Review

# Carbonation of cement-based materials: Challenges and opportunities

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## HIGHLIGHTS

- Carbonation kinetics of alternative binder materials requires further investigation.
- Carbonation resistance of OPC is higher than that of alternative binder materials
- Cement-based materials can be used as $CO_2$ storage systems.
- Recently developed carbonate binders are reviewed.

## ARTICLE INFO

## ABSTRACT

This article summarizes the existing knowledge regarding the carbonation of cement-based materials and identified the areas which require further investigations. Available studies regarding the carbonation test scenarios, influences of supplementary cementitious materials (SCMs) on carbonation resistance, and effects of carbonation on the properties of cement-based materials are reviewed here. In addition to ordinary portland cement (OPC) based materials, this article has reviewed the performances of sulfoaluminate belite and alkali activated materials (AAM) while subjected to carbonations. Some very recent topics such as the potential of $CO_2$ storage in concrete and the newly developed carbonate binders are also discussed.

## Contents

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## 1. Introduction

Carbonation is one of the most well-discussed research topics in cement and concrete industry. Almost all of the cement-based materials have to undergo a certain extent of carbonation reaction during their service life due to the presence of $CO_2$ in earth's atmosphere. Conventionally, carbonation reaction of concrete is considered as an unfavorable event as it demeans the durability performances of such materials. In the case of OPC-based systems, carbonation reaction reduces the alkalinity of concrete and hence, making the reinforcement susceptible to corrosion. For alkali activated materials (AAM) and sulfoaluminate belite cements, carbonation reaction possesses a greater risk as it causes the disintegration of the binding matrix (detailed discussion are in Section 6.4.2). However, only a limited number of studies have been performed to investigate the behavior of these alternative binder matrices in the $CO_2$ bearing environment.

In last decade, research interests focusing on the beneficial aspects of carbonation of cement-based materials have been observed to be growing. Briefly, there are two major beneficial features involved in the carbonation of OPC based systems including (i) rapid strength gain of the cementitious matrix when subjected to curing in the presence of $CO_2$ (this is because the presence of $CO_2$ accelerates the reaction of calcium silicates [1]), and (ii) sequestration of $CO_2$ in concrete. Concrete is the second largest commodity (in terms of total volume of the material) consumed by any society annually after water [2,3]. Hence, if successful, concrete and other cement-based materials have the potential to be one of the largest global $CO_2$ sequestration sectors [4], leading towards possible reduced $CO_2$ footprint of the cement industry. Varieties of approaches can be followed to sequester $CO_2$ in concrete. Some of these approaches include accelerated carbonation curing, atmospheric carbonation, adding $CO_2$ with concrete mixing water, etc. Moreover, several new cementitious systems have been developed in the last decade based on the concept of storing $CO_2$ in concrete in the stable forms of carbonates.

This paper presents a comprehensive review on the following: (i) various experimental scenarios and kinetics of carbonation of cement-based materials; (ii) influence of SCMs addition on the carbonation resistance; (iii) effects of carbonation on the properties of OPC, AAM, sulfoaluminate belite cements and their microscopic phases; and (iv) recent studies focusing on the potential of storing $CO_2$ in cement-based materials and newly developed carbonate cementitious systems. At this point, it should be acknowledged that Bertos et al. [5] presented an elaborate discussion on the carbonation of cement-based materials with the focus on the utilization of solid wastes. On the other hand, Torgal et al. [6] comprehensively reviewed the carbonation behavior of concrete containing SCMs and recycled aggregate concretes (RAC). Detail discussions on these particular topics are not included in this article.

## 2. Accelerated vs. natural carbonation

The carbonation reactions of cement-based materials occur in natural environment at a very slow rate due to the low $CO_2$ concentration in the atmosphere (400 ppm or 0.04% [7]). Usually, accelerated carbonation schemes are used in the laboratory to investigate the effects of carbonation on concrete. The carbonation rates of accelerated carbonation tests are considerably higher than those of atmospheric condition [8,9]. The higher carbonation rates are obtained by using higher $CO_2$ concentration and controlled environment (i.e., temperature, RH). Nonetheless, a wide range of variation in the accelerated curing environment can be observed in literature (Table 1). From Table 1, it can be seen that a RH within the range of 50–70% is commonly used in the experiments. This is because the carbonation reaction rate of concrete is highest within this RH range [10,11].

**Table 1**
Accelerated carbonation curing test conditions.

| Binder types | RH (%) | $CO_2$ concentration/ partial pressure | Temperature (°C) | Maximum exposure duration | References |
|---|---|---|---|---|---|
| OPC | 55 ± 5 | 4% ± 0.5% | 20 ± 2 | | [21] |
| OPC | 70 | 20% | 20 | | [22] |
| OPC | – | 0.15 MPa | – | 28 days | [23] |
| OPC (concrete with recycled aggregate) | ~0 | 0.01 MPa | 23 | 24 h | [24] |
| OPC | 70 | 20% | 23 | 16 weeks | [25] |
| OPC | 65 ± | 50% ± 5% | 20 ± 2 | 42 days | [26] |
| OPC | 35, 55, 80 | 40% | – | 3 days | [27] |
| OPC | – | 1.5 MPa | – | 2 weeks | [14] |
| OPC | 65 | 3%, 10%, 100% | 22 | 103 days | [18] |
| OPC + fly ash (FA) | 62 | 10% | 25 | 16 weeks | [28] |
| OPC + FA | 65 ± 5 | 5% | 20 | 3 months | [29] |
| OPC + FA | 55 | 4% | 40 | 28 days | [30] |
| OPC + FA | 65 ± 5 | 50 % ± 5% | 20 ± 2 | 120 days | [31] |
| OPC + FA/ blast furnace slag (BFS) | 65 ± 5 | 50 % ± 5% | 20 ± 2 | 123 days | [32] |
| OPC + FA/ BFS + silica fume (SF) | 50 | 4% | 20 | 30 weeks | [33] |
| OPC + BFS | 60 | 10% | 20 | 24 weeks | [34] |
| OPC + BFS | 50 | 3% | 20 | 9 weeks | [35] |
| OPC + BFS | 40 ~ 90 | 10% | 20 | 21 days | [10] |
| OPC + PFA, GGBS, MgO, talc | 70–90 | 20% | 20 | 7 days | [36] |
| Self-compacting concrete | 75 ± 5 | 100% | 19 ~ 24 | 240 days | [37] |
| High initial strength and sulfate-resistant Portland cement (HS SR PC) | 60 | 20% | 25 | 24 h | [38] |
| White cement, OPC | 70 ± 2 | 100% | 25 ± 1 | 150 days | [39] |
| GGBFS, metakaoline (MK), alkali activated slag | 50 ± 5, 65 ± 5, 80 ± 5 | 1.0 ~ 5%, | 25 ± 2 | | [20,40–43] |
| Alkali activated slag | 70 | 10–20% | – | 4 months | [44] |
| Basic oxygen furnace (BOF) slag | 0–80 | 0–40% | 25–250 | | [45] |
| MgO | 55–98 | 5–20% | 20 | 7 days | [46] |
| MgO / GGBFS | 98 | 99.9% | 23 ± 2 | 56 days | [47,48,49] |
| Rice husk ash, hemp fiber | 65 ± 5 | 50% | 20 ± 2 | | [50] |
| Ladle slag | | 0.15 MPa | | 24 h | [51] |

Carbonation of cement-based materials is largely controlled by the diffusion rate of $CO_2$ through the microstructure if it is already hardened [5,12,13]. In the case of hardened concrete samples, most of the test schemes given in Table 1 can be expected to produce only partially carbonated samples. Complete carbonation of the samples might be the requirement if the effects of carbonation on the mechanical properties of concrete or corrosion are the primary research objectives. Al-kadhimi et al. [14] have prepared a test setup which is able to prepare fully carbonated samples (up to 150 mm diameter or 100 mm × 100 mm sections within two weeks) by applying a very high $CO_2$ pressure (~1500 kPa).

