposition of carbonate crystals formed by the reaction of Ca from both inner and outer C-S-H. The influence of this can be seen in micromechanical tests, as described later.

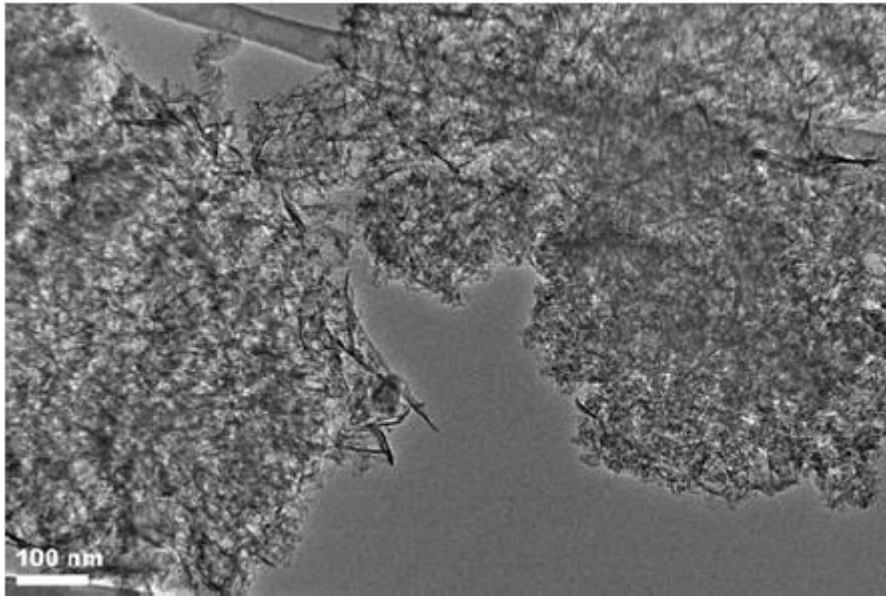


Figure 5. TEM micrograph of C-S-H before carbonation. Tobermorite-like needles typical for low density C-S-H as well as a disordered particulate mesoporous structure (high density C-S-H) are clearly visible [42]

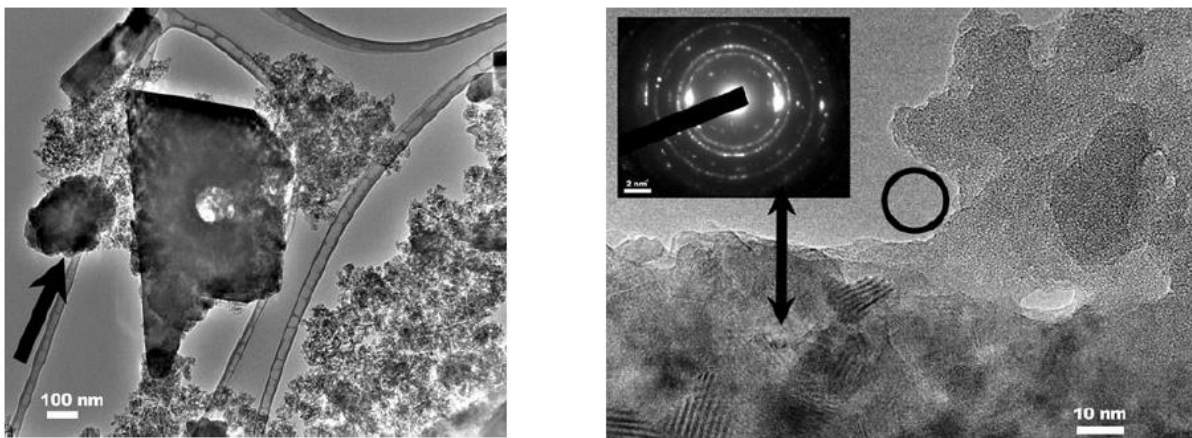


Figure 6. TEM micrograph of C-S-H after carbonation [42]. Left: CaCO_3 microcrystals together with films covering the porous matrix are visible (pointed by the arrow); Right: Two different morphologies – HD C-S-H with embedded nanocrystals (lower part) and the silica gel resulting from C-S-H carbonation (upper right part). Inset shows a diffraction pattern focused on the disordered area indicated by the arrow

The degree of carbonation of C-S-H gel also depends on the CO_2 concentration and environmental conditions [31, 43]. From a cross-analysis of XRD and DTA/TGA, it was found that the C-S-H carbonation rate depended on the CO_2 partial pressure, increasing with the

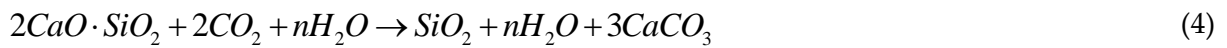
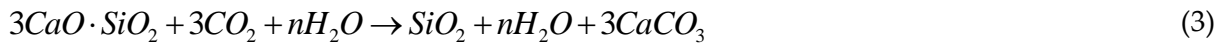
increase in CO₂ concentration [44]. On the other hand, X-ray diffraction analyses showed that other calcium bearing phases, such as CH, ettringite, and aluminates, seem to be completely “carbonatable” irrespective of the CO₂ partial pressure (concentration) [44].

Carbonation of C-S-H in general results in formation of calcite, aragonite and vaterite [16, 28, 30], with the the formation aragonite and vaterite vaterite seemingly related to the presence of highly decalcified C-S-H, and hence to a high CO₂ concentration [18, 32, 45].

2.3. Carbonation of other phases

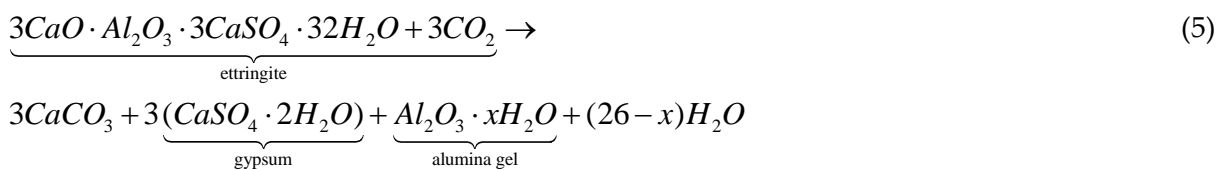
As already stated, other calcium bearing phases are also susceptible to carbonation [1, 15, 20].

Han et al.[33] observed that the number and size of unhydrated cement particles decreases due to carbonation because of reactions of tricalcium silicate (C₃S) and dicalcium silicate (C₂S) with CO₂. These reactions result in formation of CaCO₃ and silica gel, as follows [21, 33]:



Similar findings were reported by other authors [43].

In a study by Hyvert et al. [44], X-ray diffraction data showed that, apart from CH, also ettringite and aluminates were effectively carbonated at low partial CO₂ pressure. It is suggested that ettringite decomposes upon reaction with CO₂, resulting in formation of gypsum and alumina gel [46-50]:



The numerical value of x in equation (5) is close to 3 [48]. Although this reaction was found to satisfactorily describe behaviour for (synthesized) ettringite powder specimens, Zhou and Glasser [48] suggested that it should be modified for compact specimens. Similar to the behaviour of CH, they also found a definite induction period prior to decomposition of ettringite. Furthermore, Xiantuo et al. [47] found that the reaction rate increases with the increase of temperature at constant CO₂ partial pressure and 100% RH. The carbonation of ettringite leads to the formation of vaterite crystals [51].

Carbonation of all calcium bearing phases contributes significantly to formation of CaCO₃, and it is commonly reported that the total amount of CaCO₃ formed far exceeds that which could result from complete CH dissolution [18, 26, 32, 40, 43, 52].

3. Microstructural consequences of carbonation

3.1. Changes in porosity

It is expected that, as a consequence of carbonation, porosity of cement paste might change. This change can be a decrease (in case of Portland cement paste), or an increase (in case of blended cement paste) [17, 20, 40, 52-57]. Similar findings were reported for concrete [1, 19, 58, 59].

Porosity changes are caused by dissolution of cement phases. Carbonation of portlandite results in a net increase of volume and precipitation of calcium carbonate in the pore network. The extent of this expansion depends on the calcite polymorph formed in the reaction with portlandite (Table 1).

