Understanding the Process of Carbonation in Concrete using Numerical Modeling

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Abstract

The objective of the study is to develop a model that will help in understanding the process of carbonation. This study investigates the influence of different physical, chemical and environmental parameters on the carbonation process in concrete. The model incorporates the influence of change in porosity on carbonation and the variations in the internal relative humidity of concrete due to drying on the rate of carbonation. The pore saturation and porosity were found to control the rate of carbonation in concrete. The model demonstrates the preconditioning duration and amount of water released on carbonation have an insignificant effect on the extent of carbonation in the long-term. Increased tortuosity and higher alkalinity could help in improving the carbonation resistance of system.

1. Introduction

Carbonation in concrete is a complex physiochemical process involving various steps (Papadakis et al. 1989; Saetta and Vitaliani 2005). In simple terms, it is a reaction between CO2 diffused in concrete and hydration products of cement. The reaction front progresses steadily from the surface of the concrete to the core. The rate of movement of carbonation front is governed by the concrete properties and exposure conditions (Papadakis et al. 1991a; Richardson 2002; Šavija and Luković 2016; Da Silva et al. 2009).

Carbon dioxide diffuses in the concrete through the air-filled pores and reacts with the hydration products, precipitating calcium carbonate and moves forward. Simultaneously, due to the difference in the relative humidity between the concrete and external environment water diffuses in or out of the concrete depending on the concentration gradient. Water present in the concrete pores provides the medium for dissolution of most major phases present in hydrated cement. Carbonation of other phases are not completely established (Georget et al. 2020). This indicates that in order to model the extent of carbonation accurately a coupled approach involving CO2 and alkali diffusion alongside wetting or drying of concrete is necessary.

The microstructure of concrete is altered with the advent of carbonation. Changes in the pore volume due to the difference in solid volume of the hydration products carbonated and calcium carbonate formed along with micro-cracks originating on the concrete surface due to carbonation shrinkage modify the diffusion characteristics of CO2 in concrete (Chen et al. 2006; Shah et al. 2018; Song and Kwon 2007; Suda et al. 2021; Wu and Ye 2015).

Thermodynamically, calcium hydroxide has the highest propensity to undergo carbonation amongst all the major phases present in hydrated cement. Carbonation of calcium hydroxide leads to an increase in molar solid volume by 11 to 14% depending on the type of polymorph of calcium carbonate being formed, leading to a reduction in overall porosity of concrete (Lagerblad 2005; Morandeau et al. 2014). The influence of carbonation of hydration phases other than calcium hydroxide (CH) has been generally neglected in the models developed in the past (Isgrò and Razaqpur 2004; Maekawa et al. 2009; Saetta et al. 1993; Talukdar et al. 2012a). Moreover, not all the calcium ions present in cement are available for the carbonation reaction. The decalcified C-S-H formed on carbonation restricts the movement of calcium ions sandwiched between long silicate chains and also formation of calcium carbonate layer around hydrated phases impedes their further dissolution (Morales-Florez et al. 2012; Omikrine Metalssi et al. 2020; Šavija and Luković 2016; Sevelsted and Skibsted 2015; Shah et al. 2018). Moreover, carbonation of alumina containing hydration products along with anhydrous clinker grains has also been reported (Shah et al. 2018; Shi et al. 2016). In addition, apart from calcium hydroxide, the volume changes occurring on carbonation of other phases are not completely established.
yet. Most available models of carbonation, either neglect the influence of the change in porosity, or assume that carbonation would lead to a reduction in pore-volume (Bahador and Cahiyyadi 2009; Isgor and Razaqpur 2004; Khunthongkeaw and Tangtermsirikul 2005; Maekawa et al. 2009; Saetta et al. 1993; Talukdar et al. 2012a; Zhang 2016). Such models are not appropriate for use in systems that are predominated by phases like C-S-H, ettringite, monosulfaloaluminate and monocarboaluminate that could lead to an increase in the porosity upon carbonation (De Ceukelaire and Van Nieuwenburg 1993; Justnes et al. 2020; Shah and Bishnoi 2018a; Shi et al. 2016; Wu and Ye 2015).

To predict the long-term performance of concrete structures under carbonation, use of empirical model is common (Bahador and Cahiyyadi 2009; Ekolu 2015; Ho and Lewis 1987; Sanjuán et al. 2003; Shah and Bishnoi 2019; Ta et al. 2016). It has been shown earlier that for the purpose of extrapolation and prediction, empirical models perform very well. Numerical models that take into consideration various complex physical processes are also developed (Georget et al. 2018; Isgor and Razaqpur 2004; Maekawa et al. 2009; Papadakis et al. 1991a; Phung et al. 2016; Saetta et al. 1993; Zhang 2016). Such elaborate models may not be required for the purpose of prediction. This is because either the understanding of the processes involved in itself is limited or the models that are available require much more data that is not available. Additionally, the error in the measurement of individual datum required for such numerical models may add up to errors that are higher than those seen in the predictions from the empirical models. Therefore, the main objective of this study is to understand the influence of different parameters (tortuosity, drying diffusion coefficient, saturation index, preconditioning duration, alkalinity, porosity and exposure condition) on the carbonation process itself. Use of diffusion law will be made to model the processes involved. It is understood that there are a large number of parameters involved, which would make the process of fitting unreliable. Hence, focus on the sensitivity of the results to individual parameters is emphasized rather than prediction of carbonation depth.