The correlation between the effects of natural and accelerated carbonations on the cement-based materials has remained as a challenge [8,15,16]. This is mostly because the differences in $CO_2$ concentration or pressure produce different amounts of carbonates [17] and alter the carbonation rate of calcium silicate hydrates (C-S-H) [18]. The pH of the pore solution, mineralogy, and pore structure of the carbonated specimens also depend on the $CO_2$ concentration [19] used during the carbonation. Additionally, Bernal et al. [20] reported that the reaction products formed during the natural and accelerated carbonation of alkali activated slags are considerably different due to the dependence of the alkali-carbonate phase equilibrium on the $CO_2$ concentration. Considering these findings, it is expected that the applicability of accelerated carbonation test results largely depends on the selection of appropriate exposure conditions. For OPC-based materials the carbonation induced microscopic changes at 3% $CO_2$ concentration is similar to that of the 0.03% $CO_2$ (~natural $CO_2$ concentration) and hence, 3% $CO_2$ can be used to replicate the natural carbonation scenario [18].

## 3. Experimental techniques to evaluate the effects of carbonation on cement-based materials

Phenolphthalein pH indicator solution is the most widely used test method to identify the carbonation front in cement-based systems. This solution changes from colorless to red (or pink) color when the pH is more than 9.0. During the carbonation reaction, the pH of the concrete system reduces and as a result, phenolphthalein solution stays colorless in the carbonated region and red (or pink) in the non-carbonated region. It should be noted that the red or pink color during this test indicates a region with the pH higher than 9.0, but that area can still be partially carbonated. Therefore, this method provides only an approximate measurement of the carbonation depth. Thermogravimetric analysis (TGA) provides quantitative information regarding the extent of carbonation in cement-based materials. This test method determines the relative proportions of the microscopic phases such as Ca (OH)₂ or CaCO₃ from which the degree of carbonation or carbonation profile within the samples can be obtained. Occasionally, TGA coupled with a mass spectrometer (TGA-MS) [52] or an infrared spectrometer (TGA-IR) is used to study the carbonated samples. Such test techniques provide the benefit of analyzing the gas phase released during the heating of the carbonated samples and thus, identify the decomposing microscopic phases. Fourier transformed infrared (FTIR) spectra can be used to obtain either qualitative [53–55] or semi-quantitative [56] assessments of the carbonated cement-based materials. Raman spectroscopy provides the qualitative information regarding the changes of microscopic phases that occur due to the carbonation reaction, such as the formation of CaCO₃, polymerization of C-S-H, decomposition of ettringite etc. [57,58]. Scanning electron microscopy (SEM) is mostly used to obtain qualitative information to assess the effects of carbonation on the microstructure of cement-based materials, while this equipment can also be used to obtain quantitative information, such as

porosity from SEM image analysis [59] or changes in the chemical composition of C-S-H when using along with energy dispersive spectra (EDS) [60]. $^{29}Si$ (also $^{27}Al$) nuclear magnetic resonance (NMR) spectra are widely used to assess the effects of carbonation on the polymerization of silicate (and aluminate) species [61–63]. One of the recent studies have showed that the $^{13}C$ {$^1H$} cross polarized NMR can be used to identify the presence of carbonate species in a hydrous environment [61]. X-ray diffractions (XRD) are widely used to both, identify and quantify the changes of the microscopic phases of cement-based materials that evolve due to the carbonation reaction. Some of the recent studies have shown the utilization of gamma rays to monitor the evolution of the density of cementitious matrix due to the carbonation reaction [28,52,64]. Morandeau and White [65] have utilized X-ray pair distribution function to monitor the atomic scale changes in C-S-H during the carbonation reaction.

## 4. Kinetics of concrete carbonation

Numerous studies involving model based simulations as well as laboratory experiments have been performed to enhance the understanding of the kinetics of concrete carbonation [17,30,35,66–80]. The most general, simplified, and widely used [66–68,81–83] expression to predict carbonation depth in cement-based materials is given in Eq. (1).

$$X_c(t) = A\sqrt{t} \tag{1}$$

here, $X_C$ = carbonation depth after time t, t = carbonation exposure duration, and A = empirical constant. As pointed out by Houst and Wittmann [83], the derivation of Eq. (1) is based on the assumption that the diffusion rate of $CO_2$ is constant. However, the diffusion rate of $CO_2$ is practically not a constant and depends on multiple factors including the degree of hydration, porosity, $CO_2$ concentration, RH, amounts and types of microscopic phases, etc. Thus, more accurate physical models to predict carbonation rate of cement-based materials are developed [69,70,78] considering the microstructural features of OPC based concrete systems. One of such models as given in eq.2 has been proposed by Papadakis et al. [78].

$$X_c(t) = \sqrt{\frac{2D^C_{e,CO_2}[CO_2]^0}{[Ca(OH)_2]^0 + 3[CSH]^0 + 3[C_3S]^0 + 2[C_2S]^0}t} \tag{2}$$

here, $D^C_{e,CO_2}$ = effective diffusivity of $CO_2$, the denominator of the Eq. (2) represents the total molar volume of CaO in the form of carbonatable phases. The sequence of following physicochemical processes is the basis of this model [78]:

  (i) The chemical reactions from which carbonatable materials are produced.
 (ii) The diffusion of atmospheric $CO_2$ in the gaseous phase of the concrete pores.
(iii) The dissolution of solid Ca(OH)₂ in the pore water and the diffusion of dissolved Ca(OH)₂ in the aqueous phase of the pores.
 (iv) The dissolution of $CO_2$ in the pore water and its reaction with dissolved Ca(OH)₂.
  (v) The reaction of $CO_2$ with the other solid carbonatable constituents of hardened cement paste.
 (vi) The reduction of pore volume due to the solid products of hydration and carbonation.
(vii) The condensation of water vapor on the walls of concrete pores, in equilibrium to the ambient temperature and RH conditions.

In addition to C-S-H and $Ca(OH)_2$ carbonation, this model (Eq. (2)) incorporates the carbonation effects of anhydrous cement clinker phases (i.e., $Ca_3SiO_5$ [$C_3S$], $Ca_2SiO_4$ [$C_2S$]). Effects of concrete porosity and degree of saturation are also considered here. Recently, another model has been proposed by Haghighi et al. [71] incorporating the effects of carbonation on both the hydrated and unhydrated phases present in the OPC concrete.

