

Review article

Dimensional change of cement paste subjected to carbonation in CO₂ sequestration and utilization context: A critical review on the mechanisms



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ABSTRACT

With the utilization of mineral CO₂ sequestration technology, the volume stability of cement paste exposed to carbonation is catching significant interest. This review attempts to summarize the state-of-the-art knowledge on the volume stability of cement paste upon carbonation and thereby benefit the decision-making process in the utilization of CO₂ sequestration technology in the concrete industry. In this work, the dimensional change caused by carbonation of each major cement hydration product was analyzed individually, with a special focus on the carbonation of calcium silicate hydrate (C-S-H). Key parameters affecting carbonation reactions and the associated volume stability of cement paste were examined, e.g. CO₂ concentration, temperature, relative humidity, and supplementary cementitious materials. On that basis, the typical evolution of dimensional change of cement paste upon carbonation was presented and elucidated, with the critical research gaps identified. Overall, carbonation of calcium hydroxide and calcium silicate (C₂S and C₃S) tends to cause a volume expansion, whereas carbonation of ettringite and C-S-H phases leads to the opposite. The change in micropore structures of cement paste upon carbonation depends mainly on the competition between the clogging of capillary pores filled with calcium carbonate and the formation of additional capillary pores induced by the decalcification of C-S-H. To assess the volume stability of cement paste carbonated at early ages, the coupling effect between hydration and carbonation requires further studies. For the measurement of linear carbonation deformation of cement-based materials, a standard test procedure is urgently needed.

1. Introduction

Mineral carbon dioxide (CO₂) sequestration has been an emerging approach, e.g. in the (precast) concrete industry, to reduce the carbon footprint as well as to improve the performance of cement-based construction materials [1–6]. However, with the extensive utilization of CO₂ sequestration technology, the volume stability of cement-based composites subjected to carbonation is becoming a big concern, because mainly of the potential cracking risk induced by carbonation shrinkage of cement paste [3,7–9]. Once such cracking occurs, the impermeability against the ingress of harmful agents of the cement-based composites may be seriously compromised, and the mechanical properties (e.g. strength and elastic modulus) may reduce considerably. Another significant issue related to the carbonation induced cracking is the accelerated corrosion of reinforcement embedded in cement-based materials [7,9–11]. Undoubtedly, the undesirable cracking can affect the decision-making process in the

utilization of mineral CO₂ sequestration technology in the concrete industry.

Most studies had focused on the CO₂ uptake capacity, carbonation depth, and mechanical properties (e.g. strength and elastic modulus) of cement-based composites exposed to carbonation [12–15]. Few studies had paid attention to the dimensional stability of the composites upon carbonation, due mainly to the lack of functional test setups and the complexity of carbonation reactions of cement hydration products. Nowadays, with the application of, e.g. advanced microscopy and spectroscopy technology [16–21], more and more research has focused on the detailed carbonation process of hydration products of cement paste as well as the nanostructures and particle sizes of main carbonation products. This enables the establishment of a comprehensive understanding on the volume stability of cement-based composites exposed to accelerated carbonation. In this study, based on a critical review of those relevant studies, the volume stability of cement paste upon carbonation is discussed and investigated in-depth.

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Generally, major hydration products of cement (by mass) consist of 50–70% calcium silicate hydrate (C-S-H), 20–25% calcium hydroxide (or portlandite, CH), and some Aft and AFm phases [22–24]. One common AFm phase in hydrated cement is aluminate ferrite monosulfate, and the most common Aft phase is ettringite (around 15–20%, by mass). Additionally, un-hydrated cement compounds also exist [24], e.g. dicalcium silicate (C₂S) and tricalcium silicate (C₃S). Theoretically, all those calcium bearing phases can react with CO₂ under suitable conditions, but the carbonation rate and kinetics of each calcium bearing phase appear to be different [25–27]. In this study, the effect of carbonation of major calcium bearing phases on the volume stability of cement paste was reviewed comparatively (see Section 2), with a special emphasis on the carbonation of C-S-H. Following that, factors affecting carbonation process of calcium phases in cement paste were examined systematically (see Sections 3 and 4). On that basis, the typical volume evolution of cement paste exposed to carbonation was presented and elucidated (see Section 5). At last, key knowledge gaps in the establishment of a comprehensive understanding on the volume change of carbonated cement paste were identified, with innovative research perspectives put forward correspondingly. Overall, the discussion and conclusions presented in this review aim to provide valuable insights for assessing the dimensional change of cement paste upon carbonation and thereby promoting the development of intelligent CO₂ sequestration and utilization technology in the concrete industry.

In addition, it should be clarified that the current review aims at discussing the carbonation performance of Portland cement paste mainly exposed to gas-solid (carbonation) conditions [1,28,29], i.e. CO₂ is in the gaseous form. It is well acknowledged that geologic carbon sequestration (GCS), a process to capture and store CO₂ in deep geologic formations, is considered a key strategy to mitigate the global warming and climate issues [30]. Also, cement is a common material, if not the most common, used for plugging and sealing GCS reservoirs [31]. In this case, CO₂ is in a supercritical state (sc-CO₂) between gas and liquid due to high pressure and temperature. For cement paste exposed to wet sc-CO₂ and CO₂-saturated brine conditions [32–34], the carbonation behaviour could have distinct features than that discussed in this review. Despite the importance, it is not the intention to cover cement carbonations subject to sc-CO₂ in this work.

2. Carbonation of major hydration products

2.1. Overall carbonation process

Prior to the occurrence of carbonation reactions, gaseous CO₂ diffusion through hydrated cement paste takes place at first (as shown in Fig. 1), which is strongly related to the microstructural features (e.g.

micropore sizes and volume), water content, CO₂ concentration, and pressure among other factors [1,28,29,35]. As CO₂ diffuses, the dissolution of CO₂ into pore liquid (water) occurs simultaneously (see Fig. 1). According to Chen et al. [36], the dissolution rate of CO₂ can be expressed as a function of temperature, relative humidity (RH), and CO₂ concentration, as given by Eq. (1). The formed carbonate ions react with calcium ions from leaching of calcium bearing minerals, resulting in the precipitation of calcium carbonate in the pore liquid. With the consumption of calcium ions and carbonate ions, continuous dissolution of CO₂ and leaching of calcium ions happen. However, it should be noted that the precipitation of calcium carbonate may form a calcium carbonate layer on the surface of calcium bearing minerals which can hinder the further leaching of calcium ions and thereby retard carbonation reactions [1,37–40]. Besides, the precipitation of calcium carbonates can fill the micropores of cement paste, which may prevent further CO₂ diffusion and thus retard carbonation reactions too (as detailed in Section 4). After carbonation, the net mass of CO₂ that has been converted into precipitated calcium carbonate is defined as the CO₂ uptake of cement paste, which can be determined by thermogravimetric analysis [41].

$$\varphi = k_0 \cdot e^{E_a/RT} \cdot P_w \cdot P_c \quad (1)$$

where, k_0 is the surface carbonation rate (constant), E_a is the apparent activation energy (J/mol), R is the ideal gas constant (J/(mol•K)), T is the temperature (K), P_w and P_c are the partial pressure of water vapour and CO₂ (Pa).

To focus on carbonation reactions closely related to dimensional change of cement-based composites, the carbonation courses of C-S-H, CH, and ettringite were emphasized in this study. For carbonation of hardened ordinary cement paste, CH, ettringite, and C-S-H with high calcium content (or high calcium to silica ratio, Ca/Si) tend to carbonate simultaneously [20], but CH and ettringite are more susceptible to carbonation. Therefore, at an initial period of carbonation, CH and ettringite undergo rapid carbonation [38,43], while carbonation of C-S-H is relatively less significant. Following the consumption of CH and ettringite, the pH of pore liquid reduces [44–46], and gradual carbonation of C-S-H accelerates (detailed in Section 2.4) [47,48].