2. Formulation of carbonation model

2.1 Diffusion of CO2

The diffusion of a gas, like carbon dioxide, in a porous medium, like concrete, can be described using Fick’s second law, which assumes non-steady state diffusion and neglects interactions with the surface. The change in concentration of CO2 due to diffusion with time can be determined by using the following equation on a one-dimensional plane.

\[
\frac{\partial [C]}{\partial t} = \frac{\partial}{\partial x} \left( D \times \frac{\partial [C]}{\partial x} \right) + S
\]

where \( D (m^2/s) \) is the diffusion coefficient of CO2, \([C] \) (mol/m^3) is the concentration of CO2 and \( S \) (mol/m^3) is the sink term corresponding to the amount of CO2 consumed in the carbonation reaction.

2.2 Diffusion of calcium ions

The concentration gradients within concrete lead to diffusion of calcium ions from one region to another. The concentration gradients arise because of consumption of calcium ions by the carbonation reaction. The movement of calcium ions in concrete can be represented by the following equation:

\[
\frac{\partial [A]}{\partial t} = \frac{\partial}{\partial x} \left( D_A \times \frac{\partial [A]}{\partial x} \right) + S
\]

where \( D_A (m^2/s) \) is the diffusion coefficient of calcium ions in water and \( S \) (mol/m^3) is the sink term mentioned above. The amount of CO2 and calcium consumed in the carbonation reaction represented by sink term \( S \) is same.

The carbonation reaction takes place in solution between the dissolved CO2 and calcium ions. CO2 diffuses from the external environment into concrete and is dissolved in concrete, forming aqueous CO2. Henry’s law is used to relate the aqueous and gaseous concentration of CO2 (Phung et al. 2016; Talukdar et al. 2012b).

\[
\left[ C_{aq} \right] = \frac{H}{T} \left[ CO_2 \right]_{g(0)}
\]

where \( \left[ C_{aq} \right] \) (mol/m^3) is the aqueous concentration of CO2, \( H \) is Henry’s constant (mol/m^3 atm), \( R \) (m^3 atm/K mol) is the universal gas constant, \( T \) is the temperature (K) and \( \left[ CO_2 \right]_{g(0)} \) (mol/m^3) is the concentration of CO2 in gaseous state. The concentration of CO2 in aqueous form is directly dependent upon the partial pressure of CO2 in the gaseous state (Khunthongkeaw and Tangtermsirikul 2005). The dissolved CO2 reacts with the calcium ions available in the solution from the dissolution of solid hydration products (Ji et al. 2014). The rate of neutralization reaction will depend on the calcium ion concentration and it can be described as below:

\[
r_n = K \left[ C_{aq} \right] \left[ A_{aq} \right]
\]

where \( K \) (m^3/mol/s) is the reaction constant between dissolved CO2 and calcium ions and \( \left[ A_{aq} \right] \) (mol/m^3) is the aqueous concentration of calcium ions in pore solution. It has been shown in the literature that in the case of concrete carbonation, since the rate of neutralization is much faster than the rate of diffusion of CO2, it is not the rate-controlling step (Peter et al. 2008; Saetta et al. 1993). The processes of neutralization and dissolution in a pore continue until no more calcium ions are available for dissolution at the location. The amount of reactant consumed constitutes the sink term described in Eqs. (1) and (2). The dissolution of calcium in pore solution is limited by the equilibrium between calcium ions concentration in the aqueous and solid state. The equilib-
rium concentration of calcium ions at saturation at 25°C is 22 mol/m³ (Zhang 2016). As discussed above, due to the diffusion of CO₂ being the rate-controlling process, the dissolution of calcium can also assume to be instantaneous as long as solid alkali hydrates are present at the location. The rate of diffusion of calcium ions due to concentration gradient within concrete was assumed to be constant and it was taken to be as 1×10⁻¹² m²/s (Talukdar et al. 2012b).

2.3 Drying of concrete
The one-dimensional variation in water content of concrete with respect to time and space is calculated using the following equation.

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x} \left( D_w \frac{\partial w}{\partial x} \right) + S_h$$  \hspace{1cm} (5)

where $D_w$ (m²/s) is the moisture diffusion coefficient and $S_h$ is the water produced during the carbonation reaction. Section 4.4 discuss in detail on the aspect of water produced ($S_h$) from the carbonation reaction and its effect on the rate of progress of carbonation. The different phases of water (vapor, capillary and chemically absorbed) can be considered to be in thermodynamic equilibrium in concrete at any time due to the slow diffusion process (Saetta et al. 1993; Zhang et al. 2012). Therefore, relative humidity ($H$) in concrete can be expressed as a function of water content based on desorption and sorption isotherms. Thus, the diffusion equation of water can be rewritten in terms of relative humidity as (Wang and Park 2017):

$$\frac{\partial H}{\partial t} = \frac{\partial}{\partial x} \left( D_w \frac{\partial H}{\partial x} \right) + S_h + K \frac{\partial T}{\partial t}$$  \hspace{1cm} (6)

where $K$ (1/°C) is the hygrothermal coefficient taking into account the change in $H$ due to one degree Celsius change in temperature. However, for isothermal conditions, the equation can be represented as below:

$$\frac{\partial H}{\partial t} = \frac{\partial}{\partial x} \left( D_w \frac{\partial H}{\partial x} \right) + S_h$$  \hspace{1cm} (7)

