Jordan Journal of Civil Engineering, Volume **17**, No. **1**, **2023**
DOI: https://doi.org/10.14525/JJCE.v17i1.08

Study of Carbonation-depth Prediction of Unsaturated Concrete Considering Carbonation-produced Water

Juan Long 1)***, Zhigao Peng*** 2)****, Haoxiong Feng*** 3) ***and Aocheng Yang*** 4)

1) School of Humanities, Hunan City University, Yiyang 413000, China.
E-Mail: longjuan1225@sina.com
2) College of Civil Engineering, Hunan City University, Yiyang 413000, China
***** Corresponding Author. E-Mail: pengzhgg@163.com
3) College of Civil Engineering, Hunan City University, Yiyang 413000, China.
E-Mail: fenghaoxiong@hncu.edu.cn
4) College of Civil Engineering, Hunan City University, Yiyang 413000, China.
E-Mail: yac2947583035@163.com

ABSTRACT

Carbon dioxide can react with alkaline carbonate substances in cement-based materials, which harms the durability of the concrete structure. The carbonation reaction is a process of releasing water, resulting in an increase in pore water saturation, which was always neglected by previous studies. In this paper, a transient pore water saturation equation is proposed and introduced into the classical carbonation reaction kinetic model, which is simulated by finite-element software with a typical ordinary Portland cement. The model was verified by two classical empirical equations for carbonation-depth prediction. The simulation results indicated that the increment of pore water saturation originated by carbonation-produced water will weaken the CO_2 diffusivity and enhance the carbonation resistance. Besides, the growth rate of carbonation depth is slightly faster without considering the produced water and with higher initial saturation, the difference will be more significant. If the influence of carbonation water is ignored, the predicted carbonation depth of unsaturated concrete may be less accurate.

This study can provide some reference for theoretical and experimental studies on concrete carbonation. However, future work is still needed including more realistic effects in the model such as the mesoscale modeling of concrete and the integration of stress states.

KEYWORDS: Ordinary Portland concrete, Carbonization reaction, Carbon-dioxide transport, Finite-element method, Pore saturation.

INTRODUCTION

The basic constituent materials of concrete are cement, water, sand and aggregates. Generally, the liquid phase inside the concrete is strongly alkaline. Under this condition, a dense passivation film is formed on the surface of the reinforcing steel in concrete to protect it from corrosion (Chen et al., 2019). However, due to the evaporation of water in the hardening process of concrete, a large number of pores are formed (Wang et al., 2019). Under the effect of concentration or pressure gradient, carbon dioxide in the environment invades the concrete through these pores and reacts with alkaline carbonate substances in cement-based materials; i.e., carbonation reaction, resulting in the reduction of pH value in concrete (Sormeh et al., 2015). When the pH value of the cement-based materials around the rebar decreases from 12.5~13.0 to below 9.0, the passivation film on the surface of the rebar begins to activate until it disappears. Then, the rebar will corrode if sufficient water and oxygen are available. The corrosion and swelling of the reinforcement will make the passivation film spall, resulting in a reduction in the

---

Received on 30/5/2022.
Accepted for Publication on 4/9/2022.

effective bearing area of the reinforcement and shortening the service life of reinforced concrete (Borg et al., 2017; Maekawa, 2008). Therefore, the resistance to carbonation is an important indicator of the durability of reinforced-concrete structures and is receiving increasing attention. The increase in CO_2 concentration will intensify the carbonation of concrete structures and bring more adverse effects on the durability of concrete structures (Sancheti et al., 2020; Wang et al., 2011). Monitoring results show that the concentration of CO_2 in the atmosphere has increased by 25% in the last century. The average concentration of CO_2 in the atmosphere was 280×10^{-6} kg/m^3 in the middle of the 19th century, reaching 379×10^{-6} kg/m^3 in 2005 and being expected to rise to 1291×10^{-6} kg/m^3 by 2100 (Yoon et al., 2007).

Carbonation is a complex physicochemical process in which atmospheric CO_2 penetrates the concrete. CO_2 is mainly diffused in the pore-fracture system of concrete and a classical theoretical model of concrete carbonation is derived from Fick's first law, which lays a foundation for future research (Thilakarathna et al., 2020). At present, carbonization models can be divided into four categories (Han, 2012): the first category is the theoretical carbonization model based on the Fick diffusion law and chemical reaction equation. Papadakis et al. (1989, 1991a; c) analyzed the process of carbonation reaction of concrete, studied the rate of cement hydration and carbonation using the method of chemical kinetics reaction and established a mathematical model in the form of a system of differential equations based on the mass balance condition of each carbonate compound in the carbonation process. Saetta et al. (1995) and Saetta and Vitaliani (2004, 2005) considered multi-factor correction including the moisture diffusion coefficient, heat transfer coefficient and chloride ion diffusion coefficient, introduced the source term of chemical reaction of carbonization with a multi-factor correction to the carbonization model and established the moisture-heat transfer-carbonization model. However, its deficiency is that the model parameters are not easily determined for engineering applications (Papadakis et al., 1989, 1991a; c). The second category is empirical carbonation models based on carbonation experiments; i.e., the rapid carbonation and natural carbonation experiments, where the model parameters are determined from actual data. Numerous studies have shown that the depth of concrete carbonation is proportional to the square root of the carbonation time (Han, 2012). However, this type of model is proposed based on specific material components and environmental conditions and many empirical parameters have no specific physical significance and are not sufficiently generalized. The third category is the semi-theoretical and semi-empirical models based on both the theoretical models and experiments, which comprehensively analyze the principle of carbonation reaction and the influencing factors and determine the parameters in the theoretical model by experimental methods, having high practicality (Papadakis et al., 1991b). The fourth category is the stochastic prediction model of carbonation depth, which is a multi-coefficient stochastic model under the consideration of the variability of the concrete itself and the variability of the environment. However, such models are still in the primary research stage (Ruan, 2018; Thilakarathna et al., 2020; You et al., 2022).

The carbonation rate of ordinary Portland cement (OPC) is greatly influenced by the pore water saturation of concrete, due to that CO_2 transport and carbonation reactions are both related to the concrete pore space (Wang et al., 2019). When the pore saturation is small, the water content in the pore space is low and the CO_2 diffusivity is high. However, the carbonation rate is slower under this condition, because the required water (solvent) for carbonation reaction is insufficient. When the saturation is larger, the water fills the pore space and hinders the diffusion of CO_2, also resulting in a slower carbonation rate (Anstice et al., 2005). What’s more, the carbonation reaction itself is also a process of water release and the produced water will fill the concrete pore space and increase the pore saturation, which in turn affects the carbonation reaction. These inner effects were always neglected in previous studies. Therefore, in this paper, a transient pore saturation model is introduced into the kinetic equation of carbonation reaction to consider the influence of produced water on the kinetic process of carbonation reaction.