2.2. Carbonation of portlandite

The chemical reaction between CH and CO₂ inside cement paste [49] can be expressed as



According to the thermodynamic model proposed to approximate

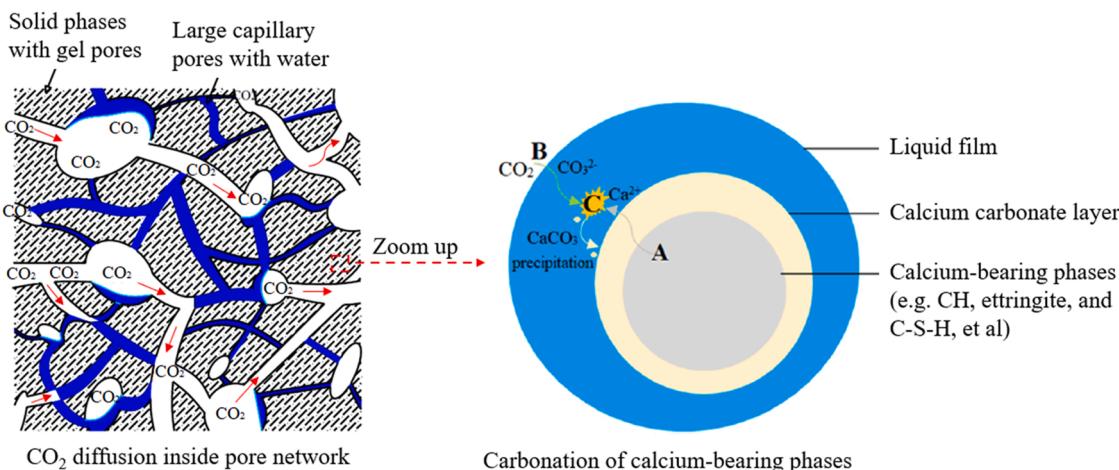


Fig. 1. Diagram of CO₂ diffusion and carbonation reactions inside cement paste (adapted from [1,42]).

the rate of carbonation of CH [49], it was assumed that for cement paste with RH lower than 50%, there is no carbonation of CH taking place. For cement paste with RH between 50% and 90%, the higher the RH, the faster the carbonation of CH. As long as the RH is higher than 90%, the carbonation of CH is no longer restrained (or affected) by RH change.

Theoretically, the volume change (ΔV_{CH}) induced by carbonation of 1.0 mol CH can be calculated by

$$\Delta V_{CH} = 100 \cdot \left(\frac{V_{M,CC}}{V_{M,CH}} - 1 \right) \quad (2)$$

where, $V_{M,CC}$ and $V_{M,CH}$ are the molar volumes of calcium carbonate and CH [37], respectively.

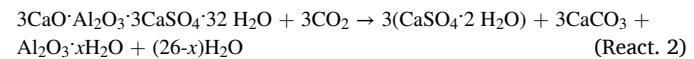
In Eq. (2), the positive volume change means expansion, while the negative represents the opposite. Literally, due to the high molar volume of calcium carbonate than that of CH, carbonation of CH tends to cause a volume expansion. In practice, because calcium carbonate generally precipitates unevenly, additional porosity is usually generated [1,19, 37]. Moreover, due to the volume expansion during the transformation of CH into calcium carbonate, microcracks may appear at the rim zone of solid CH where carbonation occurs. Those microcracks may accelerate the carbonation of CH [37].

The molar volume of calcium carbonate ($V_{M,CC}$) depends mainly on its polymorph [50]. Generally, through transmission electron microscopy (TEM) imaging, three major calcium carbonate polymorphs can be detected, such as calcite, aragonite, and vaterite (as shown in Fig. 2). $V_{M,CC}$ of the three calcium carbonate polymorphs is approximately 36.9, 34.2, and 37.6 cm³/mol, respectively. According to Eq. (2), the formation of aragonite upon CH carbonation can generate 7.8% volume expansion, whereas the formation of calcite and vaterite generates 16.4% and 18.6%, respectively. According to [51–55], the polymorph of the produced calcium carbonate in React. (1) is affected by carbonation conditions (temperature, RH, and CO₂ concentration). Besides volume

change, the transformation of CH into calcium carbonate could increase intrinsic modulus from ~40 GPa for CH to around 67 GPa for calcite (and even to a much higher value for vaterite) [56].

2.3. Ettringite's carbonation process

The carbonation process of ettringite is essentially similar to that of CH, as illustrated in Fig. 1. Briefly, the carbonation of ettringite [27,50, 57] can be given as



Thus, the volume change (ΔV_{AFt}) induced by carbonation of 1.0 mol ettringite can be calculated by

$$\Delta V_{AFt} = 100 \cdot \left(\frac{3 \cdot V_{M,CS} + 3 \cdot V_{M,CC} + 2 \cdot V_{M,A}}{V_{M,E}} - 1 \right) \quad (3)$$

where, $V_{M,E}$ is the molar volume of ettringite (approximately 710.3 cm³/mol), $V_{M,CS}$ is the molar volume of calcium sulfate (~46.0 cm³/mol), and $V_{M,A}$ is the molar volume of aluminium hydroxide (~33.5 cm³/mol).

It can be noted from React. (2) that upon carbonation of ettringite, a great deal of crystal water is released and converted into liquid form. Since carbonation leads to the conversion of ettringite into products (with low molar volume) that occupy less space [58], a substantial volume decrease tends to occur, as determined by Eq. (3). Like the carbonation of CH, decomposition of ettringite upon carbonation is also affected by carbonation conditions [27,36]. In the absence of pore liquid (low RH) of cement paste, ettringite is hardly carbonated, whereas in the case of plenty pore liquid, ettringite can easily be decomposed to gypsum, calcium carbonate, and alumina gel [59]. Factors affecting the carbonation process of ettringite are discussed in Sections 3 and 4.

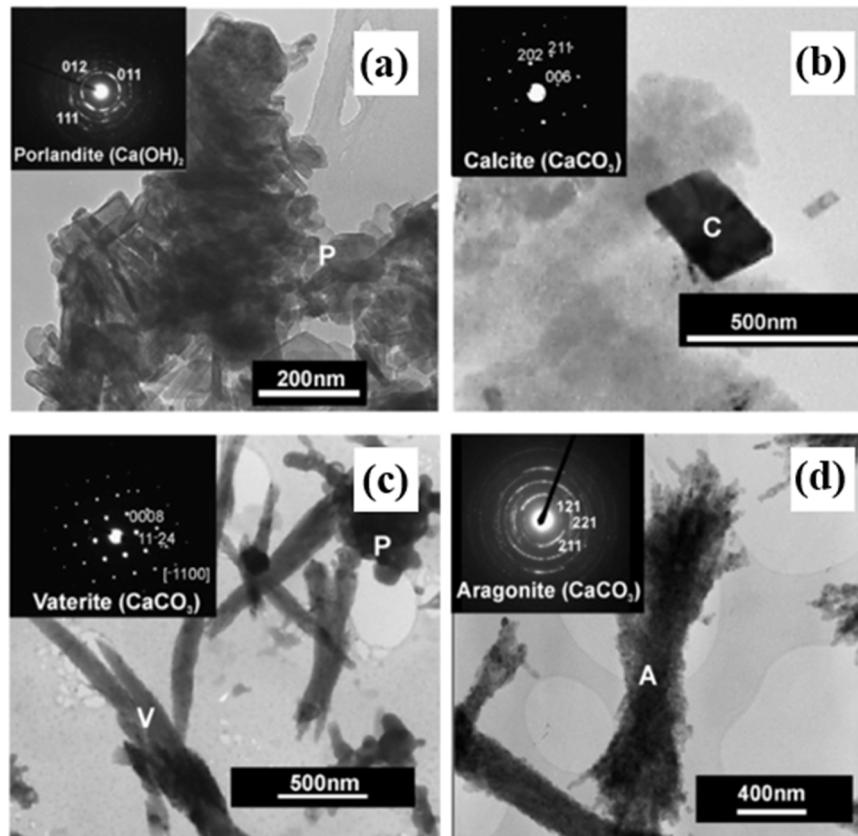
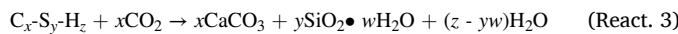


Fig. 2. TEM images of (a) CH, (b) calcite, (c) vaterite, and (d) aragonite (adapted from [55]).

2.4. C-S-H's carbonation process

2.4.1. Volume change of C-S-H upon carbonation

Compared with CH and ettringite, the carbonation process of C-S-H tends to be more complex. Generally, C-S-H phases in hydrated cement paste can be classified into different types according to grain sizes and morphology [60]. The morphology of C-S-H is affected by many factors, e.g. cement types, chemical additives, hydration conditions, and hydration degree of cement, etc. According to Morandieu et al. [26], the complete carbonation of a specific C-S-H phase can be given as follows.



where, x , y , and z are the amount of CaO, SiO₂, and H₂O in the C-S-H phase, respectively. w is the amount of water chemically bound within the produced silica gel.