2.4 Finite difference formulation
The finite difference method was used in this study to solve Eqs. (1), (2) and (7) numerically. The forward Euler method in time and central difference in space was used to solve the differential equations. Equation (8) represents the general form of the diffusion equation, where $u$ is a dependent variable (either [C], [A] or [H]), $x$ and $t$ are the independent variables and $D$ is the diffusion coefficient.

$$\frac{\partial u(x,t)}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial u}{\partial x} \right)$$  \hspace{1cm} (8)

$$\frac{\partial u(x,t)}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial u}{\partial x} \right) + D \frac{\partial^2 u}{\partial x^2}$$  \hspace{1cm} (9)

The diffusion coefficient is a temporal and spatial function of porosity and saturation of the system. The entire domain is discretized into a two-dimensional uniform mesh, with the first dimension representing space and the second dimension representing time. Using Taylor series expansion, the term on the left side of Eq. (9) can be written as Eq. (10). Similarly, the term on the right side of the Eq. (9) can be written as Eq. (11). In Eqs. (10) and (11), $h$ and $k$ are the spatial and time step respectively by which the domain is discretized. The modified diffusion equation can be represented by Eq. (12), which has one term from the next time level $u(x,t+k)$ whereas all the remaining terms are from the time level ($t$). Hence, given the initial values at a particular time level, Eq. (12) can be used to find the values at next time step.

$$\frac{\partial u(x,t+k)}{\partial t} = u(x,t+k) - u(x,t)$$  \hspace{1cm} (10)

$$\frac{\partial u(x,t)}{\partial t} \approx u(x,t+k) - u(x,t)$$  \hspace{1cm} (11)

The computed values at time ($t+k$) can be used to compute values at time ($t+2k$). By incrementing time the steps, the values at all the points in the domain considered can be computed. After arranging, Eq. (12) can be rewritten as:

$$u(x,t+k) = u(x,t) + \frac{k}{h^2} (D_{xx} u_t + D_{xy} u_{xy}) + \frac{k}{2h} (D_{yy} u_{xy})$$  \hspace{1cm} (13)

The stability of the simulations was ensured by satisfying the Courant-Friedrichs-Lewy Condition - i.e., $kD/h^2 \leq \frac{1}{2}$, and the spatial and temporal step sizes were fixed at 1 mm and 1 second respectively.

2.4.1 Initial and boundary conditions
The domain for the Eqs. (1), (2) and (7) is $0 \leq x<n$ and $0 \leq t<\infty$.

At time $t=0$,

$$[CO_2(g)](x,0)=0;$$  \hspace{1cm} (14)

$$[A_{aq}](x,0)=22 \text{ mol/m}^3;$$  \hspace{1cm} (15)

$$H(x,0)=100;$$  \hspace{1cm} (16)

At any other time $t=t$,

$$[CO_2(g)](0,t)=CO_2(\text{exposure}) \text{ for } t=0;$$  \hspace{1cm} (17)
\[
\frac{d[CO_{2g}](n,t)}{dx} = 0; \\
\frac{d[A_w](0,t)}{dx} = 0; \\
\frac{d[A_w](0,t)}{dx} = 0; \\
H(0,t) = H_{\text{exposure}} \text{ for } t > 0; \\
\frac{d[H](n,t)}{dx} = 0; 
\]

(18) (19) (20) (21) (22)

3. Experimental data for validation

A sensitivity analysis was carried out to identify the influence of different parameters on the rate of carbonation in concrete. The values of parameters identified were changed and their influence on the model output was assessed. The modeled carbonation depth was compared with the experimental carbonation depth measured for a range of binders exposed to different environmental conditions (Table 2) and sheltered natural condition. The carbonation depth was measured after 1, 3, 7, 14, 28, 60, 90 and 120 days of exposure to CO2 for samples placed in accelerated exposure conditions, whereas samples placed in natural condition, the carbonation depth was measured after 6, 12, 18, 24 and 48 months using phenolphthalein indicator.

3.1 Concrete

The compositions of the binders used in the study are given in Table 1. Concretes were cast at a water to binder ratio of 0.35 and 0.45 for all the binder types. The details of the concrete mix design are included in the in Table A1 in the Appendix to this paper. After casting, the concrete samples were cured in lime-saturated water for 120 days. After the end of the curing regime, the concrete samples were preconditioned at a temperature of 27°C and 60% relative humidity, for a duration of 15 days in accordance with EN 13295:2004 (EN 2004). Thereafter, the concrete samples were exposed to different accelerated CO2 environmental conditions (Table 2) and sheltered natural condition. The carbonation depth was measured after 1, 3, 7, 14, 28, 60, 90 and 120 days of exposure to CO2 for samples placed in accelerated exposure conditions, whereas samples placed in natural condition, the carbonation depth was measured after 6, 12, 18, 24 and 48 months using phenolphthalein indicator.