An elementary model (Eq. (3)) for OPC-based systems has been developed by Hyvert et al. [17] to predict the carbonation depth considering the partial pressure induced by $CO_2$ and the carbonation of primarily the hydrated phases (i.e., C-S-H, ettringite, aluminates, $Ca(OH)_2$).

$$X_c(t) = \sqrt{\frac{2P_0}{\varphi_P(CH_i + \frac{CSH_i}{n+1}(\frac{P_0}{P_{atm}})^n)RT} \frac{D_0}{(1 - \alpha CSH_i(\frac{P_0}{P_{atm}})^n)}t} \qquad (3)$$

here, $CH_i$ (mol/l cement paste) = initial calcium content in $Ca(OH)_2$, ettringite and aluminates, $CSH_i$ (mol/l cement paste) = initial calcium content of C–S–H gel, $\varphi_p$ = volume fraction of paste in the concrete, $P_0(Pa)$ = $CO_2$ pressure, $P_{atm}$ = atmospheric pressure (101,325 Pa), R = ideal gas constant (8.31 $J\,K^{-1}\,mol^{-1}$), T = temperature (K) and $D_0$ = diffusion coefficient of $CO_2$ under natural carbonation condition. $\alpha$(l/mol) reflects the sealing of porosity due to C–S–H gel carbonation and n reflects the chemical affinity of C–S–H gel towards the $CO_2$ pressure (need to be determined experimentally).

A probabilistic approach for designing the carbonation resistance of concrete can be found in Fib model code [84] (Eq. (4)). This model has incorporated the stochastic nature of concrete induced during the curing procedure and laboratory scale accelerated carbonation experiments.

$$X_c(t) = \sqrt{2.K_e.K_c.(K_t.R_{ACC,o}^{-1} + \varepsilon_t).C_s}.W(t).\sqrt{t} \qquad (4)$$

here, $k_e$ = environmental function that considers the influence of the humidity level on the diffusion coefficient, $k_c$ = execution transfer parameter that considers the curing effect on carbonation resistance, $R_{ACC,o}^{-1}$ = inverse effective carbonation resistance of concrete determined at a certain point of time on specimens with the laboratory based accelerated carbonation test [$(mm^2/years)/(kg/m^3)$], $k_t$ = regression parameter which considers the influence of test method on the accelerated carbonation tests, $\varepsilon_t$ = error term considering inaccuracies that occur when using the accelerated carbonation test methods [$(mm^2/years)/(kg/m^3)$]. This model (Eq. (4)) has taken into consideration both the concrete properties and environmental factors.

All of the kinetic models for predicting the depth of carbonation discussed here (Eq. (1) to (4)) are applicable primarily for the OPC-based systems. It is evident that only a few research works are performed on the carbonation kinetics of the concrete containing SCMs [35,68,85] or other alternative binder systems (AAM [40]). Incorporation of SCMs in the model to predict carbonation behavior of concrete can be complicated as it requires taking into consideration the pozzolanic reaction, effective water content, and all other differences in the microscopic phases. Jian et al. [85] have developed a model for predicting carbonation behavior of high-volume fly ash (HVFA) concrete as given in Eq. (5).

$$X_C(t) = 839(1 - RH)^{1.1}\sqrt{\frac{W/B^* - 0.34}{\alpha k' C}C_0 \sqrt[n]{t}} \qquad (5)$$

here, $W/B^*$ = effective w/c ratio, $\alpha$ is the degree of hydration, $C_0$ = concentration of $CO_2$, C = cement content, $k'$ = coefficient related to carbonation reactivity depending on the contents of cement and fly ash, n is a parameter related to the pore system of concrete and reported to have a value between 2.0 and 2.1.

Model for describing the carbonation kinetics of the alternative binder systems (such as AAM or sulfoaluminate belite cement etc.)

**Table 2**
Effects of SCMs addition on the carbonation resistance of concrete.

| Types of SCM | Carbonation resistance | Proportion (%) | References |
|---|---|---|---|
| Fly ash | Decrease | 10–70% | [30,68,35,85,92,93] |
| Pulverized fuel ash (PFA) | Decrease | 0–40% | [94] |
| Blast furnace slag (BFS) | Decrease | 0–85% | [68,34] |
| Silica fume | Decrease | 0–20% | [95,94] |
| | Increase | 5–10% | [68] |
| Nano and micro silica[a] | Increase | 0–5% | [96] |

[a] Nano and micro silica usually are not considered as SCM, but these materials also take part in pozzolanic reaction.

is not readily available in existing literature. Considering the increasing popularity of the alternative binder systems, additional studies need to be performed to develop appropriate physical models for understanding their carbonation kinetics.

Regarding the carbonation kinetics of cement-based materials, it is also important to note that most of the studies predict/measure the carbonation depth of concrete samples with primary focus on the diffusion rate of $CO_2$ through the hardened microstructure of concrete. However, carbonation reaction of cement-based materials is a chemical reaction. In cases where the concrete samples are subjected to carbonation in fresh state (within few hours after mixing [51,86]), the chemical reaction kinetics can be expected to play a vital role on the extent of carbonation. Only a few studies [72,87,88] have investigated the chemical kinetics of carbonation reaction of cement-based materials. Information related to the kinetics of the reaction (i.e., reaction rate constant, activation energy etc.) between $CO_2$ and individual cement hydrate or anhydrous phases (i.e., C-S-H, $Ca(OH)_2$, $C_2S$, $C_3S$, ettringite, monosulphate etc.) are still not well explored and warrant further investigations.

## 5. Effects of SCMs on the carbonation resistance of concrete

In comparison with the vast number of research works that have been conducted on the carbonation behavior of OPC concrete, studies focusing on the concrete with SCMs as partial replacement of OPC are substantially limited. Table 2 summarizes the influence of SCMs additions on the carbonation resistance of OPC based concrete systems. As it can be observed from Table 2, usage of the pozzolanic materials (i.e., ash, slag, silica fume etc.) reduces the carbonation resistance of concrete. According to Papadakis et al. [89], this reduction in carbonation resistance is due to the increased porosity at early ages (resulted from the dilution effect of cement clinker) and the lesser amount of the carbonatable phases (i.e., $Ca(OH)_2$) present in concrete prepared using cement with pozzolanic replacements.

Similar to that of SCMs, studies on the carbonation behavior of alternative binder materials are also limited. Literature supports that the carbonation resistances of AAM-based concretes are lower than that of the OPC-based systems [20,54,63,90]. Carbonation resistance of concrete containing sulfoaluminate belite cement is also lower than that of the OPC-based concrete [91].

## 6. Effects of carbonation on concrete properties

### 6.1. Mechanical properties

It was first revealed in 1970's that the addition of $CO_2$ accelerates the hydration reaction of $C_3S$ and $C_2S$ [1,60,87,97,98]. Because of this faster reaction rate, the accelerated carbonation curing of OPC-based systems results in rapid strength gain [99]. Carbonation curing also results in rapid strength gain in the case of ladle slag binder [51] and solidified waste materials [100,101]. However, it

**Table 3**
Effects of carbonation on the mechanical properties of concrete.

| Properties | Materials | Effects | References |
|---|---|---|---|
| Compressive strength | OPC concrete | Increase | [103–105] |
| | Hemp and rice husk based concrete | Increase | [50] |
| | Ladle slag binder | Increase | [51] |
| | Alkali activated fly ash geopolymers (in situ carbonation) | Increase | [106] |
| | Solidified waste forms | Increase | [100,101] |
| | High strength cement paste | Increase (1 h of carbonation) | [38] |
| | High strength cement paste | Decrease (24 h of carbonation) | [38] |
| | Alkali-activated slag/metakaolin | Decrease | [40] |
| Electrical resistivity | OPC concrete | Increase | [14,104,105,107,108] |

should be noted that this beneficial effect of $CO_2$ on the mechanical properties of OPC based systems are observed when the fresh concrete mix is subjected to carbonation. When the hardened (or matured) concrete samples are subjected to carbonation, the $CO_2$ penetration depth is mostly limited to the outer layer of the samples because of the slow diffusion rate through the dense microstructure. In such condition, the increase in strength of OPC-based systems due to the carbonation is not prominent.