Table 1. Properties of the minerals which can be involved in the carbonation process [29]

Mineral	Density (g/cm ³)	Molar volume (cm ³)	Crystal shape	Variation of volume (%)
Portlandite	2.23	33.20	Laminar	/
Calcite	2.71	36.93	Prismatic	11.2
Aragonite	2.93	34.16	Fibrous	2.9
Vaterite	2.54	39.40	Spherical	18.7

Therefore, the reduction of total pore volume is associated with CaCO₃ deposition. Precipitation of CaCO₃ takes place preferentially in smaller pores, due to better water condensation [29]. This results in shifting the pore size distribution curve towards smaller pore diameters (Figure 7) and total volume of pores per gram of paste [29]. Carbonation of Portland cement paste also causes loss of pore connectivity [52]. On the other hand, coarsening of the pore structure may be associated with the formation of additional silica gel due to decomposition of C-S-H [55]. The fact that blended cement pastes contain significantly lower amounts of portlandite, as a consequence of pozzolanic reactions of fly ash or hydraulic reactions of blast furnace slag, results in coarsening of their pore structure. Furthermore, it seems that Portland cement paste reacts in a similar way, albeit delayed by carbonation of portlandite: Rimmelé et al. [17] found a porosity decrease in Portland cement paste specimens exposed to wet supercritical CO₂ (from 33%-15% in the first weeks), and then an increase (15%-27%) from 6 weeks-3 months, and a stabilization until 6 months. In CO₂ saturated water, it decreases from 33%-9% in first 3 weeks, increasing to 28% after 3 months, and 30% after 6 months. In both exposure conditions, MIP shows an initial sealing stage is followed by a dissolution stage. It seems, thus, that carbonation of Portland cement paste is not a continuous process which plugs the porosity [17]. In fact, some authors even suggest that the C-S-H carbonation is the main factor in the variation of paste porosity [60].

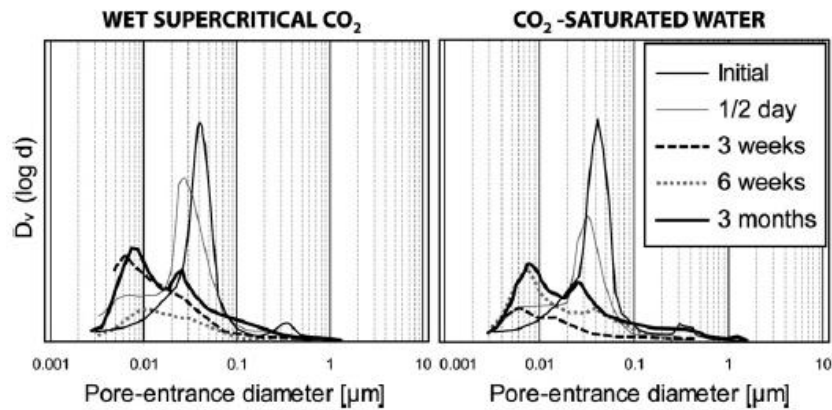


Figure 7. Evolution of the threshold diameter with time estimated from mercury intrusion porosimetry (MIP) on Portland cement samples exposed to wet supercritical CO₂ and CO₂-saturated water up to three months [17]

Mercury intrusion porosimetry (MIP) is a widely used technique for characterizing the distribution of pore sizes in cement-based materials [61], despite being heavily criticised [62]. It can be useful for comparing the pore-size distributions of a cement paste before and after carbonation. The major drawback of this technique in this respect is that it does not provide any information on local variations of porosity in different areas of the paste. For this, some modern techniques, such as image analysis of BSE images [63, 64] and micro-computed tomography (CT scanning) [65-67], can be used. For example, Rimmelé et al. [17] used image analysis of BSE images to show a gradient of porosity in carbonated Portland cement paste (figure 8). A decrease in porosity can be seen at the exposed surfaces, followed by a slight increase (the dissolution front, see also Figure 1), and constant porosity in the intact portion of the sample. Han et al. [68] used computed tomography to visualize in-situ the progress of the carbonation front (figure 9). Using this method, it is also possible to see the development of carbonation cracks.

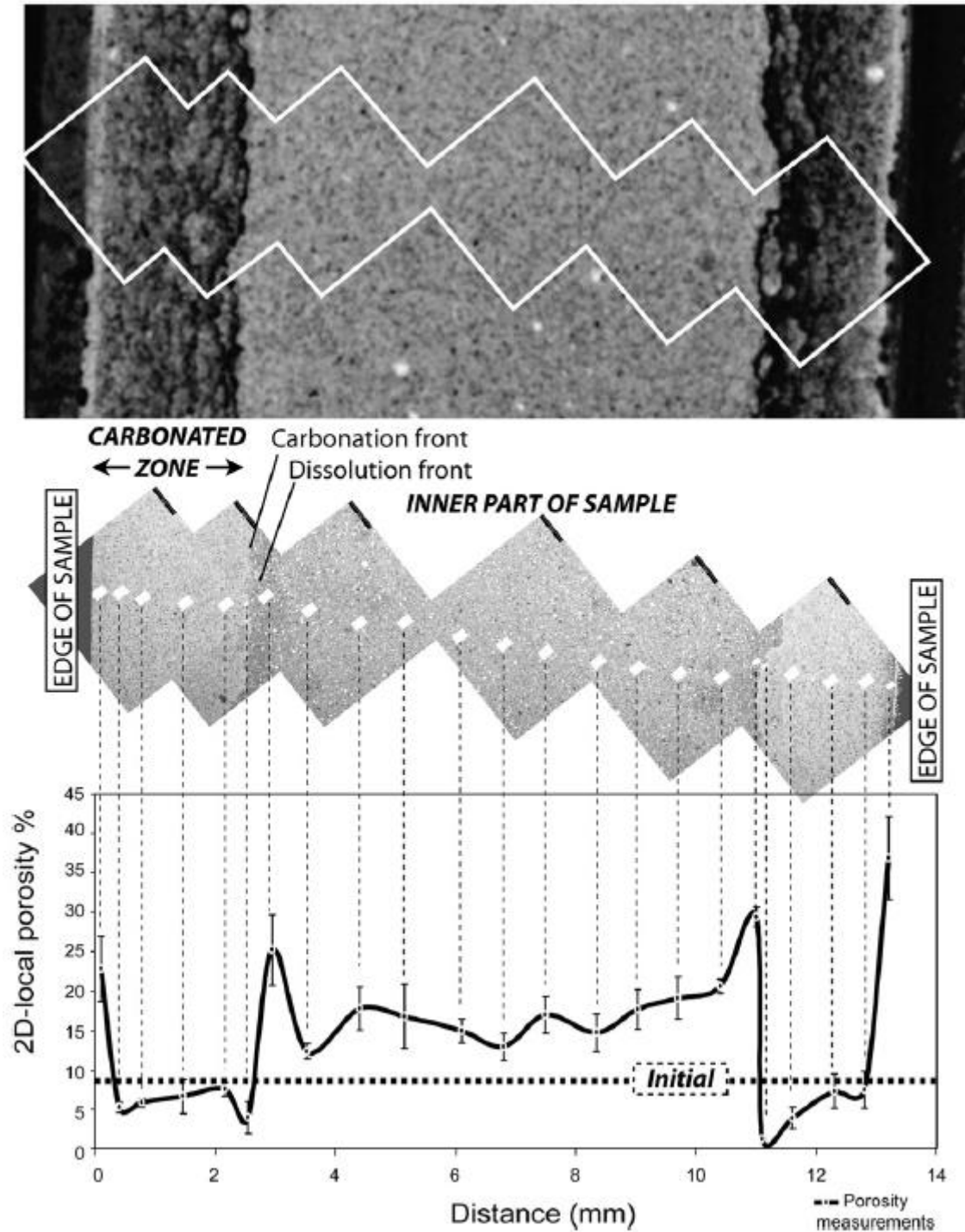


Figure 8. Polished section (above) and SEM-BSE image profile (middle) through a Portland cement core attacked during four days in CO_2 -fluid at 280 bars and 90 °C. The different carbonation and dissolution zones are identified. The white rectangles locate the areas where local porosity was measured by thresholding the BSE images. The results of the local porosity estimates with their error bars along the profile are reported below. Note that the porosity in the inner part of the sample is higher than the initial porosity (~15% compared to ~8%), confirming that it is not a sound zone [17].