3.2 Reserve alkalinity and porosity

The amount of calcium available for carbonation in blended cements is lower in blended cements due to the dilution effect of SCMs. Therefore, it is important to consider carbonation of all the hydration phases and not only calcium hydroxide. For this reason, the alkalinity content determined through acid neutralization of hydrated cement samples was used for modeling carbonation. The alkalinity content was measured on cement paste samples cast at the same water to binder ratios as concrete. A thin slice of cement paste was cut and ground after 120 days of curing and subsequently sieved through a 150 µm sieve. A solution of one gram of powdered sample and 100 ml of double distilled water was prepared. Thereafter, 2-3 drops of phenolphthalein indicator were added in the solution and titrated against 0.1 M sulphuric acid, until the pink colour of the solution disappeared. The amount of acid required to completely neutralize the alkalinity was measured. The reserve alkalinity values obtained is given in Table 3, which denotes the total concentration of alkalinity available for the carbonation reaction. The lower the clinker factor the lower is the reserve alkalinity value. More details have been reported earlier (Shah et al. 2020; Shah and Bishnoi 2018b).

| Clinker | Clinker | Gypsum | Fly ash | Slag | Limestone | Calcined clay |
|---------|---------|--------|---------|------|-----------|---------------|
| PC      | 0.97    | 0.03   | -       | -    | -         | -             |
| FA30    | 0.67    | 0.03   | 0.30    | -    | -         | -             |
| LC3     | 0.50    | 0.04   | -       | -    | 0.15      | 0.31          |
| S30FA15 | 0.50    | 0.04   | 0.15    | 0.31 | -         | -             |

Table 2 Accelerated exposure conditions used for carbonation.

| CO2 concentration (%) | Temperature (°C) | Relative humidity (%) |
|-----------------------|------------------|-----------------------|
| 3                     | 27               | 40, 60, 80            |
| 1                     | 27               | 60                    |

Table 3 Reserve alkalinity of different mixes (mol/m³ of concrete).

| W/B | PC | FA30 | LC3 | S30FA15 |
|-----|----|------|-----|---------|
| 0.35| 3270| 2235 | 1841| 1791    |
| 0.45| 2492| 1654 | 1281| 1388    |
the carbonation process itself, which can alter the rate of diffusion of CO$_2$ in concrete. As it is difficult to calculate the exact volume change occurring on carbonation with the existing knowledge, experimental results were used in the model. Mercury intrusion porosimetry (MIP) was used to measure the changes occurring in pore structure of cement paste on carbonation. Thin discs of 2 to 3 mm were cut from the cement paste samples cast to measure the porosity. The discs were subjected to carbonation in an environmental chamber having CO$_2$ concentration of 3%, relative humidity of 60% and temperature of 27°C for 2 months. The MIP measurements on the uncarbonated samples were made after the end of the curing regime whereas the MIP measurements of the carbonated samples were done at the end of the exposure period of 2 months. The procedure adopted for MIP measurements is given elsewhere (Shah et al. 2018). Since the diffusion of external agents in concrete is predominantly governed by capillary pores (Gruyaert et al. 2013; Van Den Heede et al. 2010; Kumar and Bhatcharjee 2003), the porosity of cement pastes corresponding to 10 nm and greater (capillary pores) measured using MIP were used. The porosity was assumed to linearly depend on the degree of the carbonation - i.e., starting from the porosity of the uncarbonated sample and ending with that of carbonated sample for all the exposure conditions.

4. Results

4.1 CO$_2$ Diffusion coefficient

The diffusion coefficient of CO$_2$ plays an important role in the progress of carbonation in concrete. Different methods for the determination of diffusion coefficient of CO$_2$ have been reported in literature (Bahador and Cahyadi 2009; Khunthongkeaw and Tangtermsirikul 2005; Papadakis et al. 1991a; Phung et al. 2016; Saetta et al. 1993; Song et al. 2006). Although, a wide variety of diffusion models have been described in the literature, the basis of their formulation is similar. Each model considers a function of porosity and tortuosity on which the diffusion of CO$_2$ is primarily dependent. Therefore, the diffusion coefficient of CO$_2$ can also be described using Eq. (23):

$$D = 1.65 \times 10^{-5} \times \tau \times P^{1.73}$$  \hspace{1cm} (23)

where 1.65$\times$10$^{-5}$ (m$^2$/s) is the diffusion coefficient value of CO$_2$ in air (Talukdar and Banthia 2015), $\tau$ is the factor that takes into account the tortuosity of the system and $P$ is the porosity.

The porous volume of concrete comprises of both air and water-filled pores. Diffusion of CO$_2$ through water is slower by 4 orders of magnitude as compared to that in air (Pacheco Torgal et al. 2012; Papadakis et al. 1991b; Visser 2013) and can therefore be ignored; it can be assumed that the diffusion of CO$_2$ in concrete takes place only through air-filled pores. In most of the existing models, either the entire porosity of the system is considered to be available for the diffusion of CO$_2$ or an empirical coefficient is used to include the influence of relative humidity. However, given that drying is a slow process and it progresses along with carbonation, it is incorrect to assume a time-invariable influence of relative humidity on diffusion. In the current model, the saturation of the pores is calculated as a function of both space and time. The procedure used to obtain the saturation index of concrete corresponding to different relative humidity is described in the Appendix. The porosity term in the equation is therefore replaced by the unsaturated porosity, as shown in Eq. (24).

$$D = 1.65 \times 10^{-5} \times \tau \times \left(1 - \text{Saturation} \right)^{1.73}$$  \hspace{1cm} (24)

Table 4 summarizes the carbon dioxide diffusion coefficient values calculated using Eq. (24) using $\tau$ of 0.06 at the end of the preconditioning period. The obtained diffusion coefficient values are in the similar range as reported in literature measured using experimental methods. A difference in the values is obvious because of the difference in the water to binder ratio, extent of drying, sample size and binder type.