Effect of Water Produced by Carbonation Reaction on Pore Saturation

The initial pore water saturation of concrete is affected by the environmental relative humidity, which affects the carbonation efficiency. The water produced by the carbonation reaction will lead to an increase in saturation and the transient pore water saturation can be obtained from Eqs. (1)~(3).

$$s = s_0 + \Delta s = \frac{V_w}{V_V} + \frac{V_{wp}}{V_V} \tag{1}$$

$$V_{wp} = \frac{m_w}{\rho_w} = \frac{n_{H_2O} \cdot M_{H_2O}}{\rho_w} = \frac{c_{H_2O} \cdot V_w \cdot M_{H_2O}}{\rho_w} \tag{2}$$

$$\Delta s = \frac{V_{wp}}{V_V} = \frac{V_w}{V_V}\frac{V_{wp}}{V_w} = s_0 \cdot \frac{c_{H_2O} M_{H_2O}}{\rho_w} \tag{3}$$

where s_0 is the initial saturation of concrete, %; Δs is the saturation variation caused by produced water, %; V_w and V_{wp} are the initial and produced water contents in the pores, respectively, m^3; V_V is the total volume of the pores, m^3; c_{H_2O} is the concentration of the produced water, mol/m^3.

The model can adaptively adjust the variation of pore saturation according to the amount of water produced by carbonation at each instant; however, the effect of the produced water content on the concentration of each substance is not considered, for the sake of computational simplicity. Figure 1 shows the variation of pore saturation caused by the reaction that produced water at different initial saturations. It is suggested that the water produced by the carbonation reaction with a high level of the initial saturation will significantly increase the pore saturation and the results obtained may be inaccurate if the amount of produced water is not considered in the carbonation reaction.

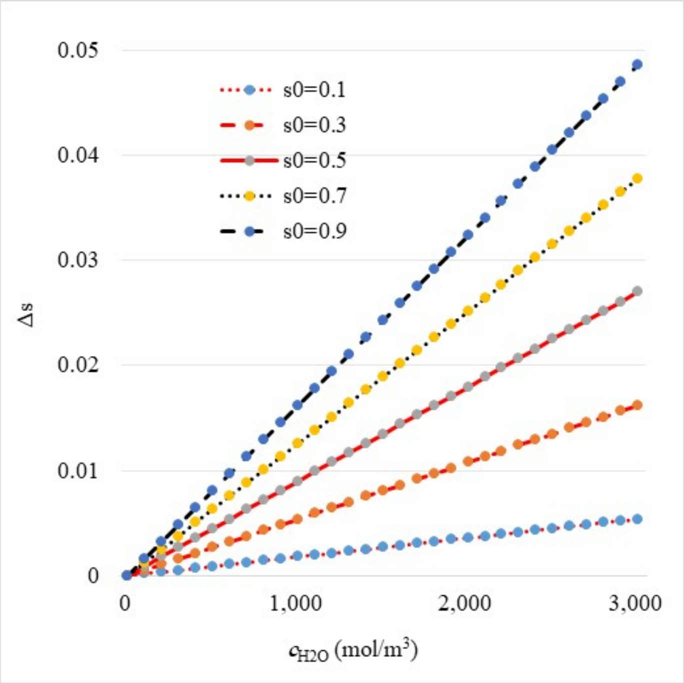


Figure (1): Variation of pore saturation caused by the amount of water produced by the carbonation reaction at different porosities

RESULTS AND DISCUSSION

Initial and Boundary Conditions

In this paper, the finite-element software COMSOL Multiphysics is employed to simulate the kinetic process of concrete carbonation, in which the diffusion reaction of each component involved in the reaction is governed by the coefficient partial differential-equation module. The initial and boundary conditions are set as follows:

$$c_{\mathbf{CO_2}} \,|\, (x,0) = c_{\mathbf{CaCO_3}} \,|\, (x,0) = 0$$

$$c_{\mathbf{CH}} \,|\, (x,0) = 2694.6(mol\,/\,m^3)$$

$$c_{\mathbf{CSH}} \,|\, (x,0) = 345.6(mol\,/\,m^3)$$

$$c_{\mathbf{CO_2}} \,|\, (0,t) = 10\%$$

$$\mathbf{n} \cdot (D_i \nabla c_i) = 0$$

Other parameters can be seen in Table 1.

Table 1. The input parameters for COMSOL simulation

Parameters	Quantities
Initial pore water saturation s_0 (%)	65, 75
Water-cement ratio $R_{w/c}$	0.5, 0.6, 0.7
Aggregate-cement ratio $R_{a/c}$	4
Temperature T_0 (°C)	20
Dissolution of CH μ	0.165
Initial diffusion coefficient of CO_2 $D_{0,CO2}$ (m^2/s)	1.64×10^{-6}
Diffusion coefficient of CH D_{CH} (m^2/s)	1.00×10^{-12}
Diffusion coefficient of CSH D_{CSH} (m^2/s)	1.00×10^{-12}
Diffusion coefficient of H_2O D_{H2O} (m^2/s)	1.00×10^{-11}
Diffusion coefficient of $CaCO_3$ D_{CaCO3} (m^2/s)	1.00×10^{-12}
Reaction constant of CH K_{CH} [m^3/(mol*s)]	5.0×10^{-6}
Reaction constant of CSH K_{CSH} [m^3/(mol*s)]	3.9×10^{-8}
Water density ρ_w (kg/m^3)	1000
Concrete density ρ_c (kg/m^3)	3100
Aggregate density ρ_a (kg/m^3)	2800

Effect of Pore Water Saturation and Water-Cement Ratio on Carbonation Depth

Figure 2 shows the variation of carbonation depth of concrete with time for the initial percentage of CO_2 $[CO_2]^0$=10%, initial pore water saturation s_0=65% and water-cement ratio $R_{w/c}$=0.6. It can be found that the initial carbonation depth is 0. There are three regions of complete carbonation (blue), partial carbonation (yellow) and uncarbonated (red) when carbonation depth increases with time. After 500 days, the carbonation depth is 42.8 mm when the amount of produced water in the carbonation reaction is considered, which reached 45.4 mm when ignoring the influence of produced water.

Figure 3 shows the carbonation depths at different s_0 and $R_{w/c}$ and the results are compared with those of two classical empirical carbonation depth prediction models of Papadakis et al. (1991a) and Zhang and Jiang (1998), respectively. The results in Figs. 3 (a)~(c) and (d)~(f) show that the carbonation depth grows faster with larger w/c for the same s_0. This is because the carbonation reaction depends not only on the amount of cement hydration product CH, but also on the diffusion of CO_2 into the concrete interior, both of which are very closely related to the water-cement ratio. When other conditions are the same only the water-cement ratio is different, the amount of CH generated by hydration is the same and the diffusivity of CO_2 is dominant in the carbonation resistance of concrete. Under these conditions, a larger water-cement ratio will result in more pores in the internal structure of the concrete, making the concrete less dense and CO_2 easier to diffuse, which accelerates the carbonation rate. Comparing the simulation results with those of these two empirical models, it can be found that the results of both two cases are between these two empirical models and are more consistent with the results predicted by Zhang and Jiang (1998), which suggest that the accuracy of our model is sufficient to predict the carbonization depth. Besides, the growth rate of carbonation depth is slightly faster when the effect of produced water of carbonation reaction on the carbonation kinetic process (the marks of s_0) is neglected and with higher initial saturation, the difference between the two cases will be larger, which agrees well with the prediction of our model in Fig. 1.