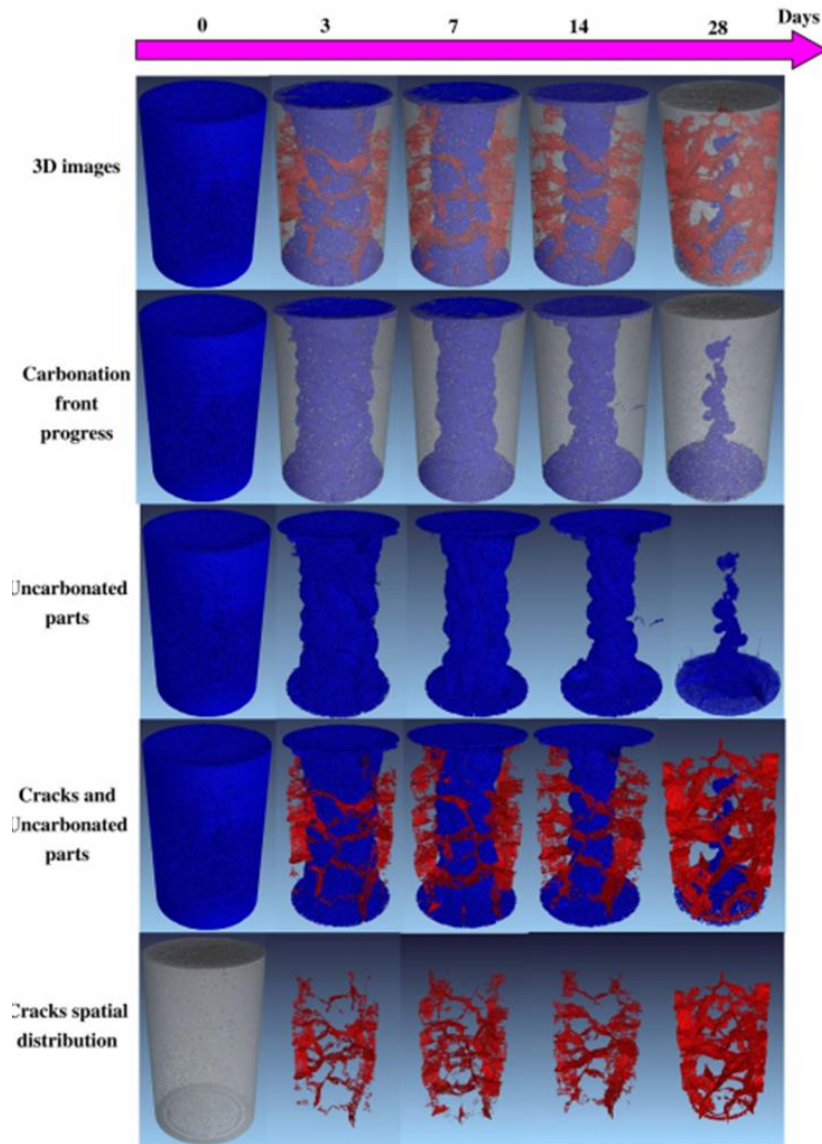


Figure 9. 3D images of carbonation front progress and cracks spatial distribution with different carbonation times [68]. Carbonation cracking is discussed later.

It is possible that the decrease in porosity due to carbonation could contribute to an increase in strength of Portland cement paste, mortar, and concrete [19]. However, it is improbable that this is the only contributing mechanism, as will be discussed later [69].

3.2. Changes in transport properties

Calcium carbonate which forms due to carbonation has a very low solubility and thus contributes significantly to clogging of the pore system, at least in the early stage of

carbonation [17, 19]. However, possible occurrence of microcracks makes it difficult to predict the change of transport properties of liquids and gasses through carbonated cement paste [19, 70].

Houst and Wittmann [71] noted that carbonation of Portland cement paste samples caused a decrease in their water absorption compared to uncarbonated samples. Ngala and Page [55] found that carbonation of cement pastes has a large effect on their transport properties, affecting blended pastes more than plain OPC pastes. They found an increase of chloride diffusion coefficient in blended pastes following carbonation of two orders of magnitude (figure 10), and an increase in oxygen diffusion coefficient by one order of magnitude (figure 11). Borges et al. [40] found that, in blended paste specimens (with 75-90% BFS), extensive cracking occurred as a consequence of carbonation, which significantly increased the oxygen permeability. Similarly, an increase of oxygen permeability for specimens exposed to supercritical carbonation was reported by Yuanhua et al. [72], coupled with a decrease in compressive strength, probably implying occurrence of cracks. Phung et al. [73] found water permeability to decrease by a factor of six and three after 4 weeks of carbonation for OPC and OPC paste blended with 10% limestone powder, respectively.

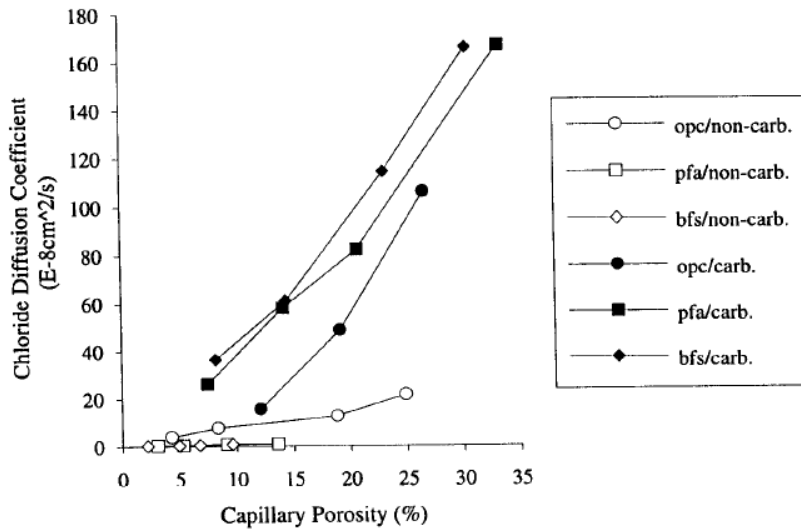


Figure 10. Chloride diffusion coefficient for carbonated and non-carbonated pastes (OPC- ordinary Portland cement; PFA- pulverized fly ash; BFS- blast furnace slag) [55]

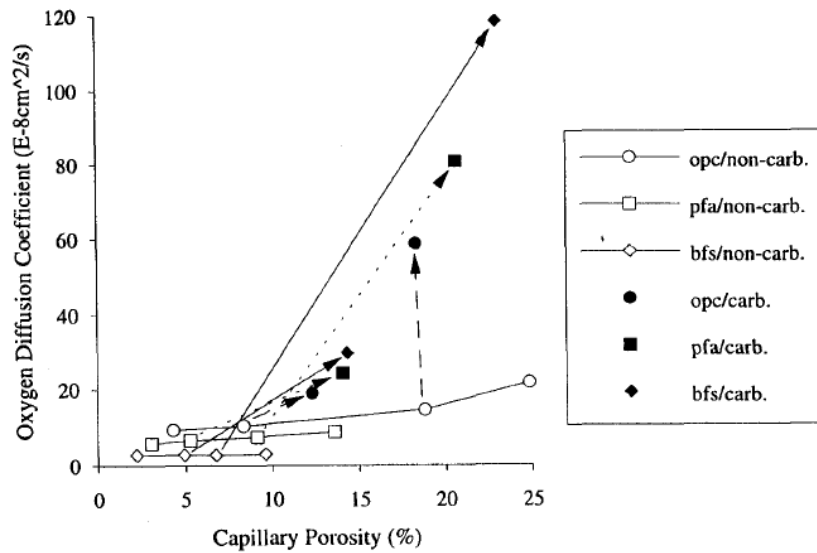


Figure 11. Oxygen diffusion coefficient for carbonated and non-carbonated pastes (OPC- ordinary Portland cement; PFA- pulverized fly ash; BFS- blast furnace slag) [55]

3.3. Micro- and macro-mechanical changes

Compressive and tensile strength of Portland cement paste (and concrete) can be significantly improved by carbonation [19, 74]. This is related to the decrease of porosity and possibly also structural changes of the C-S-H gel as the main binding component in cement [69]. It seems that the cement paste becomes stiffer and stronger macroscopically with

carbonation while a large reorganization of the microstructure takes place at small scale [75-77]. Hardness and elastic modulus measured by nanoindentation have a tendency to shift towards higher values in Portland cement paste (Figures 11 and 12), but towards lower values in blast-furnace slag paste (Figure 12).