Carbonation depth predicted using the model for different values of $\tau$ is shown in Fig. 1. The grey colour bands in Fig. 1 represent the range in which the experimentally measured carbonation depth varied after 120 days of exposure in 3% CO$_2$, 60% R.H. and 27°C. Higher the value of the tortuosity factor faster is the rate of diffusion of CO$_2$ in concrete. For a factor of 0.03, the modeled data is less than the experimental data for most of the mixes. Whilst the predicted data shows a good correlation with the experimental data for the tortuosity factor values of 0.06 and 0.09. The results imply that binder systems even with a similar porosity could exhibit contrasting carbonation performance due to the difference in the tortuosity of the system. The pore structure or the tortuosity varies significantly between

| Table 4 Calculated diffusion coefficient values. |
|-----------------------------------------------|
| W/B: 0.35                                      |
| PC                                            |
| $7.7 \times 10^{-5}$                          |
| FA30                                          |
| $3.93 \times 10^{-5}$                        |
| LC3                                           |
| $1.36 \times 10^{-5}$                        |
| S30FA15                                       |
| $4.44 \times 10^{-5}$                        |
| W/B: 0.45                                     |
| $7.05 \times 10^{-5}$                        |
| $2.25 \times 10^{-4}$                        |
| $1 \times 10^{-7}$ to $1 \times 10^{-11}$     |
| $4.00 \times 10^{-9}$                        |

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binder systems depending on the composition. Therefore, using the same value for different binders could result in inappropriate estimation of carbonation depth. The higher carbonation depths for 0.45 water to binder ratio mixes are due to their inherently higher porosity. The influence of porosity on progress of carbonation is discussed further in Section 4.5.

4.2 Drying diffusion coefficient

The drying of concrete occurs due to the difference in relative humidity levels at the concrete surface and interior of the concrete. Figure 2 shows the changes occurring in the saturation index and CO$_2$ diffusion coefficient with time and distance for LC3_0.35 mix. The results clearly depict a reduction in the saturation of concrete and a corresponding increase in the CO$_2$ diffusion coefficient due to the availability of more space (air-filled porosity) associated with the drying of the concrete.

A few models are available to determine the drying diffusion coefficient for PC concrete (Bažant and Najjar 1972; Isgor and Razaqpur 2004; Sarkar 2015), however, a generic model that could predict the diffusion coefficient for different binder systems is not available. Drying diffusion coefficient can be determined experimentally by placing sensors in concrete or by measuring the change in weight of concrete sample with time at different relative humidity levels (Huang et al. 2015; Sarkar 2015; Zhang et al. 2012). However, due to the high cost of the sensors and longer testing duration the determination of drying diffusion coefficient for blended cements is difficult. Therefore, due to the lack of an appropriate method to compute drying diffusion coefficient use of Eq. (25) was made. The drying of moisture from saturated concrete involves flow in both vapor and liquid phases. The diffusion of gas in concrete is influenced by the air-filled porosity whereas diffusion of water is primarily influenced by the water-filled porosity. Drying of concrete is analogous to diffusion of gas in concrete, with the added influence of capillary forces. The diffusion coefficient of water vapor was, therefore, written as a function of the porosity, a factor accounting for tortuosity and capillary forces (D$_{\tau_p}$) and its value in bulk ($2.82 \times 10^{-5}$ m$^2$/s).

$$D_w = 2.82 \times 10^{-5} \times \tau_p \times (P \times \text{Saturation})^{-0.73}$$ (25)

A sensitivity analysis was carried out to arrive at an appropriate factor to account for the influence of the tortuosity and surface forces in concrete. The implications of change in this value of proportionality constant on the rate of carbonation in concrete were studied. The value of proportionality constant was varied between $10^{-2}$ to $10^{-7}$. The simulations were carried out by decreasing the proportionality constant value by one order at a time, starting with the value of $10^{-2}$. Figure 3 shows the effect of variation in drying diffusion coefficient on the extent of carbonation and compared with experimental carbonation depth (grey and red bands) for sam-
samples exposed in 3% CO₂, 60% R.H. and 27°C for 120 days. The extent of carbonation reduces significantly, as the value of drying diffusion coefficient is reduced. As the rate of drying of water reduces, more number of pores in concrete is filled with water, thereby reducing the effective volume of air-filled porosity for CO₂ diffusion. The carbonation depth seems to be minimally affected beyond a certain value of drying diffusion coefficient. This is because of rapid drying of concrete resulting in equilibrium between the internal relative humidity of concrete and the external humidity in a short time. In such cases, the volume of air-filled porosity available for the CO₂ diffusion will remain the same. This means that the estimation of the extent of carbonation is sensitive to the chosen value of the drying diffusion coefficient. Georget et al. (2018) also postulated that the advancement of the carbonation front is limited for slow drying concrete due to high saturation.