As it can be observed from Table 3, carbonation curing increases the mechanical strength for most of the cementitious mix. However, in the case of AAM, carbonation directly affects the binding gel phase which results in the disintegration of the matrix and hence, reduces strength [102] (details are in Section 6.4.2). Puertas et al. [54] have shown that the waterglass activated slag mortar is more susceptible to carbonation induced strength loss than that of the NaOH activated slag mortar. Similar observation can be found in [90]. Effects of carbonation on AAM can vary depending on the dose of the activators as well [41].

### 6.2. Corrosion

Steel bars in reinforced concrete are protected from corrosion by a thin oxide layer that forms on their surface due to the highly alkaline (pH of 12–13) environment of the OPC-based concrete. During the carbonation reaction, $Ca(OH)_2$ is gradually converted into $CaCO_3$ which reduces the alkalinity of the concrete. Hence, carbonation of OPC based concrete makes the reinforcement more vulnerable for corrosion [109]. Although the addition of silica fume up to 10% reduces the carbonation resistance of concrete, it increases the resistance to carbonation induced corrosion [95]. However, the resistance to carbonation induced corrosion can be reduced for a silica fume proportion higher than 10% [95].

A risk of carbonation induced corrosion in alkali activated fly ash geopolymer concrete has also been detected by Badar et al. [110]. Geopolymer concretes prepared from the low-calcium class F fly ash have the lesser risk of corrosion of reinforcing steel than that of the high-calcium class F fly ash [110].

### 6.3. Porosity and pore size distribution

In the case of OPC based systems, carbonation reaction leads to a reduction in total porosity as the volume of the carbonation reaction product (i.e., $CaCO_3$) is higher than the primary reactant (i.e., $Ca(OH)_2$) [108,111]. The reduction of porosity due to the carbonation reaction is also evident in the case of concretes containing FA and BFS [112], high initial strength cement paste [38], reactive MgO [48], and cementitious waste forms [113]. Because of the reduction of total porosity, carbonation reaction also reduces the permeability [114–117] and increases the microhardness of the paste matrix [48]. Although the carbonation reaction reduces the total porosity of OPC based systems, it changes the pore size distribution by increasing the proportion of capillary pores (pore sizes greater than 30 nm) [112,118] (Fig. 1). Due to the increase in the capillary porosity, carbonation reaction increases the diffusivity of ions through the cementitious matrix [112,113]. The specific surface areas of OPC paste samples are likely to decrease with an increase in the degree of carbonation [119,120].

### 6.4. Microscopic phase changes

Effects of carbonation reaction on the microscopic phases of the cement-based materials vary depending on the types of the binder. In the following sections, the changes in the microscopic phases are discussed separately for different binder systems.

#### 6.4.1. OPC-based materials

During the carbonation reaction of OPC-based systems (with or without SCMs), $CO_2$ can react either with anhydrous cement
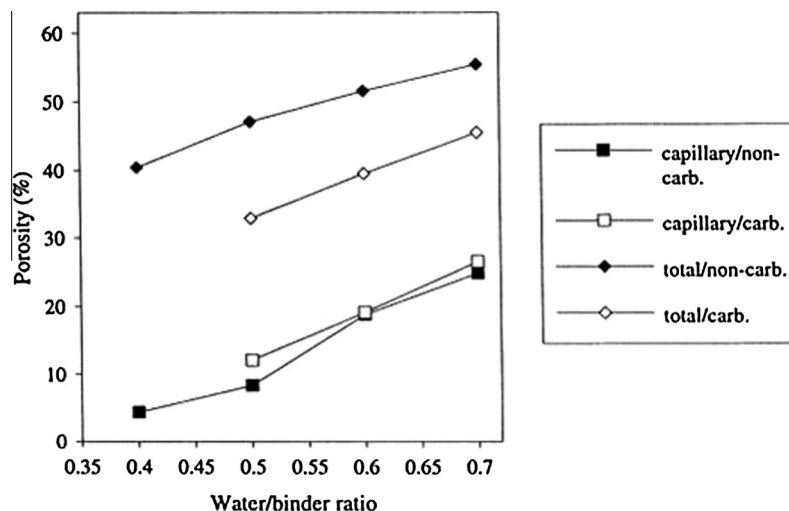


**Fig. 1.** Effects of carbonation on total porosity and capillary porosity of OPC pastes. adapted from [112].

clinker phases (i.e., $C_3S$, $C_2S$) or hydrated phases (i.e., $Ca(OH)_2$, C-S-H). A number of studies have been conducted to evaluate the effects of carbonation on both, anhydrous [1,53,55,121] and hydrated [61,65,122–124] phases.

Goto et al. [121] have presented an elaborate investigation on the morphologies of the carbonates that are formed during the carbonation reaction of pure calcium silicate phases, namely $C_3S$, $\beta$-$C_2S$, and $\gamma$-$C_2S$. In terms of crystalline structure, two types of carbonates are observed to form during the carbonation reaction of pure calcium silicates, including the poorly crystalline carbonates with decomposing temperature below 600 °C and the well crystalline phases (i.e., calcite, vaterite, and aragonite) that decompose at a temperature above 600 °C [121]. El-hassan et al. [86] have made similar observations in this regard. However, these suggestions contradict Fang et al. [125] who have shown that the carbonates which decompose below 600 °C also include vaterite and aragonite – the metastable crystalline polymorphs of calcium carbonates. Again, according to Thiery et al. [52] and Shtepenko et. al [126], the mass loss in the range of 500 °C to 600 °C is due to the decomposition of amorphous hydrocarbonate phase. In the case of carbonation reactions of $C_3S$ and $\gamma$-$C_2S$, calcite is reported to be the preferred polymorph, whereas, for $\beta$-$C_2S$, aragonite is the abundant polymorph of $CaCO_3$ [121,127]. During the carbonation reaction of OPC, calcite is observed to form as the primary polymorph of $CaCO_3$ [128], although the polymorph of the $CaCO_3$ can depend on the kinetics of the carbonation and cement types [129]. According to Goni et al. [129], all three varieties of crystalline $CaCO_3$ (these are – calcite, vaterite, and aragonite) are produced during natural carbonation process of OPC-based materials; whereas, calcite is the primary polymorph produced during the accelerated carbonation process. In addition to the crystalline calcium carbonate phases, formation of an amorphous calcium silicate hydrocarbonate phase during the carbonation reaction of calcium silicate based binders is also shown by several researchers [23,86,121,126]. Limited information is known about this phase, yet it is believed to contribute significantly to the early strength development of the cement paste matrix during the carbonation reaction [23,38]. Both, Junior et. al [38] and Ashraf et. al [130] have suggested that this phase is, in fact, a composite formed by intermixing of decalcified C-S-H (or silica gel) with amorphous calcium carbonate phase.