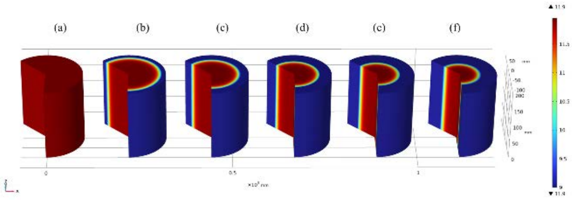
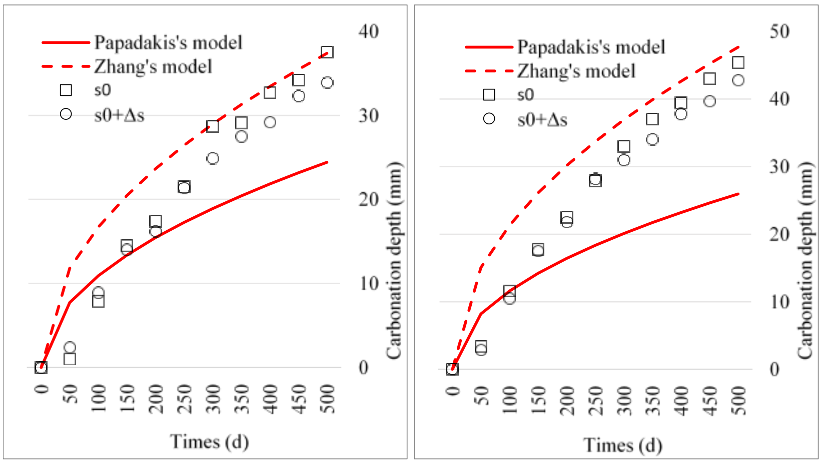
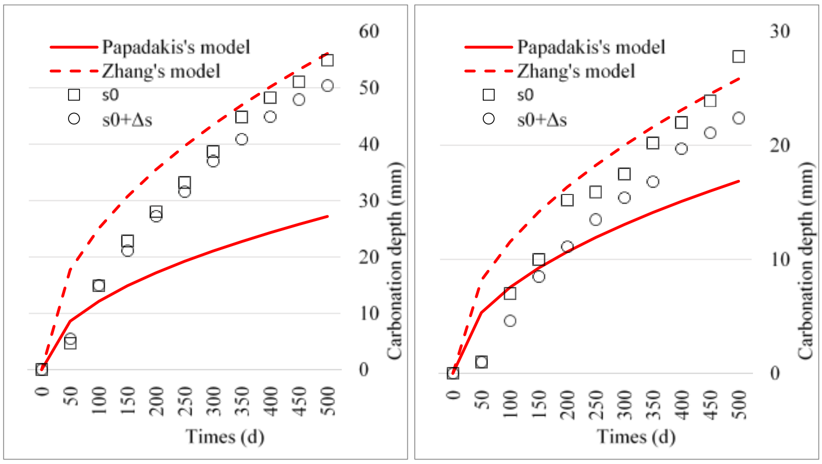


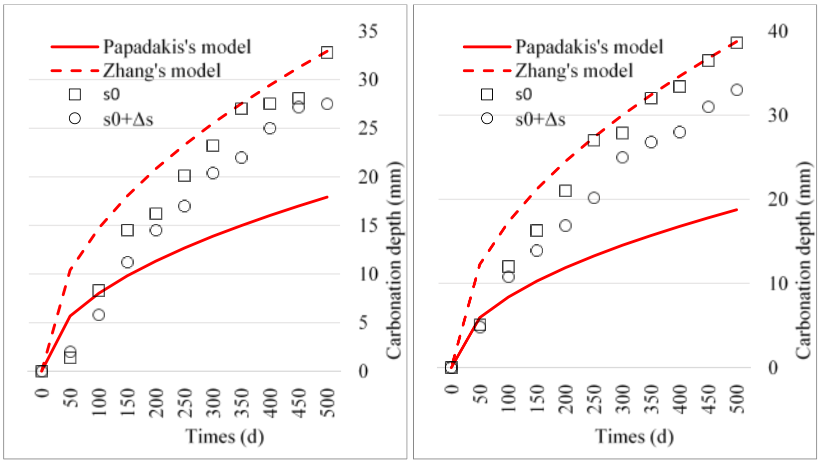
Figure (2): Variation of carbonization depth with time. (a) t=0d, (b) t=100d, (c) t=200d, (d) t=300d, (e) t=400d, (f) t=500d



(a) $[CO_2]^0$=10%, s_0=65%, $R_{w/c}$=0.5 (b) $[CO_2]^0$=10%, s_0=65%, $R_{w/c}$=0.6



(c) $[CO_2]^0$=10%, s_0=65%, $R_{w/c}$=0.7 (d) $[CO_2]^0$=10%, s_0=75%, $R_{w/c}$=0.5



(e) $[CO_2]^0$=10%, s_0=75%, $R_{w/c}$=0.6 (f) $[CO_2]^0$=10%, s_0=75%, $R_{w/c}$=0.7

Figure (3): Carbonization depth under different water saturation and water-cement ratio

Characteristics of Distribution of Each Component Concentration during Carbonation Reaction

The carbonation reaction is directly related to the concentration magnitude and distribution of CO_2. The environmental concentration of CO_2 in this paper is 10%, which is converted into 4.076 mol/m^3. The CO_2 is driven by the concentration gradient to transfer to the inner part of the concrete along the carbonation path and carbonize with CH and CSH. The process is shown in Fig. 4.