4.3 Preconditioning period

In accelerated carbonation studies, concrete specimens are preconditioned by drying at lower relative humidity levels (40 to 70%) prior to exposure to CO₂ to ensure sufficient availability of pore volume for diffusion of CO₂. Different preconditioning regimes have been suggested ranging from few days to months in a humid room or drying in an oven (Papadakis 2000; Da Silva et al. 2009; Thiery et al. 2007). However, the effect of the preconditioning period on the rate of carbonation is seldom discussed. Sensitivity analysis was carried out to understand the effect of different preconditioning period on the extent of carbonation. Carbonation depths were predicted using the model for 4 preconditioning period of 1.5, 15, 150 and 1500 days.

For all the simulations here, the values of τ and τ₀ were assumed to be 0.04 and 10⁻⁴ for CO₂ and drying diffusion coefficients respectively. At the start of the preconditioning period, the saturation was considered to be 100% throughout the depth of the concrete. Thereafter, the effect of preconditioning in an external relative humidity of 60% for 1.5, 15, 150 and 1500 days was simulated in absence of CO₂. The relative humidity at the end of the preconditioning period with depth is shown in Fig. 4. With the increase in the preconditioning duration, the internal relative humidity of the concrete reduces and approaches the external relative humidity of 60%. However, even after exposure of 1500 days (approx. 4.1 years), an equilibrium with the external environment is not obtained. This suggests in order to ensure a constant humidity level throughout the concrete prior to exposing to CO₂, an impractically long period is needed, which is not feasible for rapid study. The effect of the preconditioning period on the extent of carbonation is depicted in Fig. 5 for exposure condition of 3% CO₂, 60% R.H. and 27°C at 120 days.

The effect of the increase in the preconditioning period is distinctly observed on the rate of carbonation as seen in Fig. 5. The carbonation depth increases with the increase in the preconditioning period attributed to faster diffusion of CO₂ in concrete due to the availability of more air-filled porosity. Intriguingly the difference in carbonation depth between 1.5 days and 1500 days preconditioned period is only between 20 to 25% although a significant difference in the relative humidity is observed (Fig. 4) between them. This indicates the preconditioning period does not seem to affect the extent of carbonation substantially. The difference reduces further (5 to 12%) for a lower carbon dioxide concentration (1% CO₂) as shown in Fig. 6. The observation is consistent with the results presented in (Cui et al. 2018) where an insignificant effect of preconditioning schemes was observed on the extent of carbonation. This is an interesting observation considering the fact a lot of importance is directed towards the preconditioning regime for accelerated carbonation testing. Use of shorter preconditioning durations could help in reducing the overall test duration.

4.4 Saturation

The pore saturation directly influences the CO₂ and dry-
ing diffusion coefficient, which in turn controls the rate of carbonation. Simulations were carried out to understand the effect of pore saturation at different levels on the extent of carbonation. A saturation index level of 0.25, 0.50 and 0.75 were considered throughout the concrete for the entire duration of the simulation. Figure 7 shows the effect of different pore saturation levels on carbonation for a model LC3 mix subjected to 3% CO2 concentration. The carbonation showed an inverse relationship with saturation index. At lower saturation levels or lower external relative humidity (<50%) (Papadakis et al. 1991b; Richardson 2002), the rate of carbonation is reported to decrease; this is likely due to the kinetic effect in absence of sufficient water. Since this was not the scope of the current study, it was not investigated further. Nevertheless, the simulations clearly show the importance of pore saturation on the progress of carbonation.

The relation between saturation index and relative humidity varies with binder and water to binder ratio. In order to understand if this variation in the relation between them affects the rate of carbonation, simulations were carried out by changing the saturation index and relative humidity relation of the same mix but at different water to binder ratio. Figure 8 shows the effect of changing the saturation index relation on carbonation depth for FA30 and LC3 mixes. FA30_0.35 represents carbonation depth for FA30 at a water to binder ratio of 0.35 simulated using saturation index and relative humidity curve at 0.35 water to binder ratio whilst FA30_0.35_Sat(0.45) represents the modeled carbonation depth for FA30 at 0.35 water to binder ratio using the saturation index relationship corresponding to 0.45 water to binder ratio. The results show that carbonation depth is over/under predicted for 0.35/0.45 water to binder ratio mixes on using saturation index and relative humidity relation corresponding to 0.45/0.35. As discussed in the Appendix, the pore saturation is a function of both the porosity and pore size, and these features of pore structure are predominantly affected by the water to binder ratio. The pore saturation of mixes with lower water to binder ratio is slightly higher than pore saturation of corresponding mix at higher water to binder ratio at same relative humidity level. This higher saturation restricts the movement of CO2, hence resulting in lower carbonation depth for 0.45 water to binder ratio mixes on using saturation index relationship of 0.35. This indicates the importance of using an appropriate saturation index and relative humidity relation to accurately estimate the carbonation depth.