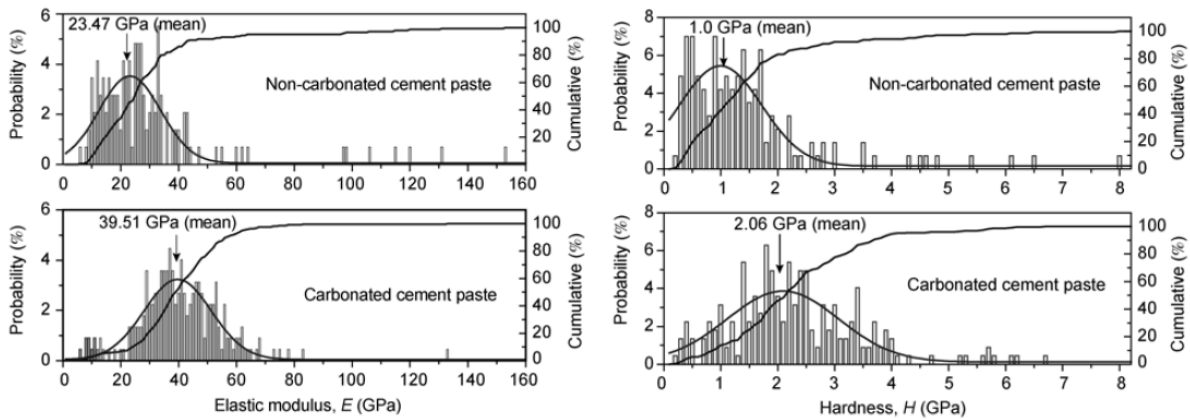


Figure 11. Histograms of the elastic modulus (left) and hardness (right) probability changes of non-carbonated and carbonated Portland cement paste measured by nanoindentation [33].

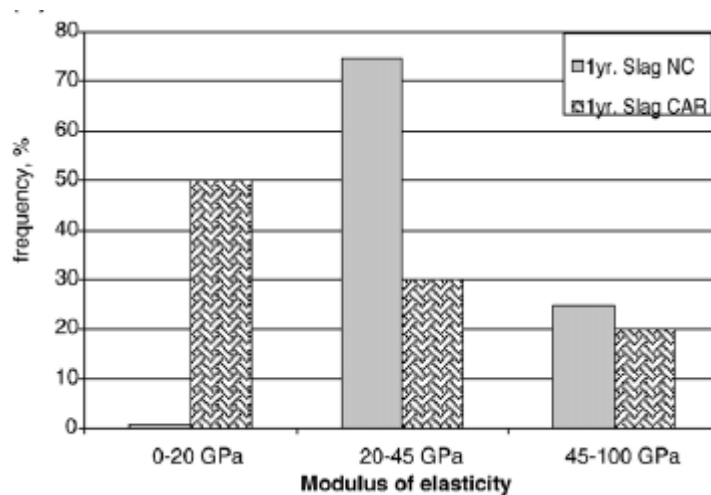


Figure 12. Moduli of elasticity for non-carbonated (Slag NC) and carbonated (Slag CAR) blast furnace slag paste measured by nanoindentation [77].

Non-destructive measurements performed on the carbonated surface, such as the rebound hammer, can be influenced by surface carbonation [78]. Due to the carbonation-induced

micromechanical strengthening, as described, locally higher rebound values may be recorded, which are not representative of the bulk strength [79-81]. Another possible mechanical effect of carbonation is an increase in (macroscopic) elastic modulus for Portland cement paste, e.g. observed by Fabbri et al. [56].

3.4. Carbonation shrinkage and cracking

Shrinkage of the cement paste can result as a consequence of carbonation [1, 82-84]. The mechanism of carbonation shrinkage is still poorly understood and under debate. Some studies (e.g. [40, 83]) suggest that carbonation shrinkage originates in the C-S-H, while others (e.g. [82]) claim that it results, at least in part, from the CH.

The following mechanism of Portlandite shrinkage has been proposed by Swenson and Sereda [82]:

They suggested that carbonation shrinkage has basically the same mechanism as drying shrinkage: it occurs due to a gradient of moisture content (resulting from the carbonation reaction of portlandite, equation (1)) within the CaCO_3 passivation layer which forms around carbonated CH (see section 2.1). Moisture held within this layer will be retained, but the moisture outside will be removed by drying due to environmental conditions, thereby creating a local moisture content gradient within the impervious coating itself and causing cracking. Shrinkage would not occur during the height of the carbonation reaction because the particular locality would be saturated with the water product. Since both lime and hydrated cement paste showed similar behaviour in their tests, they suggested that carbonation of the portlandite phase is at least one of the causes [82].

On the other hand, Chen et al. [83] suggested that carbonation shrinkage is, in fact, a special case of decalcification shrinkage. As already discussed in section 2.2., carbonation of C-S-H is

accompanied by a decrease of Ca/Si ratio. The degree of polymerization increases due to removal of interlayer Ca ions below Ca/Si=1.2. Furthermore, a morphology transition from a fractal (Ca/Si=1.7) to a sheet-like structure results for Ca/Si<1.1. Changes in content of hydroxyl groups in C-S-H are also induced by decalcification. If Ca/Si≤1 (in C-S-H), it is a highly plastic deformable material that exhibits very little cohesion [85]. Ca/Si~1.2 marks the initial point where interlayer Ca ions are removed from the C-S-H gel during decalcification. This causes an excess negative charge, which is most readily balanced through protonation and subsequent formation of Si-OH groups. Mean chain length then increases [40, 83]. Polymerization of silicate chains in C-S-H is the direct cause of shrinkage. Accompanying polymerization-induced decalcification shrinkage, the loss of interparticle cohesion in C-S-H and the subsequent propensity of C-S-H to structurally reorganize at low Ca/Si ratios is also believed to contribute to the marked shrinkage below Ca/Si~1.2. The progressive layering of C-S-H could account for the continuous decrease in specific surface area below Ca/Si~1.2 [83]. At extensive levels of decalcification (Ca/Si<0.66), when C-S-H begins to decompose, shrinkage could also result from decomposition of Ca-O sheets and the subsequent precipitation and polymerization of silica gel. Cracking is suggested to be caused by differential decalcification shrinkage due to a gradient of Ca/Si ratios across the specimen [83]. Due to their lower CH content, blended cement pastes are thought to be more vulnerable to carbonation cracking, which may be somewhat offset by their lower permeability.

Carbonation induced cracking was observed in multiple studies. For example, Fabbri et al. [56] found that elastic wave velocities of partly carbonated specimens showed significant pressure sensitivity up to a critical pressure. In rock physics, such pressure sensitivity is

commonly interpreted as resulting from elastic closure of microcracks. Borges et al. [40] observed a large number of cracks in carbonated blended slag paste (figure 13), while Han et al. [68] also found cracking in Portland cement paste (see figure 9), which accelerated the carbonation reaction close to the crack tip as expected [86].

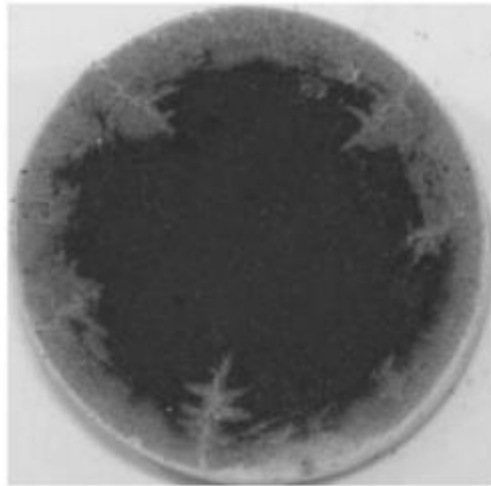


Figure 13. Carbonation induced cracking of a blended paste with 90% of blast furnace slag after 7 days of accelerated carbonation [40]

4. Factors influencing carbonation in cement based materials

4.1. Exposure conditions

Environmental factors such as relative humidity, CO₂ partial pressure, and temperature have a great effect on the carbonation process. It is commonly said that carbonation reaches its highest rate at a relative humidity between 50 and 70% [1]. In a study by Parrot [23] it was found, however, that the relative levels of carbonation for cement paste mixes with different pore structures were strongly dependent upon the moisture conditions during carbonation, with more porous mixes carbonating rapidly at high relative humidities.