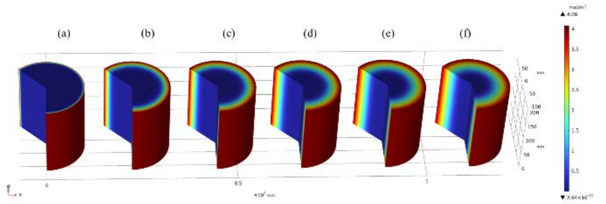
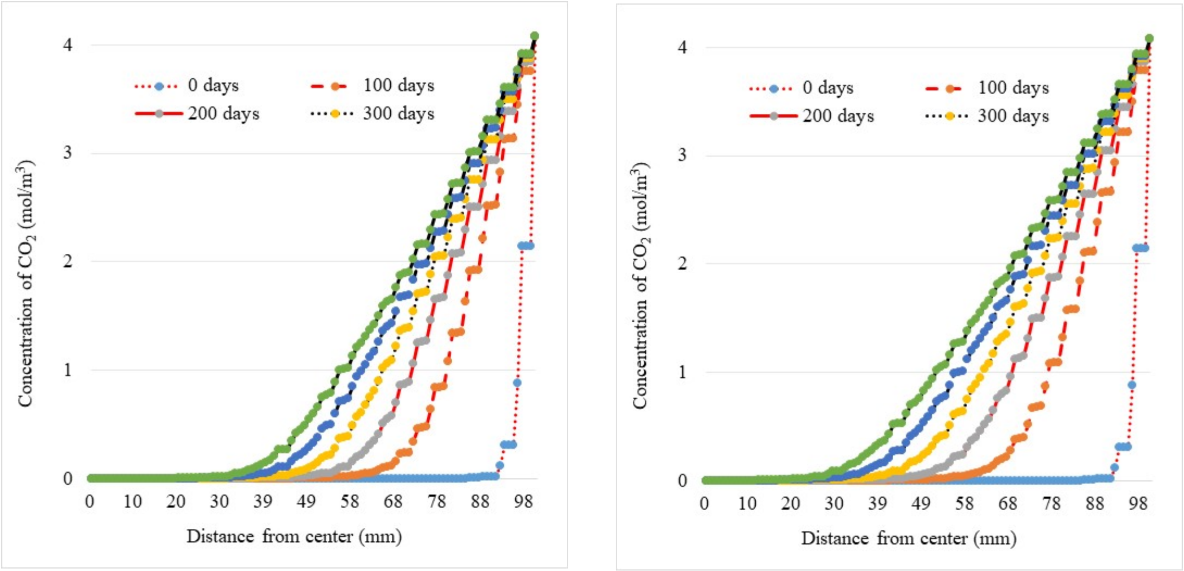


Figure (4): Distribution of CO_2 concentration at different times. (a) t=0d, (b) t=100d, (c) t=200d, (d) t=300d, (e) t=400d and (f) t=500d

Figure 5 shows the magnitude and distribution of CO_2 concentration at different times. It can be observed that the CO_2 concentration in the carbonation-reaction zone gradually increases with time, but the growth rate becomes smaller and smaller, indicating that the carbonation resistance becomes larger with increasing the carbonation depth. When the effect of carbonation-produced water is considered, both the magnitude of CO_2 concentration and the concentration increments along the carbonation direction over time are significantly smaller than the results of neglecting produced water, due to the increase of the pore water saturation, which weakens the CO_2 diffusivity.



(a) (b)

Figure (5): The magnitude and distribution of CO_2 concentration at different times. (a) without considering the effect of produced water and (b) considering the effect of produced water

Figure 6 shows the magnitude and distribution of the concentration of H_2O produced by the carbonation reaction at different times. Before the reaction, the H_2O content is 0. After 100 days of carbonization, the carbonation reaction with CH and CSH occurs after the outside CO_2 is transferred into concrete, rapidly consuming the local concentration of CH and CSH. The H_2O concentration in the fully carbonated zone reaches the maximum value of 2440.28 mol/m^3, which gradually decreases along the carbonation direction as the carbonation continues, the front line of produced H_2O concentration gradually moves forward along the carbonation direction with the carbonation reaction zone. Combined with the results of Fig.1, it can be seen that the concentration of produced H_2O has some increment in water saturation during carbonation.

Figure 7 summarizes the concentration magnitude and distribution of each reactant and product along the carbonation direction. It can be found that the initial content of CH is larger and the reaction rate with CO_2 is faster than that of CSH, which is rapidly consumed by CO_2 in the carbonation reaction zone and its content decreases sharply. The variation of CSH is similar to that of CH, but the consumption rate is slower due to its initial content being smaller and the reaction rate with CO_2 being lower.

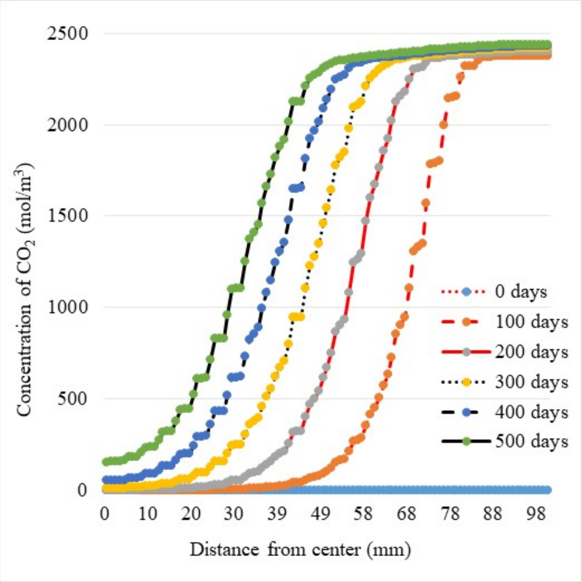


Figure (6): The magnitude and distribution of H_2O concentration at different times

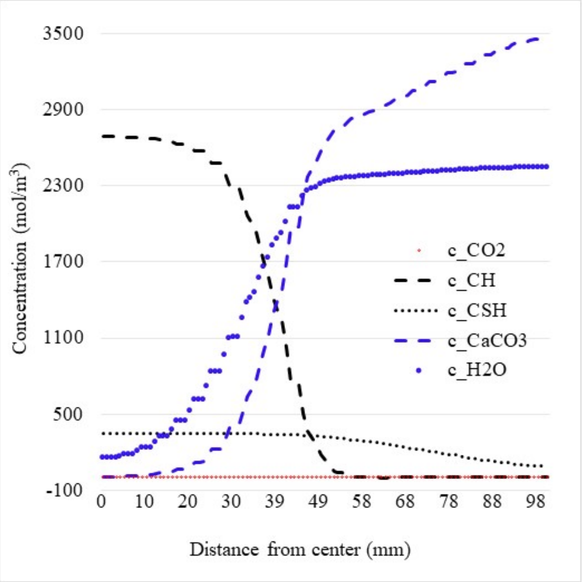


Figure (7): Concentration distribution of each component substance at 500 days

The main component of the uncarbonated zone is CH, while the main component of the complete carbonated zone is $CaCO_3$. In the carbonation reaction zone, the $CaCO_3$ content gradually increases and the CH content gradually decreases along the carbonation direction. After 500 days of carbonation, the concentration of H_2O in the fully carbonated zone is much lower than that of $CaCO_3$, while in the carbonation reaction zone and the uncarbonated zone, the concentration of H_2O is slightly higher than that of $CaCO_3$. This is because the reaction of CO_2 and CSH is slower than that of CH and the concentration of $CaCO_3$ produced in the later stage is greater than that of H_2O. Moreover, the diffusivity of H_2O in concrete is much greater than that of $CaCO_3$ and the H_2O in the fully carbonated zone will be driven by the concentration difference to diffuse to the carbonation reaction area and the uncarbonated area. This difference is smaller in the early stage of the carbonation reaction and becomes larger and larger as carbonation proceeds.