Carbonation process can change both chemical compositions and nanostructures of C-S-H, which can be featured by a progressive decrease in Ca/Si ratio and formation of lengthened silica gel chain of carbonated C-S-H [61,62], as shown in Fig. 3. In the literature, it has been concluded that carbonation can decalcify C-S-H gradually by removing or migrating calcium ions from the inner-layer to out-layer of C-S-H to produce calcium carbonate [56]. C-S-H phases with high Ca/Si tend to carbonate faster than those with low Ca/Si [63,64]. After complete carbonation, calcium carbonate and silica-rich gels without calcium that are generally intertwined together randomly are the final carbonation products.

Upon carbonation, the carbonation degree (θ) of C-S-H can be determined according to the change of Ca/Si [66], as expressed by Eq. (4).

$$\theta = \left(1 - \frac{Ca/Si_c}{Ca/Si_0}\right) \times 100 \quad (4)$$

where, Ca/Si_0 and Ca/Si_c are the Ca/Si of C-S-H before and after carbonation, which can be measured, e.g. by ²⁹Si NMR (Nuclear Magnetic Resonance).

During the decalcification and polymerization of C-S-H upon carbonation, a volumetric decrease of C-S-H phases has been widely reported, which is generally believed as the origin of carbonation shrinkage of cement paste. According to [7,67], with the carbonation degree rising, the evolution of the carbonation shrinkage of C-S-H with an initial Ca/Si of ~1.7 follows a second-order polynomial (see Fig. 4). When the C-S-H is completely carbonated, the final carbonation shrinkage can reach approximately 7.8 mm/m.

According to React. (3), the volume change induced by complete carbonation of 1.0 mol of C-S-H can be determined by Eq. (5).

$$\Delta V_{CSH} = 100 \cdot \left[\frac{V_{M,CC} \bullet (Ca/Si) + V_{M,SS}}{V_{M,CSH}} - 1 \right] \quad (5)$$

where, $V_{M,SS}$ is the molar volume of silica gel, $V_{M,CC}$ is the molar volume of calcium carbonate. $V_{M,CSH}$ is the molar volume of C-S-H before carbonation, which depends on Ca/Si and water content [68].

The variation of the molar volume of C-S-H phases over Ca/Si is summarized and plotted in Fig. 5. Usually, the higher the Ca/Si, the

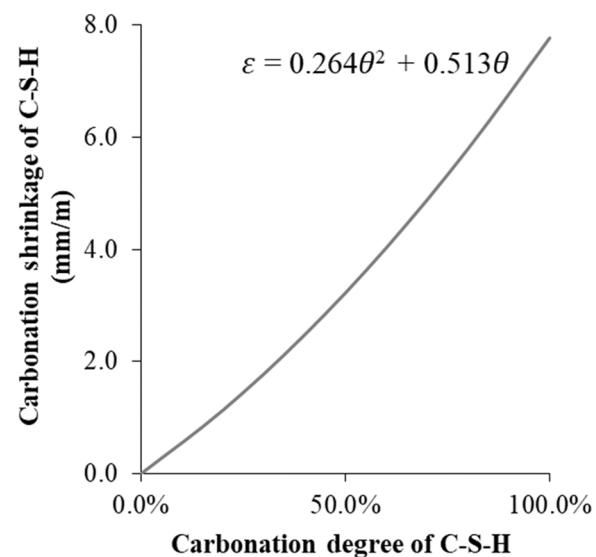


Fig. 4. Evolution of carbonation shrinkage of C-S-H with an initial Ca/Si of 1.7 (adapted from [7]).

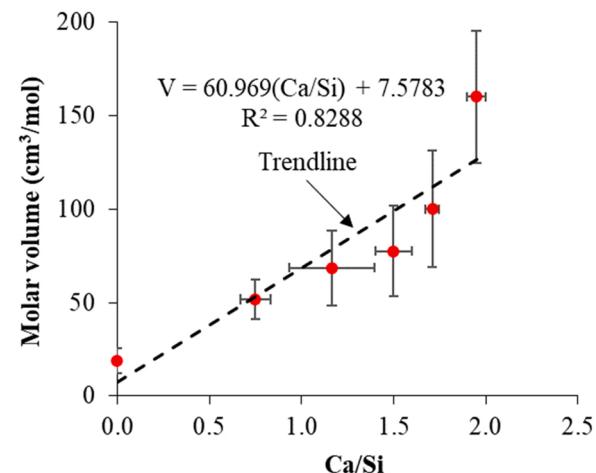


Fig. 5. Variation of molar volume of C-S-H over Ca/Si (vertical and horizontal error bars represent standard deviation of molar volume and Ca/Si, respectively), data collected from [62,68,69,71,72].

higher the molar volume of C-S-H. According to the presented data in Fig. 5, the relationship between $V_{M,CSH}$ and Ca/Si was approximated by a linear function, as reported in [68,69]. Inputting the linear relationship into Eq. (5), the volume change (ΔV_{CSH}) induced by complete carbonation of C-S-H was described as a function of Ca/Si (see Fig. 6). The negative ΔV_{CSH} indicates volume shrinkage of C-S-H after carbonation. It can be noted that when Ca/Si remains at a high level, the volume contraction of C-S-H appears to be insignificant. With Ca/Si of C-S-H decreasing, the volume contraction induced by carbonation accelerates.

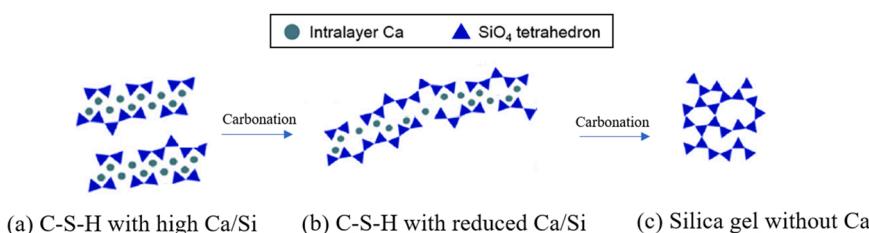


Fig. 3. Calcium removal process of C-S-H upon carbonation (adapted from [65]).

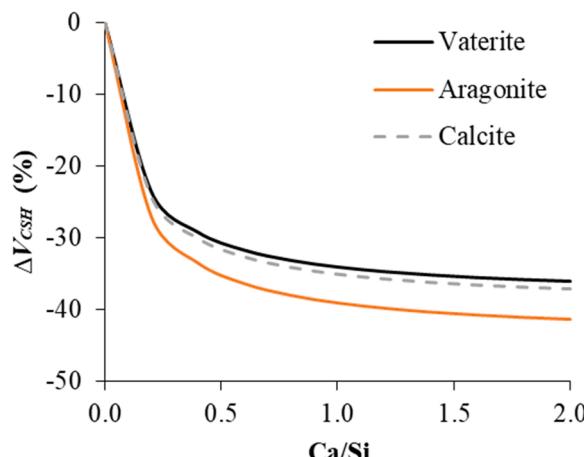


Fig. 6. Volume change induced by carbonation of 1.0 mol of C-S-H phases with varied Ca/Si (vaterite, calcite, and aragonite as main polymorphs of the generated calcium carbonate, respectively).

Such volume contraction trend seems consistent with experimental findings reported in [68,70] where the decalcification of C-S-H with Ca/Si lower than a threshold value (~ 1.2) was found to be responsible for significant volume contraction. Besides, the carbonated C-S-H with aragonite as the main carbonation product tends to shrink more significantly (see Fig. 6), due to the low molar volume of aragonite compared to that of calcite and vaterite.