The CO₂ diffusion rate in the carbonated zone depends on the partial CO₂ pressure [44] and the governing transport mechanism. Phung et al. [73, 87] studied carbon dioxide transport in cement paste by combined advection and diffusion. This was done by periodically stopping

the CO₂ influx and resuming after a rest period. Applying such cyclic CO₂ exposure resulted in a significantly increased degree of carbonation compared to continuous carbonation by clearly preventing saturation due to H₂O formation in carbonation reaction (see equation 1) and re-establishing gaseous CO₂ pathways (figure 14). The carbonation front resulting from coupled diffusion-advection was less sharp compared to pure diffusion.

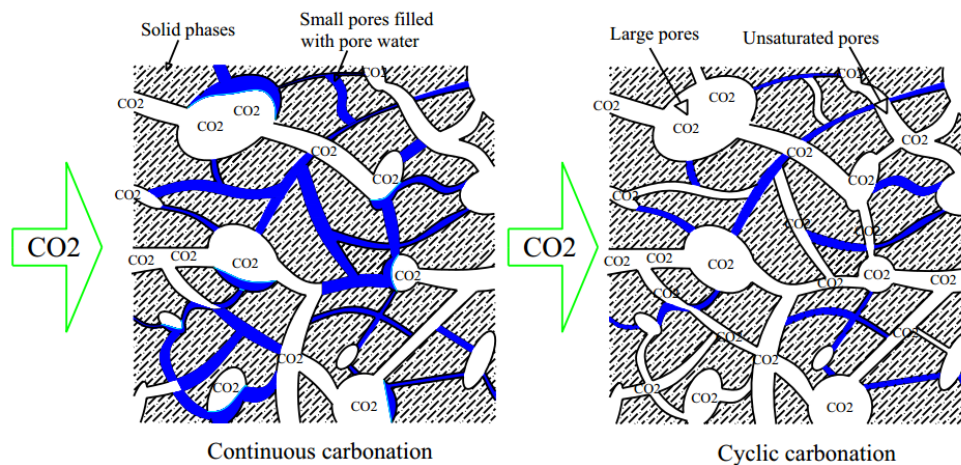


Figure 14. Conceptual comparison of aqueous and gaseous phase distribution within the cement pore structure during continuous and cyclic carbonation: Saturation degree is significantly increased due to continuous carbonation as small pores are mostly filled with released water as carbonation proceeds; while for cyclic carbonation part of small pores are emptied during drying cycle [73]

Castellote et al. [43] studied the influence of CO₂ concentration (ranging from natural ~0.03% to 100% CO₂) on microstructural changes in the cement paste. They observed that the processes are markedly different and dependent on the CO₂ concentration. For natural carbonation, a part of C-S-H decomposes to a phase close to silica gel (Ca modified silica gel), and in the 3% CO₂ sample it is still present but its intensity decreases compared to natural conditions (with appreciably higher polymerization of silicates). C-S-H is almost completely polymerised for 10% CO₂, and completely decomposed for 100% CO₂ to a silica gel with no unhydrated phase. Some uncarbonated CH remains in natural exposure conditions, while it

is absent from 3-100% CO₂ specimens. Furthermore, ettringite disappeared from 10% and 100% CO₂ samples, while C₂S decreased with increasing CO₂ concentration (being completely absent at 100%). They concluded that up to 3% CO₂ results in a microstructure similar to the natural process. This could influence conclusions made based on accelerated carbonation tests used as input for service life design of reinforced concrete structures, which commonly use higher CO₂ concentrations [88-90].

In recent years, multiple studies have focused on the interaction of supercritical CO₂ (abbreviated as scCO₂) with the cement paste [20, 69, 91, 92]. Supercritical carbon dioxide is a fluid state of carbon dioxide where it is held at or above its critical temperature and critical pressure. For CO₂, the critical point is 31.1 °C (around 304 K) and 7.39 MPa (around 74 bar) (figure 15). This is of interest both for some passive carbonation processes (such as geological CO₂ storage in exhausted oil wells, which were made with cement), as well as some active utilizations of the carbonation process (see figure 2). Supercritical CO₂ has liquid-like density but gas-like transport properties and no surface tension, which enables it to penetrate into very fine pores of the cement paste [69, 91]. In natural carbonation, the amount of CO₂ dissolved in the pore water is restricted by the low solubility of atmospheric CO₂ in water. This is not the case for scCO₂, which penetrates even small pores with ease, providing continuous availability of the fresh scCO₂ [26]. Therefore, carbonation of cement paste under supercritical conditions is not diffusion controlled [20]. As a result, carbonation of hydrated cements was greatly accelerated in a scCO₂ environment [93]. On top of this, carbonation kinetics is also different: in specimens carbonated under supercritical conditions, the C-S-H is more polymerised with lower Ca content compared to naturally carbonated specimens [26]. It also seems that, under scCO₂ conditions, the crystallized calcium carbonate comes

mainly from carbonation of C-S-H, while at the atmospheric conditions it comes mainly from CH [26]. However, supercritical carbonation process is also highly dependent on the water saturation degree of the cement paste: in dry samples, unhydrated phases and C-S-H mainly react, leaving CH present; while at high RH (95%) the mechanism is dependent on the w/c ratio – at w/c of 0.4/0.5, C₃S, C₂S, and C-S-H carbonate first, while at w/c=0.6 the CH reacts first [93]. Dependence of the supercritical carbonation process on the w/c ratio at high RH is probably related to differences in the pore structure. In a study of supercritical carbonation process by Fabbri et al. [56], wet samples showed carbonation with a sharp penetration front, while dry samples showed homogeneous carbonation, due to rapid diffusion of wet scCO₂ throughout the unsaturated porous network of dried specimens. The fact that scCO₂ can penetrate deeper into cementitious materials is often exploited in processes which utilize carbonation (figure 2), as described later.

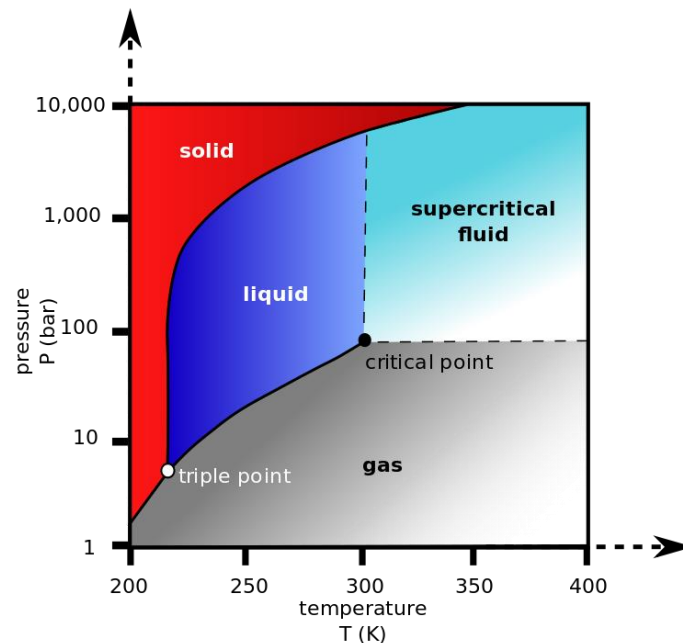


Figure 15. Carbon dioxide pressure-temperature phase diagram [94]

4.2. Supplementary cementitious materials

When supplementary cementitious or pozzolanic active materials (e.g. fly ash, blast furnace slag, or silica fume) are used as (partial) replacements to Portland cement, CH is consumed in a pozzolanic reaction, which also produces C-S-H gel [1, 53]. In that case, less portlandite is available for carbonation, which changes the kinetics and nature of the process. Furthermore, the surface of fly ash, slag or silica fume also acts as thermodynamically favourable area for the formation of nuclei of hydration products [53, 95]. Also some filler materials, such as limestone powder, form nucleation sites for hydration products [96, 97]. On the other hand, blended cement pastes show a denser microstructure compared to Portland cement paste [1]. As a result of these two (opposing) phenomena, it is not possible to a-priori assess the resistance of blended cement paste to carbonation.