A silica-rich gel phase forms due to the carbonation reaction of either hydrated cement paste or unhydrated clinker phases. It is important to clarify that this phase has been identified with different names throughout the literature including calcium modified silica gel [13,18,61,130–132], low-lime C-S-H [60,98,121], and polymerized silica gel [28,56,87,90,123,125,128,133,134]. Both Castellote et al. [18] and Morandeau et al. [64] have shown that the carbonation of $Ca(OH)_2$ and C-S-H occurs simultaneously. Additionally, Castellote et al. [18] have pointed out that the structural modification of C-S-H caused by the carbonation mostly depends on the $CO_2$ concentration as it also affects the extent of carbonation. A recent study performed by Morandeau et al. [64] have explored the carbonation mechanism of $Ca(OH)_2$ and C-S-H using TGA, mercury intrusion porosimetry (MIP), phenolphthalein test, and gamma ray attenuation (GRAM). According to this study [64], among $Ca(OH)_2$ and C-S-H, only the carbonation reaction of $Ca(OH)_2$ releases the bound water and the decalcification of C-S-H leads to the formation of a highly hydrated silica-rich gel. Sevelsted and Skibsted [61] have studied the carbonation of synthetic C-S-H using NMR spectroscopy showing that the carbonation rate of C-S-H increases with lower calcium to silica atomic (Ca/Si) ratio of C-S-H (Fig. 2). The silica rich phase formed due to the carbonation of C-S-H is consists of $Q^3$ (either hydroxylated surface sites or cross-linked silicate tetrahedrons) and $Q^4$ (fully condensed network of silicate tetrahedrons) species [18,61,126,127]
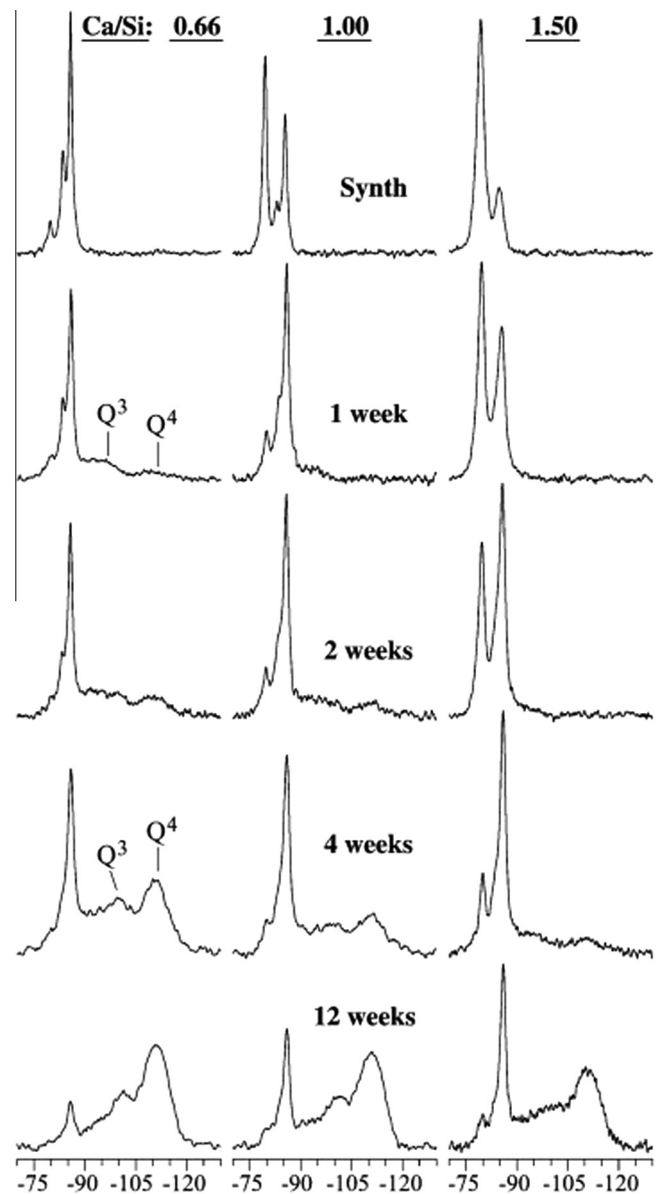


**Fig. 2.** $^{29}$Si MAS NMR spectra (9.4 T, $\nu R$ = 12.0 kHz, 30-s relaxation delay) of the synthesized C–S–H samples with Ca/Si = 0.66, 1.00, and 1.5 exposed to atmospheric $CO_2$ under humid conditions for 1, 2, 4, and 12 weeks. $Q^3$ and $Q^4$ indicate the resonances observed for the hydrous silica decomposition product. adapted from [61].

(can also be observed in Fig. 2). The hardness and elastic modulus of this polymerized silica rich phase are higher than those of the C-S-H [135,136].

### 6.4.2. Alternative binder materials

Effects of carbonation on the microscopic phases of AAM are considerably different than that of the OPC-based systems because of the presence of low calcium containing microscopic phases (Fig. 3). During the carbonation reaction, both $Ca(OH)_2$ and C-S-H phases are carbonated in OPC based systems. On the other hand, in the case of AAM, the gel phase starts carbonating immediately and hence, resulting a more severe effect than that of OPC [44,90].

Calcite, aragonite, and vaterite polymorphs of $CaCO_3$ are observed [42,63] to form during the carbonation reaction of alkali activated slag paste. Formations of these polymorphs of $CaCO_3$ also follow the Ostwald process, that is, the least stable polymorph of
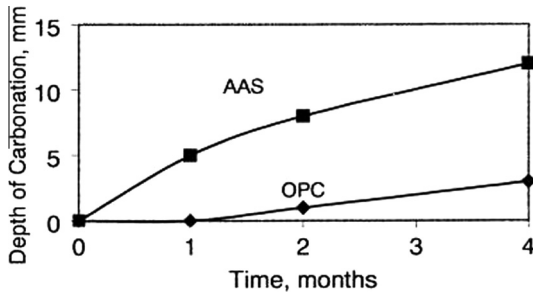
**Fig. 3.** Depth of carbonation in alkali activated slag (AAS) and OPC concretes exposed to atmosphere containing 20% $CO_2$, 70% RH. adapted from [44].

$CaCO_3$ crystallizes first [20,42,63]. During the carbonation reaction, the $Na_2SiO_3$ and NaOH activated slag pastes form hydrous sodium carbonates including thermonatrite ($Na_2CO_3 \cdot H_2O$), natron ($Na_2CO_3 \cdot 10H_2O$), and trona ($Na_3H(CO_3)_2 \cdot H_2O$) [42,43]. Mg-Ca bearing carbonate, such as huntite ($Mg_3Ca(CO_3)_4$) can form during the carbonation of Mg-containing alkali activated system [63]. Alkali activated fly ash/blend is primarily composed of two types of gel phases, namely, C-A-S-H and N-A-S-H [63]. Bernal et al. [63] have reported that the C-A-S-H gel phase is more prone to carbonation than the N-A-S-H.