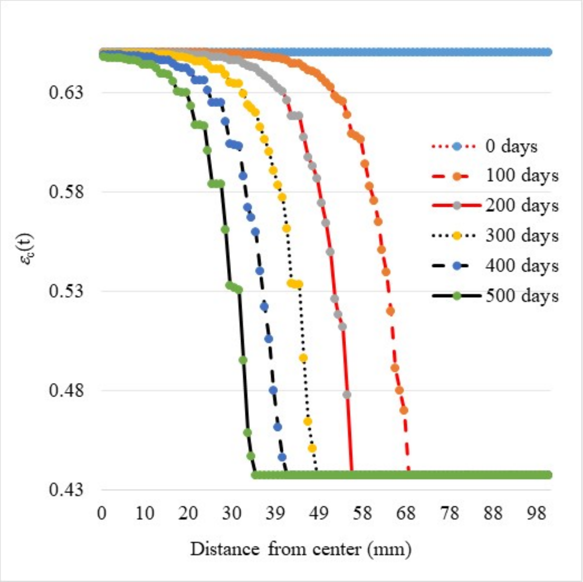
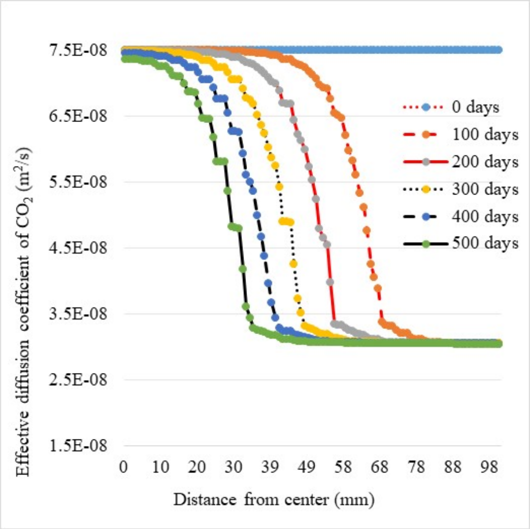


Figure (8): The variation of porosity during the carbonation reaction

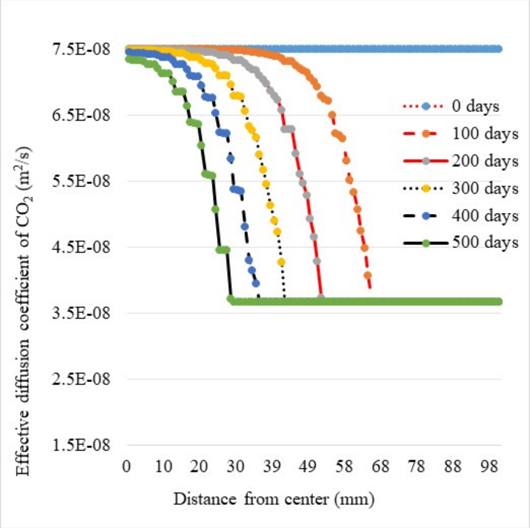
The Variation of Porosity and CO_2 Diffusivity during Carbonation Reaction

Porosity is an important factor affecting the carbonation of concrete, because it directly affects the diffusivity of carbon dioxide. Figure 8 shows the variation of porosity during the carbonation reaction. It can be observed that the initial porosity of the concrete is 0.65 after considering the amplification effect of porosity in the interface transition zone (ITZ), while porosity decreases with time in the carbonation-reaction zone and drops to the lowest point of 0.44 in the fully carbonated zone. The porosity of cementitious composites is closely related to the water-cement ratio ($R_{w/c}$) where higher $R_{w/c}$ leads to an increase in porosity and promotes CO_2 diffusivity, which increases the degree of carbonation. Therefore, the degree of carbonation usually increases with $R_{w/c}$. However, as $R_{w/c}$ increases to the limit, the degree of carbonation will not increase further due to the decrease in the amount of cement and this conclusion has also been confirmed by literature (Wang et al., 2019). According to the model proposed by Chen et al. (2019) and Papadakis et al. (1991a), the change in porosity is proportional to the difference in molar volume between the solid reactants and the solid products. Houst and Wittmann (1994), using numerical models and experimental measurements, found that the effective diffusivity increases exponentially with increasing porosity.

Generally, the water produced by the carbonation reaction does not change the porosity of the concrete, but the effect on the pore saturation will change the CO_2 transport efficiency. Figure 9 shows the variation of the effective diffusion coefficient of CO_2 during carbonation in the two cases, respectively. It can be found that the influence of carbonation kinetics on CO_2 diffusivity is greater when the effect of produced water is considered and the effective diffusion coefficient of CO_2 in the fully carbonated zone decays more, which will cause more "resistance" to the carbonation process in the carbonation-reaction zone.



(a)



(b)

Figure (9): The variation of CO_2 diffusivity during carbonation reaction.
(a) considering the effect of produced water and
(b) without considering the effect of produced water

CONCLUSIONS

In this paper, a transient pore saturation model is introduced into the carbonation reaction kinetic model to consider the influence of produced water on the process of carbonation reaction. The finite-element software COMSOL Multiphysics is employed to simulate the kinetic process of concrete carbonation, in which the diffusion reaction of each component involved in the reaction is governed by the coefficient partial differential-equation module and the physicochemical parameters involved were estimated using empirical equations. The effect of carbonation-produced water on the reaction kinetic process was analyzed and the results were compared with those of two classical empirical carbonation models. The conclusions were as follows:

1. The comparison relationship between the simulation results and these two empirical models suggests that the accuracy of our model is sufficient to predict the carbonization depth.
2. The growth rate of carbonation depth is slightly faster when the effect of produced water of carbonation reaction on the carbonation kinetic process is neglected and with higher initial saturation, the difference between the two cases will be larger, which agrees well with the prediction of our model.
3. Carbonation resistance increases with carbonation depth and the carbonation-produced water will further enhance the resistance, especially in the fully carbonated zone, due to that the increase of the pore water saturation weakens the effective CO_2 diffusivity.
4. In the process of unsaturated concrete carbonation, a large amount of water has been produced during carbonization. In our cases, the carbonation-produced water in the fully carbonated zone reaches the maximum value of 2440.28 mol/m^3, which will significantly increase the pore water saturation. When predicting the carbonation depth of unsaturated concrete, if the influence of carbonation water is ignored, the results may be less accurate.