Portland cement pastes blended with blast furnace slag have a lower Ca/Si ratio, resulting in a high risk of carbonation shrinkage [58] (figure 13). Rapid decalcification of C-S-H is expected in highly porous pastes, which is accelerated when Ca/Si ratio is reduced below 1.2. On the other hand, carbonation might not be a risk for low-permeability blended pastes [40]. Ngala and Page found a reduction in total porosity for a paste containing 30% blast furnace slag and pastes containing 30% fly ash, but with a significant increase in the proportion of large pores (>30 nm). Çopuroğlu and Schlangen [77] also observed a significant coarsening of the pore structure in BFS cement paste. Similar findings were reported for concrete [58]. The rate of carbonation of BFS concrete is significantly higher than that of OPC concrete [98]. The carbonation rate of the paste increases with increasing amount of blast furnace slag, and the mechanism of carbonation for high slag pastes seems to be governed by the amount of CH prior to carbonation [40]. Similarly, blended pastes containing fly ash show a rearrangement of the microstructure [99], with a decrease in total porosity and a creation of big pores [26,

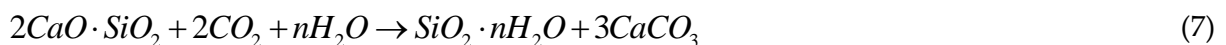
54]. Pastes become more vulnerable to carbonation with increasing percentage of fly ash [100], with an increase in C-S-H carbonation. This is probably due to rapid depletion of CH. Other pozzolanic materials (such as palm oil ash, rice husk ash, and silica fume) exhibit similar behaviour [27, 54, 101]. Similarly, increased susceptibility to carbonation was reported in ternary cement pastes containing thermally activated paper sludge and fly ash [102].

On the other hand, use of limestone filler promotes CO₂ uptake because calcite then precipitates preferentially on limestone phases (not CH or C-S-H) [73]. This process then limits the amount of calcite available for forming protective layers around CH. Therefore, in this case, CH carbonation is favoured compared to C-S-H. This can be of use for active carbon capture, as described later.

5. Possible uses of carbonation

5.1. Accelerated carbonation curing

In recent years, accelerated carbonation curing has been proposed as a way to capture atmospheric CO₂ [103-108]. This procedure involves exposure of freshly cast cement paste or concrete (mostly within the first 24 hours) to an elevated CO₂ concentration [109, 110]. In the past, mineral carbonation has been developed to prepare stable carbonate products by reacting CO₂ with magnesium silicate minerals [111]. Calcium silicate minerals can serve the same purpose [112-114]. Major chemical reactions governing carbonation curing of cement based materials are [115]:



A cementitious matrix cured using short term accelerated carbonation creates a microstructure with more strength-contributing solids than conventional curing [110, 116-120]. Unlike passive carbonation processes described previously, where all three polymorphs of calcium carbonate have been reported to form, accelerated carbonation curing seems to result mostly in formation of the stable polymorph, calcite [103, 109]. In one study, however, traces of aragonite and vaterite were also observed [120].

Accelerated carbonation curing has several important benefits over moisture curing. Initial studies showed that accelerated carbonation curing can lead to high early age strength and rapid strength gain [103] (figure 17). It seems that, in early hydration stages, the C-S-H becomes intermingled with carbonates, generating an amorphous calcium-silicate-hydrocarbonate binding phase [116], while CH is converted to CaCO_3 [109]. In fact, effects responsible for marked strength gain probably include subtle changes in C-S-H microstructure, not only simple pore filling by CaCO_3 as often stated [121, 122].

Carbonation of fresh cement paste seems to have a complex influence on the microstructure: moderate exposure to CO_2 increases the compressive strength, while prolonged exposure may negatively affect the mechanical properties [117] (Figure 18). Even though longer carbonation would result in more CO_2 captured by this process, an optimal duration of carbonation curing should therefore be selected. During carbonation, part of the bound water is lost and this causes shrinkage of the crystalline structure, without affecting its degree of polymerization. This more densified structure promotes a higher compressive strength. After this initial period, the mechanical resistance begins to decrease due to increase of carbonation degree toward the inner regions of the paste, by carbonation of inner CH phases, as well as of the hydrated C-S-H for longer carbonation times [117]. Furthermore,

appropriate time for start of carbonation curing needs to be carefully chosen. Carbonation of the fluid cement paste is not beneficial, because a high amount of CaCO_3 forms at the solid/gas interface, preventing CO_2 diffusion into the paste [116]. It seems most beneficial to apply the procedure during the hydration accelerating period, when significant production of CH and C-S-H takes place [116].

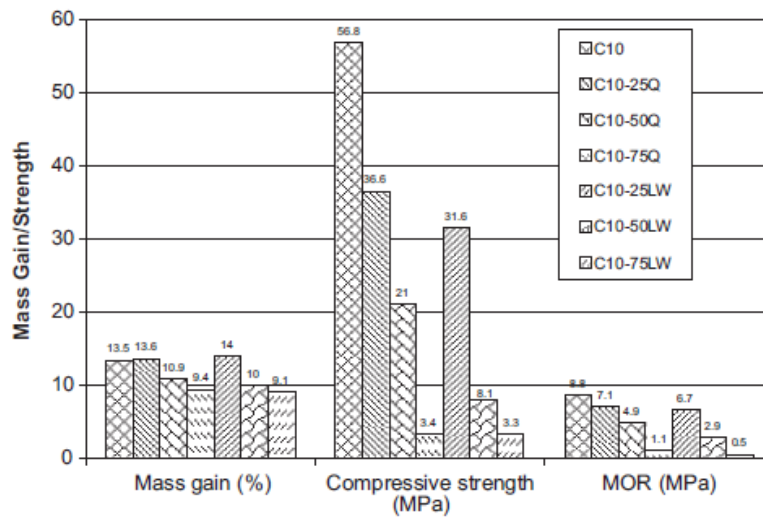


Figure 17. Mass gain, compressive strength, and modulus of rupture (MOR) for different cement paste and concrete mixes exposed to 2h accelerated carbonation (100% CO_2) and tested at 7 days (note: C10-cement paste, others- various concrete mixtures with quartz (Q) or lightweight aggregates (LW)). Note that reference paste had compressive strength of 43 MPa [103].

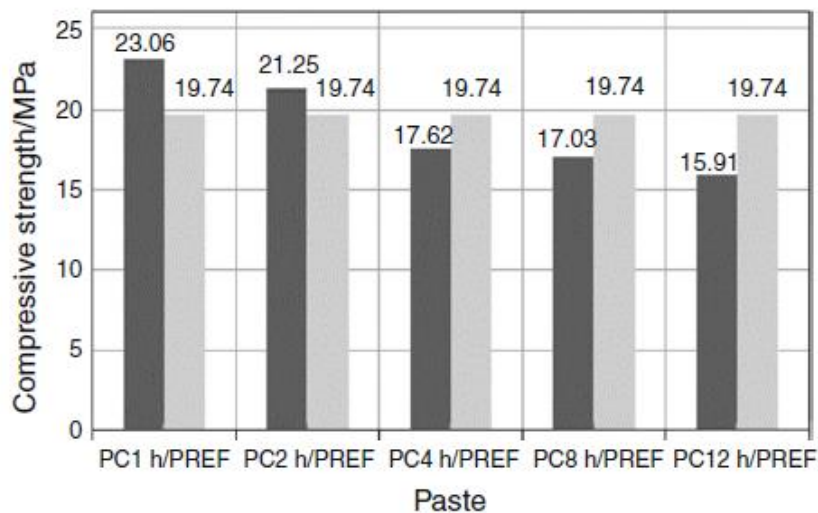


Figure 18. Influence of duration of accelerated carbonation curing on compressive strength of cement paste [117].