The water released during the carbonation reaction could bring about changes in the pore saturation that could directly affect the movement of the carbonation front. Carbonation of one mole of calcium hydroxide is known to release one mole of water. In blended cements, the amount of water released due to carbonation of calcium hydroxide will be lower due to the overall lower amount of calcium hydroxide. Moreover, for phases other than calcium hydroxide, no clear consensus exists...
on the amount of water released on carbonation. Formation of no additional water on carbonation of C-S-H has been reported in some work (Morandeau et al. 2014; Shah and Bishnoi 2018a) whereas carbonation of AFm and AFt phases has been suggested to release a large amount of water (Georget et al. 2018; Justnes et al. 2020). This makes it imperative to comprehend the influence of water released on carbonation on the process itself. Due to lack of information on the exact amount of water released on carbonation, simulations were performed considering that every mole of alkali reacted produces either 0, 1, 2 or 3 moles of water.

Figure 9 depicts the influence of different amounts of water released on the extent of carbonation after 120 days of exposure in 3% CO₂, 60% R.H. and 27°C temperature. Higher the amount of water released on carbonation lower is the carbonation depth due to the increased saturation in the system. For accelerated carbonation conditions - i.e., higher external CO₂ concentration, the implication of additional released water is distinctly visible on the carbonation depth. However, for natural exposure simulations, where the concentration of CO₂ is low and duration is quite large, the effect may wear off due to drying. To verify this, simulations were performed with CO₂ concentration of 0.035% for a duration of 4 years. Figure 10 shows the modeled carbonation depth considering 0 and 3 moles of water released per mole of alkali reacted for a duration equivalent to 4 years of exposure. No difference is observed between the carbonation depths for the two cases suggesting the effect of water released on carbonation is negligible in simulations of long duration representing the real natural exposure condition.

4.5 Alkalinity and porosity

The reserve alkalinity and porosity of the binder system significantly affect the rate of carbonation in concrete. Simulations were carried out for LC3_0.35 mix subjected to 3% CO₂ concentration, 60% relative humidity and 27°C temperature. The reserve alkalinity and final porosity of the system were varied by ±50% to assess the sensitivity of these parameters on the carbonation depth. Figure 11 shows the modeled carbonation depth for 120 days of exposure as a function of reserve alkalinity and porosity. The number in the parenthesis indicates the percentage value by which a particular parameter is varied - i.e., RA(0)P(+50) means the reserve alkalinity is kept constant whereas the final porosity is increased by 50% of its original value. The results show that changing the reserve alkalinity has a direct influence on the extent of carbonation. Higher the alkalinity better is the carbonation performance of the system. This is evident from the results presented in the previous sections, where carbonation depth of PC<FA30<LC3≈S30FA15 due to higher alkali content (Table 3). A similar effect is observed on increasing or reducing the porosity on the carbonation depth. However, the changes are considerably higher as compared to changes observed on varying the alkalinity content. This indicates that diffusion of CO₂ has a more promi-
nant effect as compared to reserve alkalinity on the carbonation rate. The increase in the rate of carbonation on increasing porosity could be compensated significantly if the reserve alkalinity of the system is also increased [see RA(+50)P(+50)] and vice-versa systems with same alkalinity but with lower porosity could improve carbonation performance. This indicates that systems with lower alkalinity - i.e., SCM incorporated binder could also exhibit carbonation performance similar to PC provided they have lower porosity, which could be achieved either by reducing the water the binder ratio or by increasing the space filling capacity of the hydration products. The analysis shows that the carbonation resistance of different binder systems could be designed as a function of alkalinity and porosity to obtain similar performance.

4.6 External exposure conditions
Figures 12 and 13 show the modeled carbonation depth of FA30 mix for different exposure conditions (CO\textsubscript{2} concentration and relative humidity). The extent of carbonation increases with CO\textsubscript{2} concentration and decreases with relative humidity. The modeled results agree well with the experimental data demonstrating the robustness of the model. These are important features as it depicts the necessity to incorporate various parameters to develop a proficient carbonation model for a wide range of conditions. It was observed that while the carbonation depths are predicted well for blended systems, they are over-predicted for PC. This is because although a linear variation of the porosity with the carbonation is considered in the model, in the case of PC, there is a slight reduction in the porosity at first (Shah et al. 2018; Shi et al. 2016), leading to a significant reduction in the rate of carbonation. This reduction leads to clogging of the pores and a reduction in the rate of carbonation notably for lower water to binder ratio mixes.

5. Conclusions
In this study, a sensitivity analysis was performed to understand the intrinsic changes different parameters could bring in terms of carbonation performance of concrete. The key findings from the study based on the developed model and input data used are summarized below.

The CO\textsubscript{2} diffusion coefficient was found to be dependent on the tortuosity of the system along with the saturation and porosity. The advancement of carbonation reaction was found to be strongly influenced by the rate of drying of concrete. The study clearly demonstrated that the preconditioning duration has an insignificant effect on the extent of carbonation. The effect of preconditioning duration tends to wear off further at lower external CO\textsubscript{2} concentrations.

The pore saturation showed a dominant effect on the progress of carbonation. Higher the saturation lower is the extent of carbonation due to limited diffusion of CO\textsubscript{2} through the water-filled pores. The rate of carbonation was found to be affected with a change in the relation between saturation index and relative humidity. The water released during the carbonation reaction appears to slow down the overall carbonation process due to an increase in the pore saturation. However, the difference in the extent of carbonation was indiscernible in natural exposure conditions for different amounts of water released due to the simultaneous drying of concrete. Reserve alkalinity and porosity were found to be equally important in governing the rate of carbonation in concrete.