The methods and results of this study can provide some reference for theoretical and experimental studies on concrete carbonation. However, future work is still needed including more realistic effects in the model, such as the mesoscale modeling of concrete and the integration of stress states.

Data Availability

The data used to support the findings of this study is included in the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was supported by the Natural Science Foundation of Hunan Province (Grant No. 2021JJ50141), Hunan College Students Innovation and Entrepreneurship Training Program General Project (Grant No. S202111527028).

Supplementary Materials

This part contains two sections. The details of modeling the concrete carbonation process are stated in Sec. S1, while the description of parameters in the simulation is shown in Sec. S2.

Supplementary Material

S1. Modeling of the Concrete Carbonation Process

S1.1 Simplified Model of Concrete Carbonation

The carbonate component in concrete is mainly $Ca(OH)_2$ (hereafter referred to as CH), hydrated calcium silicate ($3CaO\cdot 2SiO_2\cdot 3H_2O$, CSH), un-hydrated tricalcium silicate ($3CaO\cdot SiO_2$, C3S) and dicalcium silicate ($2CaO\cdot SiO_2$, C2S) in the presence of water. The concrete carbonization process mainly involves the following four chemical reactions:

$$\mathbf{Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O} \tag{S1}$$

$$\mathbf{3CaO\cdot 2SiO_2\cdot 3H_2O + 3CO_2 \rightarrow 3CaCO_3 + 2SiO_2\cdot \mathit{x}H_2O + (3-\mathit{x})H_2O} \tag{S2}$$

$$\mathbf{2CaO\cdot SiO_2 + 2CO_2 + \mathit{n}H_2O \rightarrow SiO_2\cdot \mathit{n}H_2O + 2CaCO_3} \tag{S3}$$

$$\mathbf{3CaO\cdot SiO_2 + 3CO_2 + \mathit{n}H_2O \rightarrow SiO_2\cdot \mathit{n}H_2O + 3CaCO_3} \tag{S4}$$

Generally, the value of x in Equation (S2) is 2.5 (Maekawa, 2008: 241). According to the research of

Papadakis et al. (1989), the content of C3S and C2S in the OPC is very small and has a limited effect on the whole carbonation process (Papadakis et al. 1991a). Therefore, in this paper, we only consider the chemical reactions between CH, CSH and CO_2. Based on the law of conservation of substances' mass, the evolution equation for the substances' transport of each component in the carbonization process can be obtained (Maekawa, 2008) from Eq. (S5).

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + R_i \tag{S5}$$

where C_i is the concentration of each component, mol/m^3; D_i is the corresponding diffusion coefficient, m^2/s; R_i is the source/sink term.

S1.2 CO_2 Transport in Concrete

The CO_2 diffusion coefficient in concrete cannot be derived from experiments due to the carbonation reaction between CO_2 and cement, resulting in inaccurate test results, which are generally obtained by multiplying the transport coefficient of nitrogen or oxygen in concrete by the molar mass ratio of nitrogen or oxygen to CO_2. Papadakis (Millington, 1959) considered the effect of porosity and pore saturation and proposed the effective diffusion coefficient of CO_2 in concrete as in Eq. (S6).

$$D_{CO_2} = 1.64\times10^{-6}\cdot\phi^{1.8}(1-s)^{2.2} \tag{S6}$$

where ϕ is the porosity of concrete; s is the saturation of pores in concrete.

S1.3 Carbonization Reaction Rate

The carbonation simulation results of Du (2009) show that the effect of the concrete pore solution saturation should be considered in the CH carbonation reaction constant K_{CH} under the partially saturated state as in Eq. (S7).

$$K_{CH} = K_{CH}^0 \times s^{3.7} \tag{S7}$$

The simulation results of Park (2008) show that initial carbonation reaction constants K_{CH}^0 of CH under the saturated state ranged from 5×10^{-6} to 5×10^{-4}. According to the results of thermo-gravimetric analysis (TGA) from Papadakis et al. (1989),

$$\frac{K_{CSH}}{K_{CH}} = 7.8\times10^{-3} \tag{S8}$$

Therefore, the carbonation reaction rates of CH and CSH can be obtained from Eqs. (S9) and (S10).

$$R_{CH} = -\varepsilon_c(t)\times k_{CH}\times s^{3.7}\times c_{CO_2}\times c_{CH} \tag{S9}$$

$$R_{CSH} = -k_{CSH}\times s^{3.7}\times c_{CO_2}\times c_{CSH} \tag{S10}$$

S1.4 Variation of Concrete Porosity during Carbonization

The carbonation reaction in the OPC leads to a decrease in total porosity, because the volume of the product (i.e., $CaCO_3$) is higher than that of the main reactant i.e., CH (Bogue, 2008; Camilleri, 2007). Papadakis et al. (1989, 1991b) proposed Eq. (S11) for estimating the initial porosity of cement.

$$\varepsilon_0 = \frac{R_{w/c}\times\frac{\rho_c}{\rho_w}}{\left(R_{w/c}\times\frac{\rho_c}{\rho_w}+R_{a/c}\times\frac{\rho_c}{\rho_a}+1\right)} \tag{S11}$$

where ρ_c, ρ_w and ρ_a are the density of concrete, water and aggregate, respectively, kg/m^3; $R_{w/c}$ is the water-cement ratio; $R_{a/c}$ is the aggregate-cement mass ratio.

Due to the presence of pores in the interface transition zone (ITZ) between the cement paste and the aggregates, an amplification factor η_0 in the porosity of concrete should be taken into consideration (Burkan Isgor and Razaqpur, 2004; Papadakis et al., 1991b).

$$\eta_0 = \left(1+\frac{R_{a/c}\times\frac{\rho_c}{\rho_a}}{1+R_{w/c}\times\frac{\rho_c}{\rho_w}}\right) \tag{S12}$$

Therefore, the porosity of the concrete before the start of the carbonation reaction can be obtained from Eq. (S13).

$$\varepsilon = \varepsilon_0\eta_0 \tag{S13}$$

Ishida et al. (Van Belleghem et al., 2014; Zhang and Lounis, 2006) assumed that the distribution of pore size would not change during the carbonation reaction, only considering the decrease of porosity. They established the linear functional relationship between the decrease of porosity and the residual amount of calcium hydroxide and water-cement ratio as in Eqs. (S14) and (S15).

$$\begin{cases} \varepsilon_c(t) = \alpha \cdot \varepsilon \\ \alpha = \alpha_{\mathbf{f}} \qquad (R < \beta) \\ \alpha = 1.25 \cdot R - 0.25 \quad (\beta < R \leq 1) \end{cases} \tag{S14}$$

$$\begin{cases} \alpha_{\mathbf{f}} = 0.67 \cdot R_{w/c} + 0.27 \\ \beta = 0.8 \cdot \alpha_{\mathbf{f}} + 0.2 \end{cases} \tag{S15}$$

where ε_c is the porosity during the carbonation reaction; α and α_f are the degrees of porosity reduction; R is the ratio of the amount of consumed calcium hydroxide to the overall calcium hydroxide.