During the accelerated carbonation curing procedure, specimens are exposed to drying (the environment being at $RH < 100\%$) at an early age, while being exposed to CO_2 at the same time. Due to the water loss, hydration is hindered. Although water loss during this period may not be an issue, additional water curing (rehydration i.e. water spraying in most cases) after the accelerated carbonation procedure is advised to provide enough water for further hydration [103, 123]. This is because early carbonation does not hinder subsequent hydration [109]. Carbonation curing has even been found to increase durability, e.g. by decreasing capillary water uptake, chloride resistance in RCPT tests, and showing better sulphate resistance [104]. Although this procedure decreases the pH value, pH still remains above the corrosion initiation threshold (at around 10.5) [104, 123, 124].

Effectiveness of the accelerated carbonation curing procedure depends on many factors. One of the more important factors is the cement fineness: in the study of Shao et al. [103], finer cement (Blaine value $481 \text{ m}^2/\text{kg}$) was able to capture 10% more CO_2 and achieve 10% higher strength compared to a less fine cement (Blaine value $373 \text{ m}^2/\text{kg}$). The addition of limestone powder as an inert filler to the cement paste seems to promote carbon capture and therefore help the accelerated carbonation procedure [73, 124], since fine limestone powder particles (10-20 microns) serve as nucleation sites for $CaCO_3$ precipitation. Furthermore, porosity, w/c ratio, relative humidity, and CO_2 diffusivity all affect the effectiveness of the procedure [116].

A technological issue that needs to be overcome in order to fully utilize this technology is the limited CO_2 penetration depth, even in young concrete. Commonly, very thin specimens (up to 10 mm thickness) are therefore produced. Elevated CO_2 concentrations, ranging from 20% [110, 116, 117] to 100% [103, 104, 109, 123, 125], have been used to enhance the CO_2 ingress.

More complex technologies such as a flow-through reactor [105] and supercritical carbonation [121, 122] were also proposed.

An important aspect of this technology is the ability to capture atmospheric CO₂. Theoretical calculations of Shao et al. [103] suggest that, with 100% carbonation efficiency, 1 t of cement could absorb 0.5 t of CO₂ to form 1.5 t of solid calcium carbonates and silica gels. In practice, this is limited by strength and diffusivity considerations. In reality, CO₂ uptake of 9-20% by mass of cement has been achieved [103, 105, 123].

Accelerated carbonation curing therefore has great potential for creating sustainable cementitious products with high early strength and good durability. However, more research is needed before it is available to the engineering practice.

5.2. Improvement of fibre reinforced cementitious composites

Similar to accelerated carbonation curing, carbonation treatments can be used to improve the mechanical and durability properties of cementitious composites which use different types of fibres [29, 69, 91, 94, 126-129]. In addition, fibre reinforced composites are in general more susceptible to carbonation due to the increased porosity at the fibre/matrix interface. However, a major problem with some fibre types is their deterioration in the highly alkaline conditions in the cementitious matrix. Two main classes of fibres that are affected are glass and natural fibres.

Glass fibre reinforced composites (GRC) made with Portland cement are known to degrade in wet environments, resulting in a significant strength and toughness loss within 10-20 years [69, 91]. This is due to: (1) CH nucleation within the alkali-resistant glass strands that constitute the main reinforcement; (2) corrosion of fibres in the highly alkaline matrix. Carbonation of these composites converts CH into CaCO₃, while at the same time it

decreases the pH of the matrix. Purnell et al. [69, 91] treated their GRC specimens using a supercritical carbonation procedure. The treatment was beneficial in many ways: the bend over point (the stress level at which significant matrix cracking occurs, and which is used as design strength for most GRC applications) was increased by 60-70%; the design toughness (defined as the area under the stress-strain curve up to a strain of 0.1%) was enhanced 40-60%; the fracture toughness increased by 60%; the tensile strength increased by 20% and failure strain by 25%. They suggested that the effect of supercritical carbonation on C-S-H (structural changes of the gel) is of the primary importance for improvement of mechanical properties of the matrix. In addition, the fibre/matrix bond was enhanced and appeared more intimate in the treated sample, with the matrix closely following the "coastline" of the fibre strand, probably accounting for the higher bond. As a result, the frictional bond was increased by a factor of 2.3 compared to reference specimens.

Similar to GRC, cementitious composites made using natural fibres are susceptible to deterioration due to the high alkalinity of the matrix. Vegetable/cellulose fibres mineralize in the high pH of the cement matrix [126]. This is caused by the free ions from the dissolution of Portland cement phases that penetrate into the fibre cavity, leading to re-precipitation of ettringite/monosulphate and CH into the fibre and inducing the stiffening of cellulose fibres. This causes low durability of cellulose fibres, and results in reduced mechanical performance (in addition to loss of adhesion between the fibre and the matrix) [127]. Carbonation treatment can cause a drop in pH, thereby protecting the fibres, while strengthening the matrix at the same time. Also, in this case, a significant improvement of the fibre/matrix bond can result [94]. The dissolution of CH and precipitation of calcite affected the bulk density and pore volume of the fibre/matrix interface. Santos et al.[94] noted that the

fibre/matrix interface allowed the massive precipitation of calcium carbonate during a supercritical carbonation treatment, causing a decrease in capillary and gel porosity around the fibres. In their study, a change of Ca/Si ratio close to the interface was observed by EDS (Figure 19). In the non-carbonated sample, a small difference of Ca/Si was detected between regions 1 and 2 (Fig. 19), indicating a relative equilibrium of the nanostructure between the regions. Carbonated sample showed significant differences. These results indicate changes in the content of hydroxyl groups in C-S-H as a consequence of its carbonation. Due to carbonation, Ca content in the C-S-H is reduced, leading to changes in silica structure. However, it did not turn into silica gel. Supercritical carbonation reduced free water, increased CO₂ diffusion around the fibre interface, and, consequently, calcium ions were sequestered from region 2 to 1 by means of a diffusion controlled carbonation reaction (Figure 19). The matrix in the vicinity of the fibre showed a gradient of porosity, with regions of lower and higher density compared to the bulk matrix (Figure 20). Thus, carbonation in this zone can be characterised by precipitation of calcite in the pores, decalcified C-S-H gel, and production of gypsum from decomposition of ettringite, forming a semi-permeable zone around partially carbonated crystals. Mechanical properties of these composites, both before and after accelerated ageing, are significantly improved by the carbonation treatment [94, 126].

It can be concluded that accelerated carbonation treatments have potential to improve mechanical properties and mitigate ageing in various fibre reinforced composites. However, similar to accelerated carbonation curing technology, some limitations are present, especially related to the thickness of the material which can be treated. More research, possibly with

even more focus on supercritical carbonation or other alternative procedures, is needed to improve this technology.

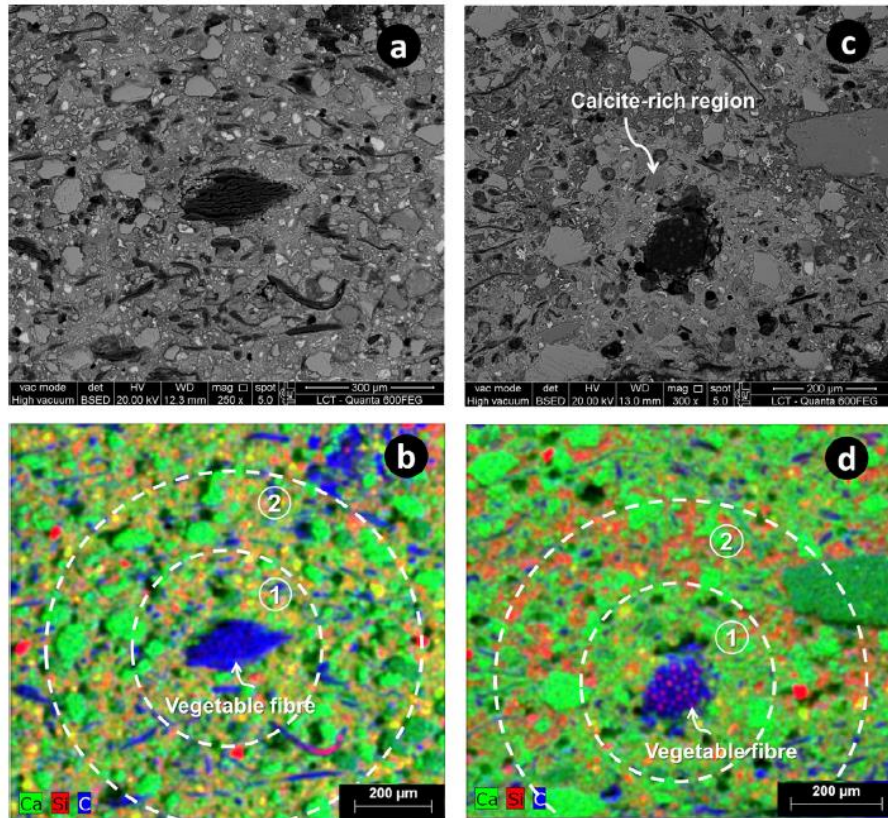


Figure 19. SEM/BSE micrographs and EDS maps of natural fibre composite: (a) and (b) non-carbonated and (c) and (d) after supercritical CO_2 treatment. Ca/Si ratio in two regions (1) and (2) in the vicinity of the fibre was measured by EDS [94]