From the limited investigations on the microscopic phases of sulfoaluminate belite cements [91,137–139], it is found that the ettringite (the primary hydration product of sulfoaluminate cement) decomposes and forms $CaCO_3$, calcium sulfate and aluminum hydroxide [138,139] during the carbonation reaction, which result in the disintegration of the matrix. The effects of $CO_2$ concentration on the microscopic phase changes and the types of carbonates form during the carbonation reaction of sulfoaluminate belite cement are yet to be studied.

### 6.5. Carbonation shrinkage

The hydrated OPC based cement system shows shrinkage while subjected to carbonation reaction. Several hypotheses have been proposed to explain the mechanism of this carbonation induced shrinkage of the cement-based materials. Powers [140] has hypothesized that under partially saturated conditions, shrinkage is due to the increase in the 'compressibility of cement paste' resulting from the dissolution of $Ca(OH)_2$. However, this hypothesis has provided an explanation only for the carbonation shrinkage of pure $Ca(OH)_2$ [141–143], but not for the total carbonation shrinkage of cement paste [144]. In accordance with Powers [140], Ramachandran and Feldman [141] have suggested that the carbonation of C-S-H occurs through a topochemical reaction in which no shrinkage is induced because dissolution does not occur. Moreover, according to Reardon et al. [142], the carbonation of C-S-H occurs through decomposition by a pseudomorphic reaction and hence, does not affect the overall shrinkage. However, a more recent hypothesis, proposed by Chen et al. [143] has explained the mechanism of carbonation shrinkage induced by the carbonation reaction of C-S-H phase as a general decalcification process. According to this study [143], Ca/Si ratio of 1.2 marks the initial point where interlayer calcium ions start removing from C–S–H gel during decalcification process. The removal of interlayer calcium ions forms Si-OH groups which then condense (i.e., increasing the polymerization of C-S-H) according to Eq. (6).

$$\equiv Si - OH + OH - Si \equiv \rightarrow \equiv Si - O - Si \equiv + H_2O \qquad (6)$$
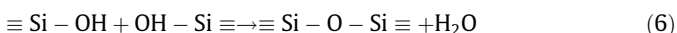
Some of these siloxane bonds (i.e., $\equiv Si{-}O{-}Si\equiv$) form bridges between neighboring surfaces or regions, thus, shrinking the sample by pulling them together. In support of this hypothesis,



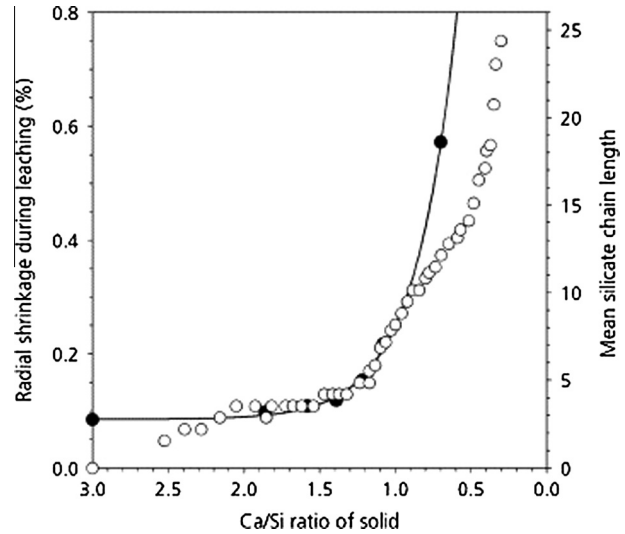**Fig. 4.** Changes in radial shrinkage ($\circ$) and mean silicate chain length (-$\bullet$-) during decalcification of a $C_3S$ paste. adapted from [143].

Chen et al. [143] have pointed out that the onset Ca/Si ratio of the decalcification induced polymerization and shrinkage of the C-S-H phase coincide at Ca/Si $\sim$ 1.2 (Fig. 4). Groves et al. [132] have also reported that the decalcification of C–S–H, particularly of the higher density (inner product) C–S–H is mostly responsible for the carbonation shrinkage of OPC-based systems.

## 7. Carbonation for sustainability: opportunities for construction industry

### 7.1. Concrete as a $CO_2$ storage system

Carbonation as a technique of storing $CO_2$ in cement-based materials has recently received substantial research interests [4,5,48,81,99,145–160]. Sequestration of $CO_2$ in concrete via carbonation reaction follows the same principal as that of the 'mineral carbonation' where the calcium and/or magnesium bearing silicate minerals are subjected to reaction with the $CO_2$ and result in the formation of calcium and/or magnesium carbonates [124,161]. Mineral carbonation is one of the safest options for the geological sequestration of $CO_2$ as it prevents the escape of $CO_2$ to the atmosphere for a long period of time [162,163]. The maximum amount of $CO_2$ that can be stored in cement-based materials depends on the chemical composition of the cement. In this regard, Steinour [164] have proposed the following formula:

$$CO_2(\%, max) = 0.785(CaO - 0.7SO_3) + 1.091MgO$$
$$+ 1.420Na_2O + 0.935K_2O \qquad (7)$$

here, CaO, $SO_3$, MgO, $Na_2O$, and $K_2O$ are the mass percentages of relevant constituent oxides. Several approaches can be followed to store $CO_2$ in concrete. These techniques are briefly discussed in the following section.

Accelerated carbonation curing is the most widely used method to store $CO_2$ in cement-based materials. In this method, the fresh cement or concrete mix (within few hours after mixing) is subjected to carbonation reaction. Shao and Hassan [4,99,107] have studied the $CO_2$ uptake during the accelerated carbonation curing process of concrete blocks and determined that one concrete block of 15 kg mass (contains 13% cement) can store up to 0.47 kg of $CO_2$ considering 24% $CO_2$ uptake of the cement. With such high efficiency, the $CO_2$ utilization in concrete blocks/bricks production can be equivalent to carbon sequestration in two geologic

formation sites [99]. Accordingly, $CO_2$ utilization in concrete block/brick production lines alone can reduce carbon emission by 2.5% for the cement industry if they adopt carbonation curing with the same carbon uptake rate [99]. During the accelerated carbonation curing, the $CO_2$ storage capacities of alkaline industrial byproducts (i.e., cement kiln dust (CKD), GGBFS, fly ash, and glass powder) primarily depend on the free CaO content, whereas, other factors including particle size distributions and moisture contents play a secondary role [81]. Similar observation has been made by Huntzinger et al. [165] for $CO_2$ sequestration capacity of CKD. It should be noted that the studies discussed here have utilized pure $CO_2$ gas for accelerated carbonation curing. Direct carbonation of cement-based materials in flue gas can save the energy required to separate the pure $CO_2$ but will also reduce the carbonation efficiency [156].

The limitation of the accelerated carbonation curing is that the samples are required to be precast as this process also results in rapid hardening of the cementitious matrix. Hence, precast concrete products including masonry units, paving stones, cement boards, and fiber boards are most suitable for $CO_2$ storage following this curing method [156]. Alternatively, $CO_2$ can be stored by incorporating it with the concrete mixing water. According to Kwasny et al. [148], a minimum of 1.655 mol $CO_2$ per litter of concrete mixing water can be incorporated. Thus, approximately 2–3.5% of $CO_2$ by mass of cement (considering w/c = 0.3 to 0.5) can be stored in concrete following this approach.