S1.5 Carbonation Depth Estimation Method

To deeply understand the kinetics of concrete carbonation, a large number of studies involving model-based simulation and laboratory experiments have been carried out (Hyvert et al., 2010; Sisomphon and Franke, 2007). The natural carbonation process of cementitious materials is very slow and may last for decades. Therefore, the accelerated carbonation method is proposed to evaluate the carbonation resistance of cementitious materials in a short period using a higher concentration of CO_2. The most general, simplified and widely used expression for predicting the carbonation depth of cement-based materials can be obtained from Eq. (S16) (Guiglia and Taliano, 2013; Houst and Wittmann, 2002; Siriwardena and Peethamparan, 2015).

$$x = b\sqrt{t} \tag{S16}$$

where *x* is the carbonation depth at t days; *t* is the carbonation exposure time; *b* is an empirical constant.

Houst and Wittmann (2002) pointed out that the derivation of Eq. (S15) is based on the assumption of a constant CO_2 diffusivity. However, the CO_2 diffusivity varies with a lot of factors, including the degree of hydration, porosity, CO_2 concentration, pore water saturation and the number and type of microscopic phases. Therefore, considering the micro-structural characteristics of OPC-based concrete systems, a more accurate physical model was developed to predict the carbonation rate of cementitious materials (Bary and Mügler, 2006; Bary and Sellier, 2004; Papadakis et al., 1991a). Papadakis et al. (1991a) proposed a theoretical model to predict the depth of carbonation:

$$x = \sqrt{\frac{2D_{e,\,\mathbf{CO}_2}([\mathbf{CO}_2]^0/100)}{0.33c_{0,\,\mathbf{CH}} + 0.214c_{0,\,\mathbf{CSH}}}} \cdot \sqrt{t} \tag{S17}$$

where D_{e,CO_2} is the effective diffusion coefficient of CO_2; $[\mathbf{CO_2}]^0$ is the initial percentage of CO_2, %; $C_{0,CH}$ and $C_{0,CSH}$ are the initial concentrations of CH and CSH, respectively, mol/m^3; *t* is the carbonation time, d.

Zhang and Jiang (1998) proposed a semi-theoretical and semi-empirical model, as follows:

$$x = 839(1-s)^{1.1}\sqrt{\frac{R_{w/c} - 0.34}{c_0}[CO_2]^0} \cdot \sqrt{t} \tag{S18}$$

where c_0 is the cement content, kg/m^3.

Generally, the theoretical model of carbonation reaction employs the pH value to estimate the carbonation depth and the pH value can be obtained from Eq. (S19).

$$\mathbf{pH} = 14 + \lg\left(2 \times 10^{-3}[\mathbf{CH}_{(aq)}]\right) \tag{S19}$$

The CH produced by hydration has two forms inside the concrete: solid and liquid, but only the liquid CH ($\mathbf{CH}_{(aq)}$) will carbonate with CO_2, so the dissolution ratio β_0 of CH should be considered in the carbonation. The solubility μ is shown in Table S.1, and the remaining solubility corresponding to temperature can be obtained using linear interpolation.

$$\begin{cases} \left[\mathbf{CH}_{(aq)}\right] = \beta_0 \times [\mathbf{CH}] \\ \beta_0 = \dfrac{\mu}{100} \end{cases} \tag{S20}$$

Table S1. Solubility μ of CH at different temperatures

T (℃) Components	0	10	20	30	40	50	60	70
$Ca(OH)_2$	0.185	0.176	0.165	0.153	0.141	0.138	0.116	0.106

Note: the value in the table is the mass of CH (g) dissolved in 100g of water.

Parrott and Killoh (1989) divided the carbonation process into three parts: the fully carbonated zone, the partial-carbonization zone (carbonation-reaction zone) and the uncarbonated zone. Generally, the region of pH=8.5~9.0 in concrete is identified as the completely carbonized zone, pH=9.0~12.5 as the partially carbonized zone and pH=12.5~13.0 as the uncarbonized zone (Conciatori et al., 2010; Papadakis et al., 1991a). In this paper, the position corresponding to pH=9.0 is taken as the depth of complete concrete carbonation.

S2. Description of Parameters in the Simulation

Many physicochemical parameters of the components are usually difficult to measure directly and need to be estimated. Papadakis et al. (1991b) proposed an empirical formula to estimate the initial molar concentration of each component in cement before hydration after full mixing. Carmel (Jolicoeur and Simard, 1998) graphically expressed the proportional relationship of each component of cement clinker. Bogue (2008) and Camilleri (2007) established an empirical formula to estimate the percentage of each mineral component of cement clinker to cement mass based on measured data. Papadakis et al. (1989, 1991b) proposed an equation for estimating the initial porosity of cement during initial hydration. Masuda and Tanano (1991) found experimentally that the hydration product CH content is about 30% of cement when hydration is complete. Based on this conclusion, Park (2008) obtained an estimation formula for the hydration product CH content. Liu (2005) found that the CSH content of concrete at complete hydration was about 60% of the cement mass.

Acknowledgement

Hunan Provincial Education Department Scientific Research Project (Grant No. 22B0794).

REFERENCES

Anstice, D.J., Page, C.L., and Page, M.M. (2005). “The pore solution phase of carbonated cement pastes.” Cement and Concrete Research, 35 (2), 377-383.

Bary, B., and Mügler, C. (2006). “Simplified modeling and numerical simulations of concrete carbonation in unsaturated conditions.” Revue Européenne de Génie Civil, 10 (9), 1049-1072.

Bary, B., and Sellier, A. (2004). “Coupled moisture—carbon dioxide-calcium transfer model for carbonation of concrete.” Cement and Concrete Research, 34 (10), 1859-1872.

Bogue, R.H. (2008). “Calculation of the compounds in Portland cement.” American Concrete Institute (ACI), Farmington Hills, MI, United States.

Burkan Isgor, O., and Razaqpur, A.G. (2004). “Finite-element modeling of coupled heat transfer, moisture transport and carbonation processes in concrete structures.” Cement and Concrete Composites, 26 (1), 57-73.

Camilleri, J. (2007). “Hydration mechanisms of mineral trioxide aggregate.” International Endodontic Journal, 40 (6), 462-470.

Conciatori, D., Laferrière, F., and Brühwiler, E. (2010). “Comprehensive modeling of chloride ion and water ingress into concrete considering thermal and carbonation state for real climate.” Cement and Concrete Research, 40 (1), 109-118.

Du, X. (2009). “Mesoscopic stochastic model for predicting concrete carbonation depth (in Chinese).” Dissertation, Tongji University, Shanghai, China.