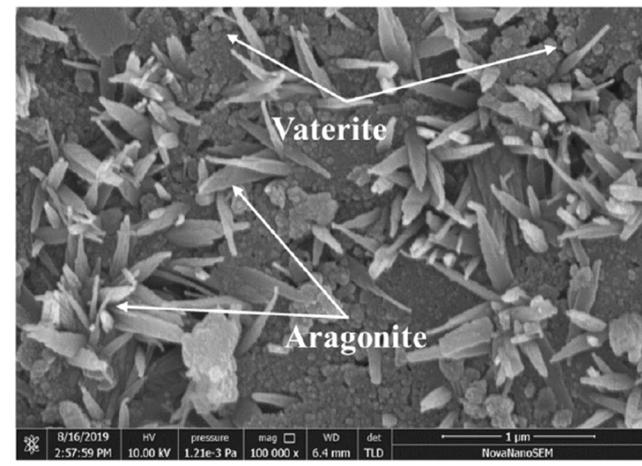
2.4.2. Carbonation products of C-S-H

In the literature, a wide range of studies have investigated the morphology of calcium carbonate produced upon carbonation of C-S-H. Liu et al. [62] reported that aragonite and calcite were the main morphologies of calcium carbonate produced by carbonation of C-S-H with Ca/Si of 1.5, while for C-S-H with Ca/Si of between 0.8 and 1.2, vaterite and aragonite were major carbonation products (as illustrated in Fig. 7 (a) and (b), respectively). Li et al. [73] concluded that the main carbonation product of C-S-H with Ca/Si lower than 0.87 was vaterite, whereas the main products were vaterite and calcite for C-S-H with higher Ca/Si than 1.02. In addition, researchers in [20] noted that for C-S-H with Ca/Si over 0.67, the formed calcium carbonate was vaterite upon carbonation, while for C-S-H with Ca/Si below 0.50, aragonite was the predominant calcium carbonate and no calcite was detected [20]. Besides, vaterite was reported as the main polymorph of the calcium carbonate produced by carbonation of C-S-H with Ca/Si of 1.4 in [7]. Overall, calcite, aragonite, and vaterite may coexist after carbonation of C-S-H, while the formation of vaterite appears to be dominant [18]. In addition to Ca/Si, external carbonation conditions can also affect the morphology of calcium carbonate (see Section 4). This may be one of the important reasons leading to varied conclusions in those previous studies. Generally, the produced calcium carbonate particles upon carbonation of C-S-H randomly precipitate in the pores of (partly) carbonated C-S-H phases and intermix with silica-rich gels after the complete carbonation [56,74].

Essentially, the carbonation of C-S-H is a gradual removal process of calcium ions from solid C-S-H phase. With calcium content reducing, the mean chain length of solid C-S-H phase extends, leading to C-S-H with low Ca/Si yet long silicate chains [7,62,76]. Literally, the mean chain length of carbonated C-S-H increases approximately exponentially as Ca/Si reduces [70], as shown in Fig. 8. Similar to the volume evolution of C-S-H subjected to carbonation (see Fig. 6), the change of the mean chain length of carbonated C-S-H tends to be marginal when the Ca/Si stays at a high level. Besides, it should be noted that decalcification of C-S-H may significantly reduce the mechanical properties of C-S-H, leading to low strength and modulus [56,62,65,77].



(a)



(b)

Fig. 7. SEM images of (a) calcite and aragonite and (b) vaterite and aragonite (adapted from [75]).

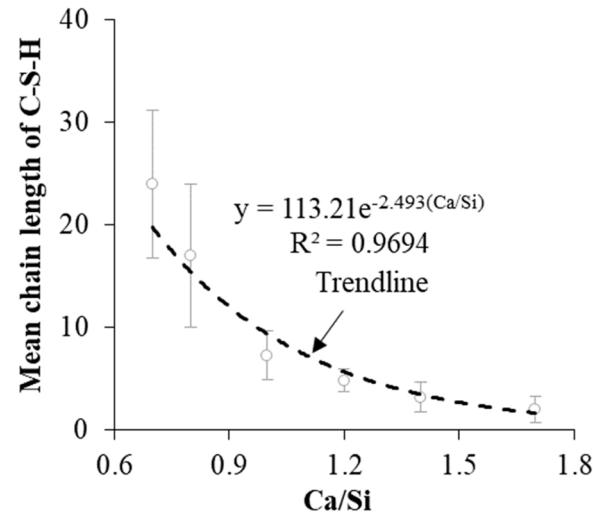


Fig. 8. Mean chain length of C-S-H with decreasing Ca/Si (error bars represent standard deviation of data collected from [16,17,62,70,76]).

3. External factors affecting the carbonation process of the calcium phases

A number of factors, i.e. both internal and external ones, can affect the carbonation process of different phases in cement pastes, and consequently the dimensional change. It should be noted that in many cases those factors are intertwined in a single system and quantitative studies in this context in general are rather limited so far. Nevertheless, the qualitative effects of various factors are summarized in Table 1, aiming to provide an overview.

For the internal factors, chemical composition of cement should be an important one, since it decides the hydration products (e.g. the amount and/or the proportion) to a large extent, while the carbonation of the hydration products differs from each other, as discussed in Section 2. Pore structure of hardened cement seems another significant internal influencing factor. Therefore, any parameters that can affect cement pore system, e.g. water-to-cement ratio and supplementary cementitious materials, may affect the concerned carbonation process as well. Relevant discussions are included in Sections 4, 5.3, and 6.4. In this section, some important external factors affecting the carbonation process of cement pastes are further highlighted and discussed.

3.1. CO₂ concentration

CO₂ concentration is one of the major factors affecting carbonation rate, carbonation degree, and even carbonation kinetics of calcium bearing phases in cement paste [1,57,85,86]. Generally, the increase in CO₂ concentration can speed up the diffusion of gaseous CO₂ in micro-pore structures and promote the formation of carbonate ions in pore liquid (see Eq. (1)) and thereby accelerate carbonation reactions of cement hydration products. As a result, significant volume changes upon carbonation of cement paste may take place. However, continuously raising CO₂ concentration does not necessarily always enhance carbonation since the solubility of CO₂ in pore liquid and the precipitation rate of carbonation products cannot be improved by high CO₂ concentration. As introduced in Section 2, CH and ettringite are prone to completely carbonate rather quickly, while carbonation of C-S-H is a relatively long decalcification process. In [57], it was proposed that to enable carbonation of C-S-H with low Ca/Si, pH of the pore liquid must be sufficiently low. In other words, each C-S-H phase with a specific Ca/Si must carbonate at a pH level below which the phase becomes unstable. For initiation of carbonation of C-S-H with Ca/Si lower than 0.85, the pH of pore liquid must be lower than 10.0 [57].

In general, high CO₂ concentration tends to promote the formation of metastable calcium carbonate (vaterite and aragonite instead of calcite) [89]. Because the molar volume and mechanical properties of vaterite, calcite, and aragonite are different, this may lead to the varied volume stability and mechanical performance of cement pastes. Additionally, the carbonation kinetics of C-S-H at low and high CO₂ concentration may be different as well [90]. In [38], it was noted that polymerization of decalcified C-S-H under different CO₂ concentration differed markedly.

3.2. Temperature

Temperature is of considerable importance in the carbonation of hydration products of cement since all carbonation reactions are controlled by chemical and thermodynamic equilibrium [1,39,75,87,88, 91–93]. Many studies had explored the carbonation behaviour of cement-based composites within the temperature range between ~20 °C and ~100 °C [39,75,91–93]. Generally, rising temperature can accelerate the diffusion of CO₂ and the leaching of calcium ions from solid calcium bearing phases [1,87,88], contributing to a fast CO₂ uptake rate and thus leading to a significant volume change upon carbonation of cement paste. Temperature change can also influence the size and morphology of the produced calcium carbonate [91]. In addition to

Table 1

Important factors affecting the carbonation (and thus the volume stability) of cement paste.

Factors	Effects	References	
Internal factors	Chemical composition	• It affects the amounts and/or the proportion of the hydration products, e.g. C-S-H, CH, and ettringite; each of the products follows a different carbonation course • It affects the Ca/Si of C-S-H, thus the carbonation process and then the volume stability • It affects the pH of pore liquid which in turn affects the carbonation process • The extent of the influence is somehow difficult to define	[20,43–48]
Pore structure		• High porosity of hardened cement allows better CO ₂ diffusion into the matrix, thus promotes the overall carbonation reactions, which typically increases the shrinkage of cement paste • Connected pores can facilitate the CO ₂ diffusion, which has a similar effect as high porosity • Pore size may also affect the carbonation process, thus the volume stability	[1,28,29, 35]
Water-to-cement ratio (w/c)		• In general, w/c affects the carbonation through the formed pore structure in hardened cement • As the w/c decreases, the porosity of cement paste reduces, leading to the reduced carbonation rate, depth, and shrinkage of cement paste, and vice versa	[78–80]
Supplementary cementitious materials (SCMs)		• SCMs in general densify the pore structure of hardened cement paste, and therefore they tend to reduce carbonation rate and shrinkage of cement paste to some extent • SCMs could affect the proportion of the hydration products, e.g. with reduced CH content and increased C-S-H generation • The inclusion of SCMs tends to generate high volume of C-S-H with low Ca/Si, which carbonates more easily than its high Ca/Si counterpart, resulting in more significant and faster volume contraction	[43,68, 81–84]
External factors	CO ₂ concentration	• The increase in CO ₂ concentration can accelerate carbonation reactions of cement hydration products, thereby leading to significant volume change	[1,57,85, 86]