Hydrated (i.e., hardened) OPC-based materials can also store a substantial amount of $CO_2$ through the atmospheric carbonation process. Pade and Guimaraes [145] have investigated the $CO_2$ uptake (using Eq. (8)) via the atmospheric carbonation process considering 100 years life cycle of concrete structures present in Denmark, Iceland, Norway and Sweden. Fig. 5 briefly explains the methodology that authors [145] have followed to estimate the $CO_2$ uptake during the 100 years life of concrete. Based on their findings [145], the concrete produced in the year 2003 can store a significant proportion (>30%) of the $CO_2$ emitted during the production process of the cements used in these structures via atmospheric carbonation process (Table 4).

$$CO_2 uptake = 0.75 \times C \times CaO \times M_{CO_2}/M_{CaO} \qquad (8)$$

**Table 4**
The $CO_2$ balance of concrete in the various countries [145].

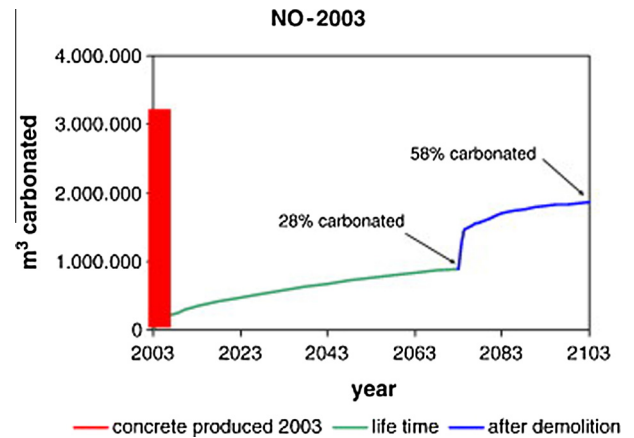| | Denmark (2003) | Norway (2003) | Sweden (2003) | Iceland (2003) |
|---|---|---|---|---|
| $CO_2$ uptake after 100 years (metric tons) | 340,000 | 220,000 | 240,000 | 21,000 |
| $CO_2$ emission from calcination (metric tons) | 600,000 | 675,000 | 730,000 | 58,000 |



**Fig. 6.** Carbonation of concrete produced in Norway during service life and after demolition. adapted from [145].

here, C = mass of Portland cement clinker per $m^3$ concrete, CaO = mass fraction of CaO in the cement clinker, $M_{CO_2}$ = molar mass of $CO_2$ and $M_{CaO}$ = molar mass of CaO. The proportions of carbonated concrete as determined in this research [145] are shown in Fig. 6 for Norway.

Considering only the atmospheric carbonation of structures during their service life (i.e., 100 years), 38% of concretes produced in USA in the year 2000 can be expected to be carbonated by the end of their service life [153,154]. However, according to Galan et al. [149], the $CO_2$ storage capacity of concrete via atmospheric carbonation process depends significantly on the environmental
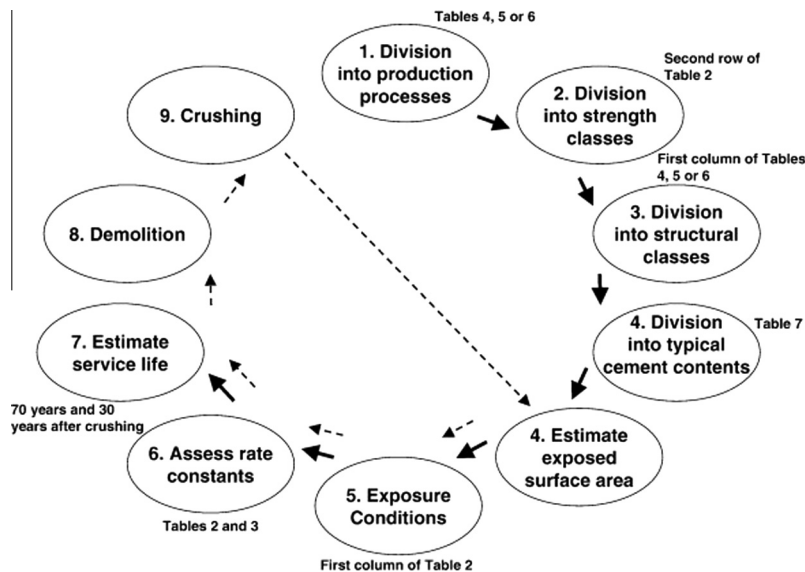


**Fig. 5.** Methodology for estimating $CO_2$ uptake for concrete structures. Full arrows indicate the service life (70 years) and dotted arrows indicate secondary life (30 years). adapted from [145].

conditions such as humidity level, wetting-drying cycles etc. Studies on the old concrete pavements [160] and sidewalks [150] have also showed noticeable $CO_2$ sequestration potential during the atmospheric carbonation process.

Another approach to sequester $CO_2$ in concrete is to submerge the specimens in sodium bicarbonate solutions [151]. Carbonation rate of concrete can be faster in this approach compared to that of the atmospheric carbonation [151] depending on the concentration of the solution.

### 7.2. Carbonate binders

During the last decade, a few binder systems have emerged, which in addition to a lower production temperature (in comparison to OPC), can also store a substantial amount of $CO_2$ through the hardening process. However, the concept behind the carbonate binders is not new. Rather, one can argue that this concept follows one of the most ancient cementing technology in the building industry involving the carbonation of pure lime [12,166,167]. The strength development in this process of converting lime to $CaCO_3$ largely depends on the morphology of $CaCO_3$ [12]. A slower carbonation rate results in well-formed crystalline $CaCO_3$ which have beneficial effect on the mechanical properties [12] of such binder systems (Fig. 7).

A recent addition to this carbonated binder system is a commercially available cement addressed as 'calcium silicate based cement (CSC)' (also known as 'Solidia cement') [130,168]. This binder is composed of low-lime calcium silicates such as wollastonite, pseudo-wollastonite, and rankinite. These low-lime calcium silicates are non-hydraulic and usually not used in conventional
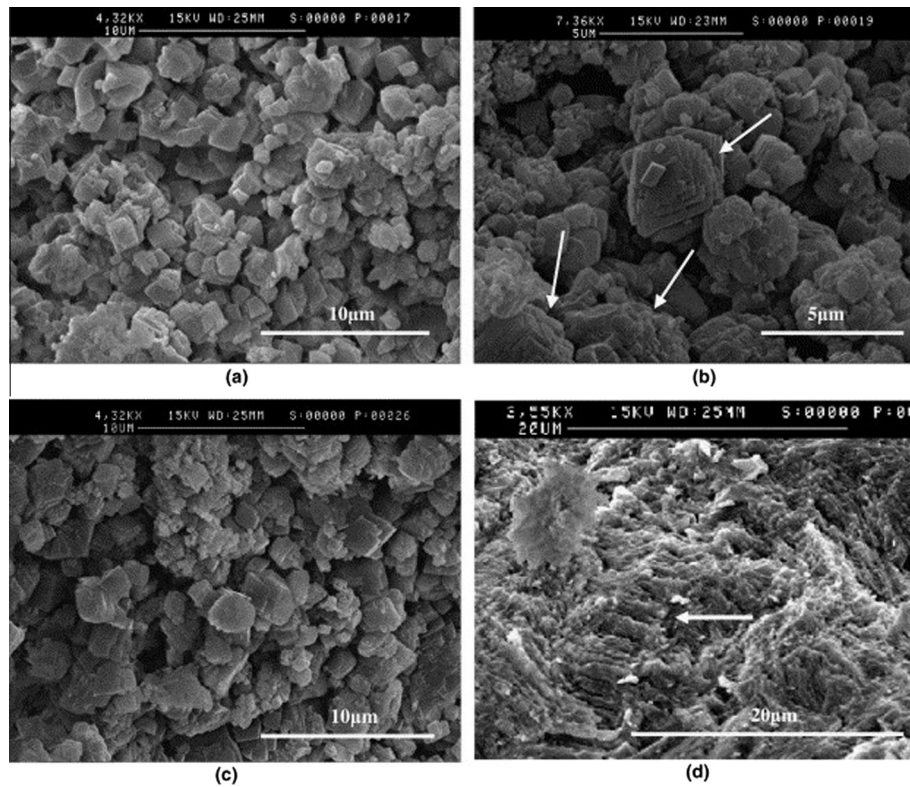