Guiglia, M., and Taliano, M. (2013). “Comparison of carbonation depths measured on in-field exposed existing R.C. structures with predictions made using fib-model code 2010.” Cement and Concrete Composites, 38 (2013), 92-108.

Houst, Y. F., and Wittmann, F. H. (2002). “Depth profiles of carbonates formed during natural carbonation.” Cement and Concrete Research, 32 (12), 1923-1930.

Hyvert, N., Sellier, A., Duprat, F., Rougeau, P., and Francisco, P. (2010). “Dependency of C-S-H carbonation rate on CO_2 pressure to explain transition from accelerated tests to natural carbonation.” Cement and Concrete Research, 40 (11), 1582-1589.

Jolicoeur, C., and Simard, M.-A. (1998). “Chemical admixture-cement interactions: Phenomenology and physico-chemical concepts.” Cement and Concrete Composites, 20 (2), 87-101.

Liu, J. (2005). “A review of carbonation in reinforced concrete (I): Mechanism of carbonation and evaluative methods (in Chinese).” Concrete, 195 (11), 11-14+24.

Maekawa, K. (2008). “Multi-scale modeling of structural concrete”. CRC Press, New York.

Masuda, Y., and Tanano, H. (1991). “Mathematical model on progress of carbonation of concrete.” Concrete Research and Technology, 2 (1), 125-134.

Millington, R.J. (1959). “Gas diffusion in porous media.” Science, 130 (3367), 100-102.

Papadakis, V.G., Vayenas, C.G., and Fardis, M.N. (1989). “A reaction engineering approach to the problem of concrete carbonation.” AIChE Journal, 35 (10), 1639-1650.

Papadakis, V.G., Vayenas, C.G., and Fardis, M.N. (1991a). “Fundamental modeling and experimental investigation of concrete carbonation.” ACI Materials Journal, 88 (4), 363-373.

Papadakis, V.G., Vayenas, C.G., and Fardis, M.N. (1991b). “Physical and chemical characteristics affecting the durability of concrete.” ACI Materials Journal, 88 (2), 186-196.

Park, D.C. (2008). “Carbonation of concrete in relation to CO_2 permeability and degradation of coatings.” Construction and Building Materials, 22 (11), 2260-2268.

Parrott, L.J., and Killoh, D.C. (1989). “Carbonation in a 36-year old, *in-situ* concrete.” Cement and Concrete Research, 19 (4), 649-656.

Siriwardena, D.P., and Peethamparan, S. (2015). “Quantification of CO_2 sequestration capacity and carbonation rate of alkaline industrial byproducts.” Construction and Building Materials, 91 (2015), 216-224.

Sisomphon, K., and Franke, L. (2007). “Carbonation rates of concretes containing high volumes of pozzolanic materials.” Cement and Concrete Research, 37 (12), 1647-1653.

Van Belleghem, M., Steeman, M., Janssen, H., Janssens, A., and De Paepe, M. (2014). “Validation of a coupled heat, vapour and liquid moisture transport model for porous materials implemented in CFD.” Building and Environment, 81 (2014), 340-353.

Zhang, J., and Lounis, Z. (2006). “Sensitivity analysis of simplified diffusion-based corrosion initiation model of concrete structures exposed to chlorides.” Cement and Concrete Research, 36 (7), 1312-1323.

Zhang, Y., and Jiang, L. (1998). “A practical mathematical model of concrete carbonation depth based on the mechanism.” Industrial Construction, (01), 16-19+47.

Borg, R.P., Gatt, E., and Sammut, S. (2017). “Chloride-ion detection in concrete through galvanic voltage and resistivity”. Jordan Journal of Civil Engineering, 11 (4), 8.

Chen, T., Gao, X., and Qin, L. (2019). “Mathematical modeling of accelerated carbonation curing of Portland cement paste at early age.” Cement and Concrete Research, 120 (2019), 187-197.

Han, J. (2012). “Recent development on theoretical model of carbonation reaction of concrete (in Chinese).” Journal of the Chinese Ceramic Society, 40 (08), 1143-1153.

Houst, Y.F., and Wittmann, F.H. (1994). “Influence of porosity and water content on the diffusivity of CO_2 and O_2 through hydrated cement paste.” Cement and Concrete Research, 24 (6), 1165-1176.

Maekawa, K. (2008). “Multi-scale modeling of structural concrete.” CRC Press, New York.

Ruan, X. (2018). “Review of two-dimensional meso-modeling methods of concrete aggregate (in Chinese).” Journal of Tongji University (Natural Science), 46 (05), 604-612.

Saetta, A.V., and Vitaliani, R.V. (2004). “Experimental investigation and numerical modeling of carbonation process in reinforced-concrete structures- Part I: Theoretical formulation.” Cement and Concrete Research, 34 (4), 571-579.

Saetta, A.V., and Vitaliani, R.V. (2005). “Experimental investigation and numerical modeling of carbonation process in reinforced-concrete structures- Part II. Practical applications.” Cement and Concrete Research, 35 (5), 958-967.

Saetta, A.V., Schrefler, B.A., and Vitaliani, R.V. (1995). “2D model for carbonation and moisture/heat flow in porous materials.” Cement and Concrete Research, 25 (8), 1703-1712.

Sancheti, G., Jain, K.L., and Bhargava, S. (2020). “Mechanical and durability performance of concrete made with waste marble and fly ash.” Jordan Journal of Civil Engineering, 14 (3), 14.

Sormeh, K.-H., Shao, Y., and Ghoshal, S. (2015). “Mathematical modeling of CO_2 uptake by concrete during accelerated carbonation curing.” Cement and Concrete Research, 67 (2015), 1-10.

Thilakarathna, P.S.M., Kristombu Baduge, K.S., Mendis, P., Vimonsatit, V., and Lee, H. (2020). “Meso-scale modeling of concrete: A review of geometry generation, placing algorithms, constitutive relations and applications.” Engineering Fracture Mechanics, 231 (2020), 106974.

Wang, J., Xu, H., Xu, D., Du, P., Zhou, Z., Yuan, L., and Cheng, X. (2019). “Accelerated carbonation of hardened-cement pastes: Influence of porosity.” Construction and Building Materials, 225 (2019), 159-169.

Wang, X., Nguyen, M., Syme, M., Leitch, A., and Stewart, M. G. (2011). “Analysis of climate-change impacts on the deterioration of concrete infrastructure-Part 1: Mechanisms, practices, modeling and simulations: A review.” Report, CSIRO, Canberra.

Yoon, I.-S., Çopuroğlu, O., and Park, K.-B. (2007). “Effect of global climatic change on the carbonation progress of concrete.” Atmospheric Environment, 41 (34), 7274-7285.

You, X., Hu, X., He, P., Liu, J., and Shi, C. (2022). “A review on the modeling of carbonation of hardened and fresh cement-based materials.” Cement and Concrete Composites, 125, 104315.