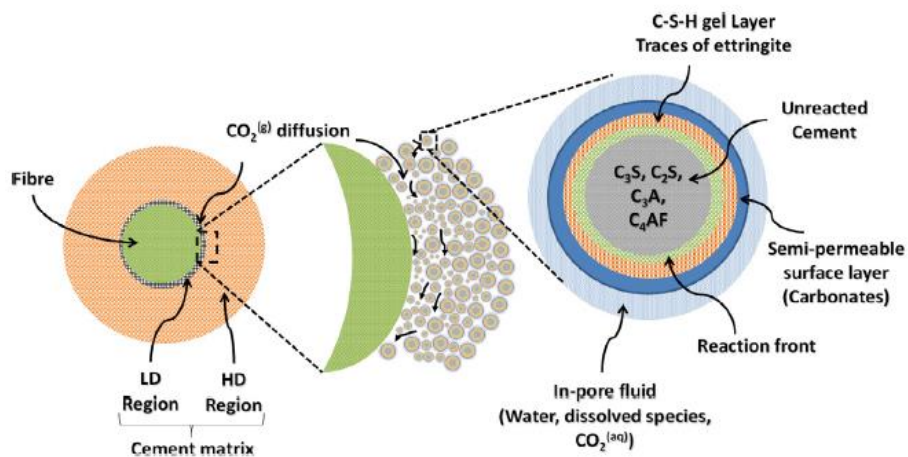


Figure 20. Left: Schematic illustration of the fibre and matrix interface with regions: lower and higher density, respectively, LD and HD, during supercritical carbonation treatment and details of the hydration reactions. Right: Schematic illustration of the carbon dioxide diffusion process [94].

5.3. Concrete recycling

In recent years, demolished concrete structures have been commonly recycled, and the material used as aggregate in new concrete production [130-134]. Recycled aggregate concrete has, in general, lower strength and durability compared to natural aggregate concrete [131, 135-137]. A major issue in this type of concrete is the fact that recycled aggregates are surrounded by a layer of mortar, which is the weakest point in recycled concrete [138]. In fact, this concrete has two interfacial transition zones – one within the recycled aggregate itself (between the aggregate and the adhered old mortar), and the other between the recycled aggregate and the new paste [139] (Figure 21). Therefore, improvement of the adhered mortar should result in improved overall properties of recycled aggregate concrete.



Figure 21. Recycled aggregate in concrete [140]

Several possible ways of improving the properties of adhered mortar in recycled aggregate concrete have been proposed. For example, Li et al. [139] suggested adjusting the concrete mixing sequence, while Zhang et al. [141] suggested using a surface treatment of recycled aggregates using nanoparticles. Another promising approach seems to be a carbon dioxide

treatment of recycled concrete aggregate [140, 142-144]. This approach uses accelerated carbonation for short periods (1 day-1 week) to improve the quality of recycled aggregates. The procedure increases the apparent density, and reduces both the water absorption and crushing value of recycled aggregate [140] (compared to non-treated recycled aggregates). Major improvements of the microhardness of the old mortar and the new ITZ are a cause of this. As a result, properties of mortar and concrete prepared using treated recycled aggregates were significantly improved: carbonation treatment increased the flowability and compressive strength of the mortar [142] and compressive and flexural strength of concrete [140]. Furthermore, a decrease in chloride diffusivity was observed [142].

Another use of accelerated carbonation in concrete recycling is found in reuse of waste hydrated cement paste. Waste hydrated cement paste is a by-product of concrete recycling, and is commonly landfilled [145]. Its quantity generated in aggregate recycling processes can be as high as 1/3 the mass of the waste concrete [146]. With accelerated carbonation of waste hydrated cement paste, CO₂ can be captured, waste reused, and building materials with good performance produced [145]. In the study of Fang and Chang [145], mixing of the waste powder with water, compaction under moderate pressure (8 MPa), and accelerated carbonation resulted in satisfactory compressive strength of the specimens (up to 30 MPa after 24 hours of carbonation in a 100% CO₂ chamber). It was observed that the compressive strength of the compacts increases with increasing CO₂ uptake. At the same time, total pore volume and pore size decrease. Phase analysis showed that carbonation mainly affected Ca(OH)₂ and C-S-H. CH has an advantage over C-S-H in the carbonation procedure. Compressive strength showed a slower gain when C-S-H carbonates at a later stage of the carbonation process.

Even though this technology is similar in principle with those described in sections 5.2 and 5.3, it is still not very mature, with only a few studies devoted to it. More research is needed to confirm and optimize the benefits of using this technology for concrete recycling.

5.4. Waste immobilization

It has been shown that carbonation can positively affect the immobilization of heavy-metals within cementitious matrixes [147-151]. Accelerated carbonation is sometimes used as a stabilisation/solidification technique for different types of cementitious materials containing various metal pollutants. An extensive review on the use of carbonation in waste immobilization was given by Fernandez Bertos et al. [147], therefore it is only briefly discussed here. Carbonation of cement-waste mixtures modifies the microstructure, increases the strength and may decrease the leaching of metals. As a result of carbonation, precipitation of calcium-metal double salts and formation of metal-silicate complexes may occur [147]. The effect of carbonation is twofold: some heavy metals form either hydroxide-carbonate or carbonate deposits on calcium silicates. Furthermore, a drop in pH reduces metal mobility for some metals, while for others leaching rate may increase. For some species, there is a stabilization of metal carbonate precipitates, due to provision of inorganic CO₂, with an increase in leaching rate at the same time [152-155] (for details, see [147]).

Carbonation treatments of waste seems, therefore, to be a good option for immobilization of certain types of waste in cementitious matrices. However, the treatment can be detrimental, depending on the waste type, so for new types of waste and different cementitious materials, additional experiments should be performed.

6. Summary and conclusions

Carbonation of cement paste is a complex process influenced by many factors, such as the binder type and composition, porosity, exposure conditions, etc. In the past, many studies have focused on carbonation induced corrosion of reinforcing steel. However, in recent years, the attention has shifted towards understanding and quantifying carbonation related microstructural changes under various conditions. A number of reasons can be given for this, ranging from use of depleted Portland cement based oil-wells to store atmospheric CO₂, to innovative uses of carbonation as a substitute for steam curing. Based on the presented review, a number of conclusions can be drawn:

- During the carbonation process, calcium hydroxide is not the only hydration product reacting with CO₂. Other phases in the cement paste, such as C-S-H, ettringite, and unhydrated cement all react with carbon dioxide. Kinetics of the carbonation process seems to be governed by both the exposure and the microstructural conditions.
- Carbonation of hydrated cement paste causes a change in porosity and pore size distribution. However, carbonation cannot be viewed as a continuous process which plugs the porosity, even in Portland cement paste: at later stages, the porosity increases, probably due to carbonation of C-S-H and its decalcification.
- Carbonation causes complex micromechanical changes in cementitious systems: an increase in strength might be observed due to structural changes in the C-S-H, which can be followed by carbonation cracking. Therefore, it is difficult to a-priori assess the influence of carbonation on mechanical and transport properties.
- Controlled carbonation can be used as an active technology for improvement of cementitious materials. For example, accelerated carbonation curing can be used to achieve high strength and improved durability for cementitious and fibre reinforced

cementitious materials. Furthermore, accelerated carbonation treatments show promising results in a number of fields, such as concrete recycling and waste immobilization.

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