**Fig. 7.** SEM micrographs of carbonated $Ca(OH)_2$ binders prepared with 0.25 water to solid ratio, 2 MPa compaction pressure and 2 MPa $CO_2$ gas pressure; (a) 2 mm depth at 0.5 h exposure and (b) 2 mm depth at 6 h exposure (arrows indicate $CaCO_3$ morphologies); (c) 6 mm depth at 6 h exposure; and (d) microstructure of beachrock (arrow indicates layered $CaCO_3$ morphology). adapted from [12].
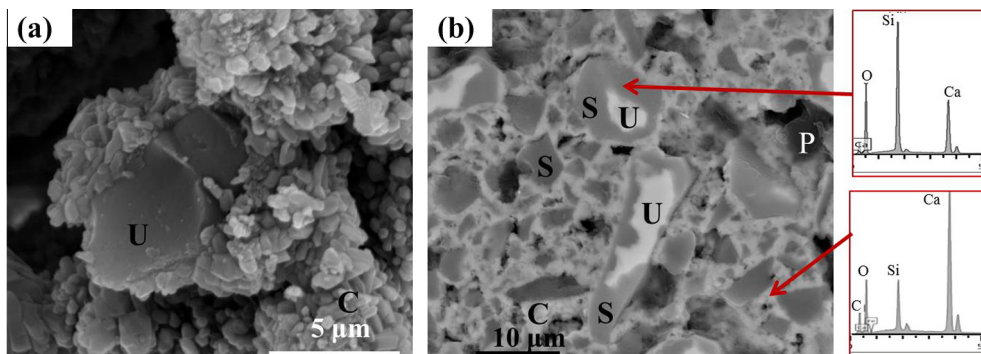


**Fig. 8.** SEM images of carbonated rankinite ($3CaO.2SiO_2$) samples showing the microscopic phases; a SE image and b BSE image. 'S' indicates Camodified silica gel, 'U' indicates unreacted/partially reacted rankinite ($3CaO \cdot 2SiO_2$) grains, 'C' indicates CaCO3, and 'P' indicates pores. adapted from [55].

OPC based system. However, these non-hydraulic calcium silicates can be readily activated during the carbonation reaction [53,55,98]. As an example, Fig. 8 shows the microstructure of the carbonated rankinite matrix. US patents [169,170] have been issued for the technologies involved in the CSC system. A preliminary study has shown that the carbonation reaction products of this binder system include Ca-modified silica gel (or silica gel), $CaCO_3$, and a composite phase containing intermixing of former two phases [130].

Higuchi et al. [171] have reported the development of a carbonated concrete named $CO_2$-SUICOM that can achieve $CO_2$ emission level below zero. The primary ingredients of the binders in this system are $\gamma$-$C_2S$ and coal-ash. Similar to the CSC system, the hardening of the $CO_2$-SUICOM is dependent on the carbonation reaction. The binding matrix of $CO_2$-SUICOM consists of $CaCO_3$ and $SiO_2$ gel like phase [171].

Das et al. [172] have studied the potential of developing new binder system by subjecting metallic iron dust powders (produced during the manufacturing of electric arc furnace) to carbonation. Paste samples containing this iron powder along with SCMs (fly ash, metakaoline) can achieve a compressive strength of around 35 MPa after 4 days of carbonation. The iron-based carbonated binder matrix also provides higher flexural strength and fracture toughness compared to that of the OPC [173].

Ladle slag can also be used as a raw material for carbonation based binder system [51]. The primary ingredient of ladle slag is $\gamma$-$C_2S$ [174] which is a latent hydraulic ingredient. However, it exhibits rapid strength gain properties when activated with carbonation reaction.

In addition to the carbonate binder systems, two other commercially available cement systems are noteworthy as these are also utilizing the general concept of carbonation. These cements are – Calera calcium carbonate [175,158] and Novacem [176]. Calera corporation [175] is promoting an approach that involves capturing $CO_2$ from industrial sources and converting them in $CaCO_3$ [177] (hence, known as Calera calcium carbonate), which can be either used as SCM [158] with OPC or itself as an individual binder system. The primary raw material of Novacem is magnesium silicate [176]. But it also requires storing of $CO_2$ (by the process of carbonation) in anhydrous cement in the form Magnesium carbonate ($MgCO_3$) [176].

## 8. Conclusion

This article presents a comprehensive review of wide ranging studies that have been performed on the carbonation of cement-based materials. Following concluding points can be drawn from this review:

(i) An appropriate selection of curing conditions, specifically the concentration of $CO_2$ is vital for accelerated carbonation tests as it influences the effects of carbonation on the microscopic phases.

(ii) Most of the existing kinetic models of carbonation are utilized to predict the depth of carbonation in the compacted cement-based materials. The chemical kinetics of the carbonation reaction of cementitious materials is still not well investigated and requires additional studies.

(iii) The carbonation resistance of concrete containing OPC as the primary binder is higher than that of the concrete containing SCMs (i.e., fly ash, silica fume, slag) or alternative binder materials (i.e., AAM, sulfoaluminate belite).

(iv) The total porosity of OPC-based systems decreases during the carbonation reaction, but the relative proportion of capillary porosity increases. The carbonation reaction of cement-based materials increases the ionic diffusivity as a result of the increased capillary porosity.

(v) Cement-based materials have the potential to store a substantial amount of $CO_2$. $CO_2$ can be stored in cement-based materials by means of (1) accelerated carbonation curing, (2) atmospheric carbonation, (3) adding $CO_2$ in the concrete mixing water, and (4) by submerging concrete specimens in water with carbonate species. Among these methods, accelerated carbonation curing ensures the highest and the fastest $CO_2$ storage in concrete.

(vi) Industrial research interest regarding the carbonate binders has been observed to grow over the past decade. Within last eight years a total of six different carbonate binders have been developed, these are: CSC, $CO_2$-SUICOM, Novacem, Calera, laddle slag based, and iron waste powder based binders. All of these binders can store a significant portion of $CO_2$ in the form of carbonates and have a significantly lower $CO_2$ footprint in comparison to that of the OPC based system.

Carbonation has been traditionally viewed as a detrimental aspect for cement-based materials. Nonetheless, it can also be regarded as an opportunity to create a sustainable concrete industry by storing $CO_2$ in cement-based materials and utilizing carbonate binders with low $CO_2$ footprint.

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