(continued on next page)

Table 1 (continued)

Factors	Effects	References
Temperature	<ul style="list-style-type: none"> Continuously raising CO₂ concentration does not always enhance carbonation and the precipitation rate of carbonation products High CO₂ concentration tends to promote the formation of metastable calcium carbonate (vaterite and aragonite instead of calcite), leading to some uncertainties of the volume stability High CO₂ concentration may change the carbonation kinetics of C-S-H, thus the carbonation process Rising temperature can contribute to a fast CO₂ uptake rate and thus lead to a significant volume change upon carbonation of cement paste Temperature can also influence the size and morphology of the produced calcium carbonates Excessive temperature (e.g. over 100 °C) yet low RH may impede the carbonation of cement paste 	[1,87,88]
Relative humidity (RH)	<ul style="list-style-type: none"> Low RH usually deters carbonation reactions because of limited dissolution of CO₂ into aqueous phase due to the lack of water in pores Fast carbonation occurs during the intermediate RH of between 50% and 70%, therefore significant volume change may take place Too high RH may saturate small pores and thereby block the diffusion of CO₂, resulting in slow carbonation reactions (or insignificant volume change of cement paste upon carbonation) The existence of additional cations (contributed by added alkali salts) helps to maintain the charge equilibrium, thus limiting the volume condensation of C-S-H chains, i.e. improving the volume stability 	[1,36,42]
Alkali salts		[46,57]
Pre-curing time	<ul style="list-style-type: none"> 'Proper' pre-carbonation curing may increase the volume stability of the paste exposed to carbonation at later ages, while a convincing definition of 'proper carbonation' is somehow missing Prolonged carbonation may lead to not only volume stability problem but also the compromise 	[1,2132, 138–140]

Table 1 (continued)

Factors	Effects	References
	of, e.g. mechanical properties	

calcite, vaterite is more favourable at low temperatures while the formation of aragonite is boosted by the increase in temperature [94–97]. Because high curing temperatures accelerate carbonation reactions and boost CO₂ uptake rate, there may exist insufficient time for calcium carbonate to precipitate uniformly. Consequently, the amorphous calcium carbonate produced upon carbonation at high temperature may be nonhomogeneous. Besides, it should be noted that under the carbonation condition with excessive temperature (e.g. over 100 °C) yet low RH, due to the increased evaporation rate of pore water and the decreased solubility of CO₂ in the liquid, carbonation of cement paste may be impeded [98].

3.3. RH

Besides CO₂ concentration and temperature, the carbonation of cement hydration products is also RH-dependent [36,54,64]. The lack of water in pores usually deters carbonation reactions, because of limited dissolution of CO₂ into aqueous phase (see Eq. (1)). At an intermediate RH of between 50% and 70%, it is generally believed that there exists an optimal RH which enables efficient CO₂ diffusion in pore structures of cement paste as well as provides sufficient water for carbonation reactions. Too high RH may saturate small pores and thereby block the diffusion of CO₂, resulting in slow carbonation reactions (correspondingly, insignificant volume change of cement paste upon carbonation) [1,36,42]. Moreover, at very high RH (over 90%), a thicker and continuous water film forms and attaches to the surface of CH, C-S-H, and ettringite, which allows the produced calcium carbonate to nucleate in the aqueous film (reducing the formation of calcium carbonate coverage at the surface). In this way, high relative humidity appears to promote the deep carbonation of hydration products. However, as the water film thickens, diffusion paths of calcium ions and carbonate ions also lengthen, which may deter the carbonation rate of hydration products of cement [40]. In [1,40,99], an optimum RH of around 75% was noticed to be able to balance the competition between carbonation rate and carbonation degree of calcium bearing phases. In [70], synthetic C-S-H in the laboratory was found to decalcify at a fast speed at RH around 66%, while at much high (85%) or low (11%) RH, C-S-H carbonated relatively slowly.

Steiner et al. [64] reported the CO₂ uptake rates of CH, ettringite, and C-S-H investigated at two RH levels (57% and 91%, see Fig. 9). It was found that increasing RH from 57% to 91% accelerated the carbonation of CH, ettringite, and C-S-H with low Ca/Si, while C-S-H with high Ca/Si was less affected by the RH change [64]. Besides, it can be observed that both carbonation rate and CO₂ uptake capacity of C-S-H are strongly related to Ca/Si (the same is reported by Liu et al. in [62]). At RH of 57%, the CO₂ absorption rate of C-S-H with high Ca/Si is faster than that of CH. This may be attributed to the water liberated by carbonation of the C-S-H which promotes following carbonation.

In addition, the polymorphs of calcium carbonate formed upon carbonation of calcium bearing phases are also affected by RH [51,52, 64,70,91]. Drouet et al. [91] proposed that the amount of metastable calcium carbonate phases would increase when RH was low. RH could also impact the crystal sizes of carbonation products, with larger crystals formed at high RH levels [51,55]. Chen et al. [36] found that the polymorphs of calcium sulfate produced by carbonation of ettringite were hemihydrate at 70% RH and gypsum at 90% RH. Steiner et al. [64] reported that for ettringite and C-S-H with low Ca/Si carbonated at high RH, the produced calcium carbonate was mainly composed of vaterite and aragonite, whereas CH and C-S-H phases with high Ca/Si carbonated at high RH produced calcite mainly.

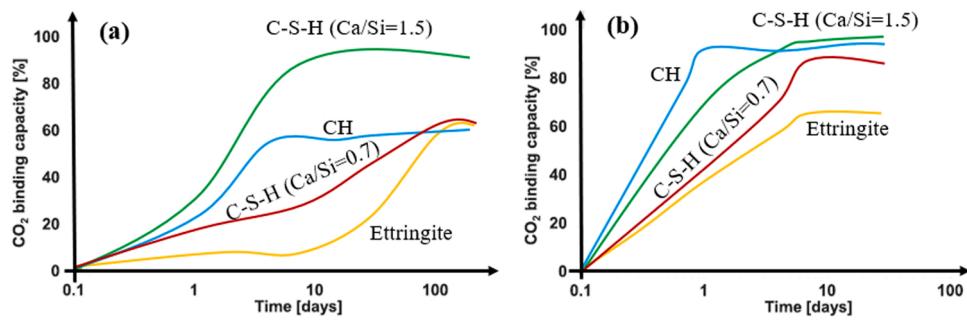


Fig. 9. Carbonation of calcium bearing phases at (a) RH= 57% and (b) RH= 91% (adapted from [64]).

3.4. Alkali salts

In recent few years, many researchers have studied the influence of alkali salts on carbonation reactions of C-S-H phases [57,73,100]. It is believed that the excess of negative charge induced by the decalcification of the interlayer calcium of C-S-H upon carbonation can be balanced by adsorption of alkali metals ions (cations) in pore liquid [46,57]. When additional cations exist to maintain the charge equilibrium, the mean chain length of C-S-H (as illustrated in Fig. 8) may be less affected by reducing Ca/Si. Therefore, the volume condensation of the decalcified C-S-H nanoparticles may become limited.

Ye et al. [100] studied the carbonation performance of cement paste with incorporations of additional sodium and potassium salts (NaOH, NaCl, and KOH). It was noted that the addition of alkali salts tended to accelerate the decalcification of C-S-H and influence the size of the calcium carbonate crystals formed upon carbonation [100,101]. Based on the measured data in [100], it was reported that the incorporation of additional alkali salts could mitigate the carbonation shrinkage of cement paste and even convert the shrinkage into an expansion. Liu et al. [61] investigated the carbonation behaviour of C-S-H incorporating aluminium ions (Al^{3+}). It was found that Al^{3+} had no remarkable influence on carbonation of C-(A)-S-H [102,103]. After complete carbonation of C-(A)-S-H, a large amount of calcium carbonate, as well as aluminium modified silica gel with a long silica chain was produced. Li et al. [73] studied the carbonation behaviour of C-S-H with the existence of additional magnesium ions, which would be introduced in Section 5.3.

4. Micropore structures and volume change of carbonated cement paste with supplementary cementitious materials

To build an in-depth understanding of the volume stability of

carbonated cement-based materials, the changes in microstructural characteristics had been broadly evaluated in the literature [42,63,68, 104–107]. However, despite substantial previous research, there only exist few consistent conclusions since the microstructural changes of cement pastes exposed to carbonation are affected by a wide variety of factors. In addition to external carbonation conditions (as discussed in Section 3), one of the key factors affecting microstructural changes of hardened cement pastes subjected to carbonation is the mineral compositions of cement and supplementary cementitious materials (e.g. fly ash, blast furnace slag, silica fume, and red gypsum) [43,68,81–84].