The study showed various parameters need to be characterized for an accurate prediction of carbonation depth using numerical modeling. The model developed takes into consideration the chemical and pore structure parameters obtained from experiments, with the physical laws governing the progress of carbonation to understand and predict the extent of carbonation. It demon-
strates the basis for the development of carbonation depth estimation models for a wide range of binders and environmental conditions. The model will be subsequently further improved to take into account the aspects of temperature and alternate wetting and drying on the rate of carbonation.

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Appendix: Computation of saturation Index

The determination of the saturation index of concrete is of utmost importance to obtain the diffusion coefficients associated with gas and vapor diffusion. The saturation is primarily influenced by the internal humidity and the pore size as expressed by Eq. (A1). The volume of the pores smaller than the Kelvin radius at any specific relative humidity is assumed to be filled with water, whereas the remaining pores can be assumed to be partially empty, with their walls covered with a layer of water to satisfy the equilibrium conditions (Maekawa et al. 2009; Papadakis et al. 1989).

\[ r = \frac{-2\gamma M}{\rho R T \ln h} \]  

(A1)

where \( \gamma \) is the surface tension of water, \( r \) is the radius of the pore, \( M \) is the molecular mass of water, \( T \) is the temperature and \( R \) is the universal gas constant.

Based on the saturation index, the volume of air and water filled porosity of the total available porosity can be obtained.

The thickness of the adsorbed layer of water can be estimated using one of many empirical equations (Maekawa et al. 2009; Sarkar 2015). In this study, model suggested by Hillerborg (1985) was used to compute the thickness of adsorbed layer \( (t_a) \) of water given by Eq. (A2).

\[ t_a = \frac{0.525 \times 10^{-8} h}{\left[1 - \frac{h}{h_m}\right] \left[1 - \frac{h}{h_m} + 15h\right]} \]  

(A2)

where \( h \) is the given relative humidity and \( h_m \) is the relative humidity required to fully saturate the pore. The degree of saturation \( (S_r) \) in an unsaturated state for a cylindrical pore can be obtained as:

\[ S_r = 1 - \left(\frac{r-t_a}{r}\right)^2 \]  

(A3)

The degree of saturation was computed for pore size corresponding to 1.5 nm (smallest pore radius that can be measured using MIP with 400 MPa pressure) for

| Blends and Water/B ratios* | Cement (kg) | Coarse aggregate (kg) | Fine aggregate (kg) | Admixture (kg) | Water (kg) |
|---------------------------|-------------|----------------------|---------------------|---------------|------------|
| PC (0.35)                 | 463         | 708                  | 472                 | 638           | 2.31       |
| FA30 (0.35)               | 463         | 688                  | 459                 | 620           | 1.85       |
| LC3 (0.35)                | 463         | 692                  | 461                 | 623           | 4.17       |
| S30FA15 (0.35)            | 463         | 691                  | 461                 | 623           | 2.31       |
| PC (0.45)                 | 360         | 720                  | 480                 | 707           | 1.44       |
| FA30 (0.45)               | 360         | 705                  | 470                 | 692           | 1.44       |
| LC3 (0.45)                | 360         | 708                  | 472                 | 696           | 2.52       |
| S30FA15 (0.45)            | 360         | 707                  | 471                 | 695           | 1.44       |

* The W/B ratios are indicated within brackets.
The cumulative porosity distribution function of the microstructure, the saturated pore volume corresponding to each size could be computed. The summation of the saturated pore volume at each pore radius level divided by the total pore volume would give the saturation index at the interested relative humidity level.

The cumulative porosity plot obtained from MIP was used as porosity distribution function in this study. The MIP curves could be represented by Morgan, Mercer, and Flodin (MMF) model due to its similarity with sigmoidal saturation curves (Kumar and Bhattacharjee 2003; Patil et al. 2008). CurveExpert 1.3 software was used to obtain the best-fit equation based on MMF model. The general MMF model for pore size and volume of mercury intruded is given by Eq. (A4) below.

\[
V = \frac{ab + c(r)^d}{b + (r)^d}
\]

where \(V\) is the cumulative porosity at radius \(r\), \(a\), \(b\), \(c\) and \(d\) are the parameters obtained from fitting. The above model was applied for all the binder systems for both the water to binder ratios. Figure A1 shows the fitted and measured MIP curve for PC and LC\(^3\) at 0.35 w/c ratio.

Using MIP results in conjunction with Kelvin’s law and adsorbed moisture layer thickness, the saturation index at different relative humidities for hydrated cement systems can be estimated. The relation of saturation index with respect to relative humidity was calculated for all the mixes using Eqs. (A1) to (A4). Figure A2 shows the plot for PC at 0.35 and 0.45 water to binder ratio. It should be noted that, certain assumptions had to be made in order to simplify the interpretation of data obtained from MIP like the shape of the pores is cylindrical, every pore is directly connected to the sample surface or through large pores (Aligizaki 2006; Moro and Bohni 2002). The plateau observed between the relative humidity levels of 95 to 100\% is due to the nature of the Hillerborg equation used to compute the thickness of absorbed layer of water in the pores. As the relative humidity inside the pore increases, the thickness of the adsorbed layer increases and at some stage the pore becomes completely saturated. The nature of the saturation curves obtained is similar to the ones reported in literature (Maekawa et al. 2009).