Shah et al. [63] investigated the effects of carbonation on the pore sizes of plain Portland cement paste, fly ash (30%, by mass) blended cement paste, and LC3 (Limestone Calcined Clay Cement) paste under natural and accelerated carbonation conditions (CO₂ concentration 0.04% and 3.0%, respectively, see Fig. 10). It can be observed that the pore size distributions of the three cement pastes all are affected by natural and accelerated carbonation. Particularly, accelerated carbonation under high CO₂ concentration significantly reduces capillary pores with sizes lower than 15–25 nm yet creates a high volume of capillary pores with sizes larger than 25–35 nm. Similar results were also reported in [108]. The clogging of fine capillary pores with sizes below 15–25 nm is highly likely due to the pore filling effect of the calcium carbonate produced upon carbonation of CH [68], while the increase in capillary pores with sizes larger than 25–35 nm is due mainly to the decalcification of C-S-H (and even associated microcracking induced by carbonation) [68,69,108,109].

In general, carbonation appears to decrease the total porosity of ordinary Portland cement paste without supplementary cementitious materials [50,68,110], but for cement paste containing different supplementary cementitious materials, the conclusion may be not always the same. Qualitatively, fly ash blended cement pastes contain much higher amounts of AFt, AFm, and C-S-H with low Ca/Si than ordinary

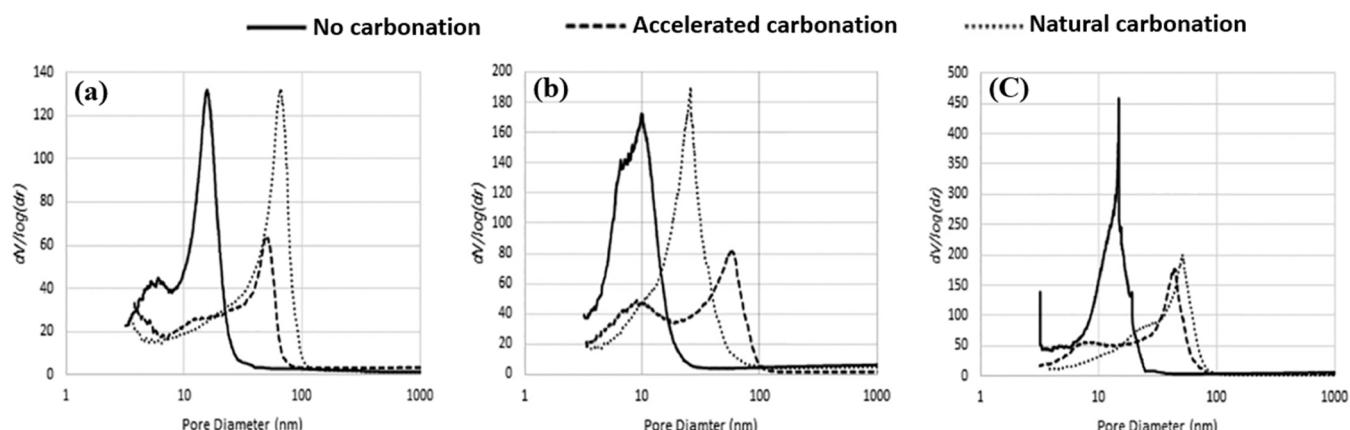


Fig. 10. Pore distribution of (a) plain cement paste, (b) fly ash blended cement paste, and (c) LC3 paste with and without carbonation, characterized using Mercury intrusion porosimetry in [63].

cement pastes. As a result, the carbonated cement pastes with a high amount of fly ash tend to have an increased total porosity [50]. The same results were also noted for cement pastes with blast furnace slag in [68]. However, there also exist some studies reporting the decreased porosity of cement pastes with fly ash and slag after carbonation [69,81,111]. To sum up, the change in the total porosity of cement pastes depends mainly on the competition between the clogging of fine capillary pores and the formation of new additional capillary pores (as discussed earlier). In addition, compared with fly ash and blast furnace slag, the porosity change of cement pastes with addition of limestone fillers seems to be less affected by carbonation [42].

Fig. 11 shows the variation of solid volume of three different cement pastes upon carbonation obtained by modelling in [63]. The relative volume change in this figure was determined by the ratio of V_c to V_0 , in which V_0 and V_c are the volume of each paste before and after carbonation, respectively. It can be observed that when the CO₂ uptake of ordinary cement paste (OPC) is lower than ~20%, a volume expansion occurs, and thereafter the solid volume starts to contract. The initial expansion can be attributed to the carbonation of CH (as introduced in Section 2.2), whereas the following contraction is due mainly to the carbonation shrinkage of C-S-H. For cement paste with fly ash, no significant volume expansion is noted upon carbonation. This is because cement pastes blended with supplementary cementitious materials (fly ash, furnace slag, and silica fume) tend to have a low volume of CH yet a high volume of C-S-H with low Ca/Si [22,43,63,68,112]. Consequently, carbonation of C-S-H with low Ca/Si occurs directly, resulting in more significant and faster volume contraction. Similar to fly ash blended cement paste, incorporation of slag as a substitute for cement can also contribute to high volume contraction, as reported in [70]. Compared with plain cement paste and fly ash blended cement paste, LC3 paste presents the lowest CO₂ uptake capacity as well as the fastest and the most significant volume contraction, due to a part of replacement of Portland cement clinker by calcined clay and limestone [63,113,114].

5. Linear dimensional change of cement paste upon carbonation

5.1. Evolution of linear carbonation deformation

Fig. 12 shows a schematic diagram of the development of linear carbonation deformation of ordinary Portland cement pastes. Typically, the linear carbonation deformation can be divided into three major periods [93,115]. At the first period, carbonation of CH plays a leading role, though C-S-H phases and ettringite carbonate at the same time [103]. As CH carbonates, an overall volume expansion takes place (as explained in Section 2.2). With the depletion of available CH for carbonation, carbonation of C-S-H becomes dominant [44–46], and the dimensional change of cement paste enters the second period. With decalcification of C-S-H upon carbonation, the volume expansion caused by carbonation of CH is offset progressively (see Fig. 12), and then carbonation shrinkage occurs rapidly. Following the reduction in Ca/Si

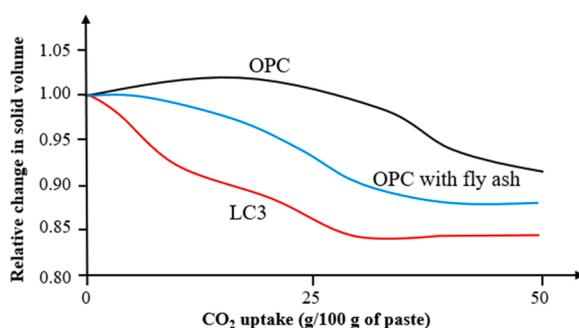


Fig. 11. Modelled volume change of different cement pastes exposed to carbonation [63].

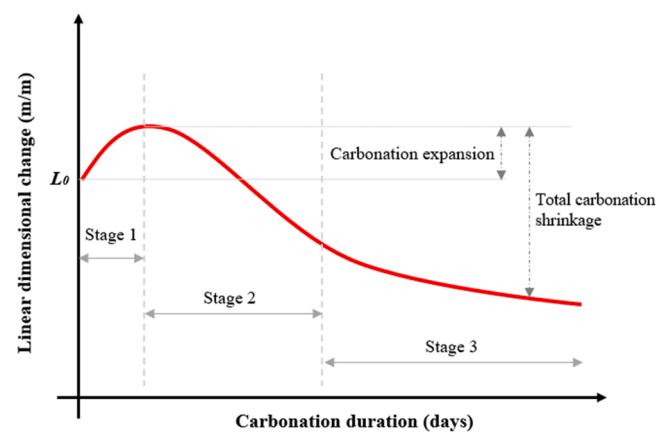


Fig. 12. Typical evolution of linear dimensional change of ordinary cement pastes upon carbonation (L_0 is the initial length of the specimen before carbonation).

and the formation of calcium carbonate layers on the surface of residual C-S-H, the carbonation rate (or decalcification rate) of C-S-H reduces gradually (see Section 2.4). Besides, the densified pore structures induced by calcium carbonate produced upon carbonation retards diffusion of CO₂ into inner parts of cement pastes, which also delays further carbonation of C-S-H [1,37–40]. In consequence, the evolution of the carbonation shrinkage slows down and enters a deceleration period. For cement paste containing supplementary cementitious materials, the carbonation expansion phase (Stage 1) may be quite short and negligible due to the low content of CH, as illustrated in Fig. 11. In that case, the evolution of linear dimensional change of carbonated cement-based materials contains two major stages only.

5.2. Measurement of linear carbonation deformation

For the measurement of the linear dimensional change of cement-based composites induced by carbonation, standard experimental procedures remain absent. In general, the total linear dimensional change (ϵ_{tot}) of cement paste exposed to a specific carbonation condition may consist of not only carbonation deformation (ϵ_c) but also autogenous shrinkage (ϵ_{as}), drying shrinkage (ϵ_d), and thermal strain (ϵ_{th}) [8,115], as expressed by Eq. (6).

$$\epsilon_{tot}(t) = \epsilon_c(t) + \epsilon_{as}(t) + \epsilon_d(t) + \epsilon_{th}(t) \quad (6)$$

where, t is the duration of specimens subjected to carbonation. ϵ_c is the deformation of cement paste induced by carbonation of hydration products of cement (including CH, ettringite, and C-S-H, etc).

For hardened cement pastes exposed to accelerated carbonation conditions with constant temperature, CO₂ concentration, and RH, the determination of ϵ_c can be simplified due to negligible ϵ_{as} and ϵ_{th} . To subtract ϵ_d from ϵ_{tot} , drying shrinkage tests need to be performed in parallel as the determination of ϵ_{tot} is performed under given carbonation conditions [116]. However, it should be noted that such an approach to quantify the dimensional change induced by carbonation may be questionable, especially for the measurement of ϵ_c under carbonation conditions with low RH. This is because water released by carbonation reactions can evaporate out of cement pastes under low RH and high temperature conditions, which causes additional drying shrinkage. Such additional drying shrinkage may lead to an overestimation of ϵ_c .

5.3. Strategies for mitigating carbonation shrinkage

Once significant carbonation shrinkage takes place, microcracking of cement paste may be the result, which has been observed in many

studies [50,63,108,117], as illustrated in Fig. 13. For cement paste exposed to a given carbonation condition, using expansive agents to mitigate the magnitude of carbonation shrinkage had been proposed in the literature [118–122] (e.g. CaO-, MgO-, and sulfoaluminato-based agents). Among those expansive agents, the use of MgO-based agent appears one of the most effective. The main mechanisms behind the shrinkage mitigation effect induced by the incorporation of MgO-based agent can be attributed to:

- (i) Upon hydration, conversion of MgO into Mg(OH)₂ causes volume expansion (due to the increased molar volume) [116], which can counterbalance carbonation shrinkage at later ages;
- (ii) Upon carbonation, leaching magnesium ions quickly react with CO₂ forming magnesium carbonate, which prevents decalcification of C-S-H phases and thereby buffers the development of carbonation shrinkage [121];
- (iii) The formed magnesium carbonate (much low solubility than calcium carbonate) densifies the micropore structures of cement paste, which prevents CO₂ diffusion and retards carbonation [116,123];
- (iv) Incorporation of MgO creates magnesium silicate hydrate (M-S-H) which has stronger carbonation resistance than C-S-H [73, 124];
- (v) Addition of MgO increases the bulk modulus of cement paste [116,123].

In addition to the employment of expansive agents, the adoption of a low water-to-cement (w/c) ratio can be another strategy [125]. With w/c decreasing, the porosity of cement paste reduces, and the bulk modulus increases, leading to the reduced carbonation rate, depth, and shrinkage of cement paste. Therefore, the dimensional change induced by carbonation can also be mitigated by adjusting the mix design of cement-based composites [78–80]. However, using MgO or a low water-to-cement ratio to mitigate the carbonation shrinkage not only reduces the rate and degree of carbonation but also leads to the reduced CO₂ sequestration capacity of cement-based composites. Therefore, a more desirable way to delay the carbonation shrinkage as well as ensure the CO₂ sequestration capacity is needed, e.g. regulate the carbonation rate of each phase of cement paste.

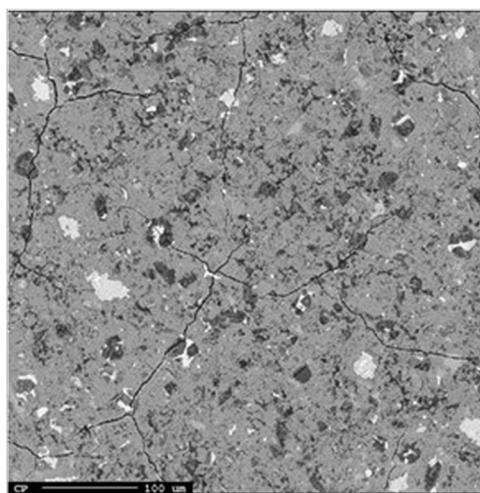


Fig. 13. Microcracking of cement paste exposed to 56 days carbonation (adapted from [50]).

6. Knowledge gaps and research perspectives

6.1. Carbonation of C-S-H of cement paste

Nowadays, a great deal of research has studied carbonation characteristics of synthetic C-S-H (with a pre-set Ca/Si) as substitutes for real C-S-H within cement paste. However, findings obtained based on synthetic C-S-H may not always be relevant for analyzing carbonation behaviours of real C-S-H [38]. This is because

- a. The nanostructures of synthetic C-S-H and real C-S-H in cement paste are generally not the same [126];
- b. The carbonation kinetics of real and synthetic C-S-H phases tend to be different [90]. For synthetic C-S-H, CO₂ can directly dissolve into gel pore liquid and react with calcium ions from the interlayer of C-S-H [90]. Therefore, the decalcification of synthetic C-S-H seems to be less influenced by CO₂ diffusion process. But for carbonation of C-S-H in cement paste, gaseous CO₂ must go into the inner parts by diffusion through capillary pores and gel pores following Fick's second law [127], and then dissolves into the gel pore liquid to form carbonate ions reacting with calcium ions. Besides, due to the existence of CH, ettringite, and other mineral phases in cement paste, the carbonation process of real C-S-H is much more complicated (as discussed in Section 2);
- c. Synthetic C-S-H phases subjected to carbonation are more susceptible to complete carbonation, whereas real C-S-H in cement paste is generally partly carbonated [26,90];
- d. Last but not least, the morphology of calcium carbonate generated upon carbonation of synthetic C-S-H and real C-S-H is also prone to be different (as discussed in Section 3.4), due to different carbonation conditions and varied carbonation degree of C-S-H.

Generally, as decalcification of synthetic C-S-H proceeds, the nanostructures of C-S-H condense, leading to the release of free water upon carbonation [128,129]. However, the water release behaviour upon carbonation of C-S-H phases in cement paste remains controversial. In [26], it was reported that there was no release of physical water upon carbonation of C-S-H, and highly hydrated silica gels were produced after carbonation. Conversely, Wu and Ye in [68] argued that the carbonation of C-S-H in cement paste produced poorly-hydrated silica gels due to the release of a high amount of water initially chemically-bound within C-S-H. In [130], physical water liberated from carbonation of CH and C-S-H in cement paste was noted. Moreover, it was observed that the water released by carbonation of C-S-H appeared to be less free (hard to be evaporated) than capillary water released by CH.

Due to the absence of substantial studies on the water release process of carbonated C-S-H in cement paste, the description of nanostructures and molar volume of C-S-H upon carbonation is still unrefined [23], which hinders the build-up of a comprehensive understanding on volume change of cement paste upon carbonation. To shed light on the carbonation characteristics of C-S-H of cement paste (with and without supplementary cementitious materials), the representativeness of the research conclusions based on accelerated carbonation of synthetic C-S-H needs to be assessed systematically.

6.2. Modelling and measurement of carbonation deformation

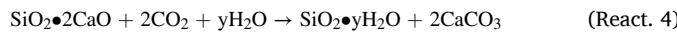
Both theoretical and empirical models for predicting the evolution of dimensional change (including both carbonation expansion and shrinkage) of cement paste upon carbonation are still absent, due mainly to the complexity of carbonation of each calcium bearing phase (in particular, C-S-H with varied Ca/Si) and the coupling effect of carbonation of different calcium bearing phases inside cement paste. Building empirical models requires a large database of reliably measured carbonation deformation of a wide range of cement pastes. However,

there are no standard experimental procedures for determining the linear carbonation deformation of cement-based materials at present.

Although linear carbonation deformation of cement pastes was measured in some previous research, the representativeness of the measured data under accelerated carbonation conditions for realistic carbonation deformation under natural carbonation conditions remains questionable. In [89,131], it proposed that using accelerated carbonation with 3% CO₂ concentration to simulate natural carbonation seemed to be reasonable. However, researchers in [102] proposed that accelerated carbonation with CO₂ concentration of 5% should be used to predict the natural carbonation process of cement paste. Besides, authors in [18,90] proposed that the decalcification process and carbonation kinetics of C-S-H exposed to CO₂ concentration of between 3% and 20% were essentially similar, indicating that accelerated carbonations with CO₂ concentration between 3% and 20% cannot stand for natural carbonation. Undoubtedly, to propose a standard test procedure for capturing linear carbonation deformation of cement-based materials, an accelerated carbonation condition that can well represent the carbonation process of materials under natural carbonation conditions is needed. Besides, further studies are in demand for linking up the volume change of cement paste under accelerated and natural carbonation conditions.

6.3. Volume stability of cement paste exposed to carbonation at early ages

The carbonation of early-age cement paste is remarkably different from that of hardened cement paste owing to different carbonation reactions and carbonation kinetics involved. Besides, while Ca/Si remains almost constant, nanostructures (sizes and shapes) of C-S-H in young and hardened cement pastes tend to be different [22]. For carbonation of hardened cement paste, major carbonation reactions occur on hydration products (e.g. CH, C-S-H, ettringite, etc) while C₂S (SiO₂•2CaO) and C₃S (SiO₂•3CaO) are hardly carbonated [132]. For early-age carbonation of cement paste, CH, C₂S, and C₃S tend to carbonate markedly (rather than C-S-H) [78,133]. According to [78,99,134,135], the complete carbonation reactions of C₂S and C₃S can be expressed as



In [135,136], it was reported that the polymorphs of the calcium carbonate produced in the two reactions mainly are calcite (at relatively low temperature) and aragonite (at relatively high temperature). According to [137], the molar volumes of C₃S and C₂S are approximately 71.0 and 52.4 cm³/mol, respectively. In accordance with the molar volume changes in Eqs. (10) and (11), it can be noted that the transformations from C₃S and C₂S to calcium carbonate and silica gels both can lead to a significant volume expansion in theory. However, the volume change induced by carbonation of young cement paste has been hardly investigated in practice. As presented in Section 5.1, upon carbonation and hydration of early-age cement paste, autogenous shrinkage, drying shrinkage, and hydration-heat induced thermal strain tend to take place simultaneously together with the volume change induced by carbonation, as given by Eq. (6). To separate carbonation deformation from other strain components measured at early ages, no reliable methodology exists.

In addition, many studies had reported that ‘proper’ carbonation curing of cement-based materials performed at early ages is favourable for improving the mechanical performance and carbonation resistance during the service life [2,132,138–140]. This implies that early-age carbonation of young cement paste may increase the volume stability of the paste exposed to carbonation at later ages [2]. However, despite extensive previous research, the mechanisms behind the increased carbonation resistance caused by early-age carbonation of cement paste remain arguable. Some research put forward that the major reason is that the carbonation of CH at early ages densifies the micropore

structures of cement pastes and thereby increases strength and reduces the CO₂ ingress at later ages [1]. Nevertheless, other studies suggested that the pore filling effect induced by carbonation of CH might be secondary. The main reason should be that ‘proper’ early-age carbonation of cement paste promotes the following hydration [76,132,139]. Besides discussion on the mechanisms, in terms of the concept of ‘proper carbonation’ of cement-based materials at early ages, a clear and convincing definition is still absent. According to [1,138], in case over-intensified (or prolonged) carbonation was applied, the mechanical properties of cement paste can be damaged.

6.4. Microscopic pore characteristics of cement paste upon carbonation

Microscopic pore characteristics are of considerable significance for assessing the volume stability and mechanical performance of cement-based composites upon carbonation [42,68,78], such as pore volume, sizes, and interconnectivity. While the pore filling effect induced by calcium carbonated produced during carbonation of calcium bearing phases has been widely recognized [81], the formation of additional capillary pores caused by decalcification of C-S-H remains not well understood [14,26,128]. To shed light on the porosity change related to the decalcification of C-S-H, the water release behaviour of C-S-H upon carbonation and the nanostructures of the (partly or completely) decalcified C-S-H must be clarified. However, substantial studies on those two topics remain few. For cement pastes with or without supplementary cementitious materials subjected to different carbonation conditions, their microscopic pore characteristics after carbonation may differ significantly (as discussed in Sections 3 and 4). Furthermore, the appearance of microcracking induced by carbonation shrinkage certainly affects the microstructures of cement pastes as well [9,108,116]. In essence, to fully understand the microscopic pore characteristics of cement paste upon carbonation, nanostructures of the decalcified C-S-H must be investigated in-depth.

7. Summary and conclusions

In this study, a comprehensive review on the volume stability of cement paste exposed to carbonation was carried out, aiming to summarize the state-of-the-art knowledge. Dimensional changes caused by carbonation of CH, ettringite, and C-S-H subjected to varied carbonation conditions were discussed and summarized. Microstructural characteristics of carbonated cement pastes with and without supplementary cementitious materials were analyzed comparatively. Critical research gaps that need further investigation were also identified with research perspectives put forward correspondingly. Based on a comprehensive overview on the dimensional change of carbonated cement-based materials, the main findings can be drawn as follows:

- According to molar volume changes, carbonation of CH, C₂S, and C₃S tend to cause a volume expansion of cement paste, whereas carbonation of ettringite and C-S-H (including C-(A)-S-H) causes a volume contraction. Notably, with decalcification of C-S-H upon carbonation, the volume contraction of C-S-H accelerates as Ca/Si reduces. When Ca/Si is lower than a threshold value (~1.2), significant volume contraction develops. For hardened cement paste, the volume expansion at an initial period of carbonation is due mainly to the carbonation CH, although CH, ettringite, and C-S-H with high Ca/Si carbonate simultaneously. For young cement paste exposed to carbonation, the volume expansion is attributed to the carbonation of CH, C₂S, and C₃S. Importantly, it should be noted that the carbonation of synthetic C-S-H and real C-S-H in cement paste appears to be evidently different. Findings obtained from synthetic C-S-H may not always be applicable for analyzing carbonation behaviours of C-S-H in cement paste.
- Microscopic pore structures of cement paste are affected by carbonation conditions and incorporations of supplementary

cementitious materials. Essentially, the change in the total porosity of cement pastes depends mainly on the competition between the clogging of fine capillary pores filled by calcium carbonate produced upon carbonation and the formation of additional capillary pores from decalcification of C-S-H. For plain cement pastes without supplementary cementitious materials, carbonation tends to lower the total porosity, while for cement pastes containing a high amount of fly ash or furnace slag, carbonation can lead to an increase in the total porosity. Overall, additions of supplementary cementitious materials as substitutes for cement in cement paste are highly likely to compromise the volume stability, resulting in significant carbonation shrinkage.

- For the measurement of linear carbonation deformation of cement-based materials, a standard test procedure is urgently needed. The conversion of the measured carbonation deformation under accelerated carbonation conditions into the deformation under natural carbonation conditions requires further research. To facilitate the deformation conversion, (accelerated) representative carbonation conditions that can realistically reflect carbonation features of calcium bearing materials under natural carbonation conditions should be investigated.
- Despite substantial previous research on carbonation of cement-based materials at early ages, the volume stability has been rarely investigated. Many studies had proposed that ‘proper’ carbonation at early ages would improve the volume stability and mechanical performance of cement pastes at later ages. However, the concept of ‘proper’ carbonation is hard to be quantified for different cement-based materials since the influences of early-age carbonation on the following hydration of C₂S and C₃S and on the growth of C-S-H remains unclear. Therefore, further studies are needed to spread the utilization of early-age carbonation technology in the (precast) concrete industry.

CRediT authorship contribution statement

Liang Li: Conceptualization, Methodology, Investigation, Funding acquisition, Writing – original draft, Writing – review & editing. **Qiong Liu:** Investigation, Writing – review & editing. **Vinh Dao:** Supervision, Methodology, Writing – review & editing. **Min Wu:** Supervision, Methodology, Investigation, Project administration, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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