

A reaction-diffusion modeling of carbonation process in self-compacting concrete

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Abstract. In this paper, a reaction-diffusion model of carbonation process in self-compacting concrete (SCC) was realized with a consideration of multi-field couplings. Various effects from environmental conditions, e.g. ambient temperature, relative humidity, carbonation reaction, were incorporated into a numerical simulation proposed by ANSYS. In addition, the carbonation process of SCC was experimentally investigated and compared with a conventionally vibrated concrete (CVC). It is found that SCC has a higher carbonation resistance than CVC with a comparable compressive strength. The numerical solution analysis agrees well with the test results, indicating that the proposed model is appropriate to calculate and predict the carbonation process in SCC. The parameters sensitivity analysis also shows that the carbon dioxide diffusion coefficient and moisture field are essentially crucial to the carbonation process in SCC.

Keywords: SCC; carbonation process; numerical simulation; reaction-diffusion modeling

1. Introduction

Fresh concrete initially contains large amount of calcium hydroxide ($\text{Ca}(\text{OH})_2$) as a primary hydrated product in cement, which creates a high pH environments and enables the formation of passivation oxide around rebar in reinforced concrete (RC) structures. However, this passivate film can disappear as pH drops as $\text{Ca}(\text{OH})_2$ is consumed due to carbonation in the atmosphere. Basically, the carbon dioxide (CO_2) in atmosphere can easily penetrate into the network of concrete and reacts with $\text{Ca}(\text{OH})_2$ and calcium-silicate-hydrate (C-S-H) gels during transportation. The precipitation of calcium carbonate (CaCO_3), the main carbonation product, can inevitably destroy the initial high pH environment around rebar, and further depassivate the film as well. Lost of this protection can trigger the corrosion of rebar in the presence of water and oxygen (Hussain 2011). Carbonation problem of concrete has gain sufficient attention recently since the corrosion of rebar can degrade the structural capability and long-term durability of RC structure (Islam *et al.* 2005, Papadakis *et al.* 2007, Zhang and Zhao 2012).

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The immersing use of self-compacting concrete (SCC) has gain much attention due to its great workability, which reduces considerable labor work (Ouchi *et al.* 2003, Fu *et al.* 2011, Fu *et al.* 2014). However, the carbonation problem still exists in SCC and performs differently as conventionally vibrated concrete (CVC) because of its unique mixing design and placing manners (Assie *et al.* 2007, Valcuende and Parra 2010). Therefore, it is reasonable to deduce that the carbonation process of SCC is also distinct with CVC. A potentially strategy of mitigating the carbonation problem in cementitious materials is to slow down the penetration rate of CO₂ in concrete. Since concrete is a porous material with very complex pore structure and networks, understanding the process of CO₂ penetration in concrete is essentially important and crucial (Demis and Papadakis 2012, Yoon 2009). According to previous findings, the carbonation depth of cementitious materials typically increases with the increasing porosity of materials, and also varies depending on the pore size distribution (Song and Kwon 2007). As a consequence, it is reasonable to postulate the different carbonation resistances between SCC and CVC in term of different pore structures (Valcuende and Parra 2010). Furthermore, the relatively higher shrinkage of SCC can potentially make it more vulnerable to restrained cracking, which accelerates the penetration of various corrosive agents (e.g. CO₂, chloride ion, and sulfate ion), as well as the depassivation of reinforcements (Ye *et al.* 2012, Ye *et al.* 2013, Ye *et al.* 2015, Fu *et al.* 2015, Loser and Leemann 2009).

In this paper, the carbonation process of SCC is assumed to be a mainly reaction-diffusion phenomenon, which indicates that the transportation of CO₂ and the profiles of CaCO₃ precipitations change under the influence of primary two processes, i.e. chemical reaction and diffusion. The chemical reaction refers to the reaction of CO₂ with Ca(OH)₂, in which the transformation of substances (i.e. Ca(OH)₂ to CaCO₃) and modification of pore structure (e.g. due to consumption of Ca(OH)₂ and precipitation of CaCO₃) occurs simultaneously. The diffusion refers to the movement of CO₂ spatially due to concentration gradient, which is modeled through different solutions of Fick's second law. Furthermore, the diffusion coefficient is affected by various factors, such as cement type and content, water-to-cement ratio, relative humidity (RH), temperature, mineral mixture and the time (Bary and Sellier 2004, Halamickova *et al.* 1995, Papadakis *et al.* 1991). In particular, the influence of multi-fields on the carbonation process of SCC is mathematically proposed and numerically simulated with the assistance of ANSYS. One the other hand, the carbonation depth of SCC is experimental investigated and compared with CVC with comparable compressive strength.

2. Theoretical framework of reaction-diffusion systems

2.1 Governing equations

Typically, the gas reaction-diffusion process in porous media is controlled both by the concentration gradient which can be simply expressed as Fick's second law, as well as the reaction rate. In the case of carbonation process, where a part of CO₂ is consumed, the conservation of mass implicitly yields

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D_{cx} \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_{cy} \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_{cz} \frac{\partial C}{\partial z} \right) + \dot{Q}_{c,s} \quad (1)$$

Where C is the CO₂ concentration (in kg/m³ concrete); D_{ci} is the CO₂ diffusion coefficient in

the direction $i(x,y,z)$, which is assumed to be identical in different directions for simplification (i.e. $D_{Cx} = D_{Cy} = D_{Cz} = D_C|_{t=0}$); $\dot{Q}_{C,s}$ is sink term due to carbonation (in $g/(m^3 \cdot h)$).

In reality, the diffusion coefficient is not constant and varies considerably with environmental conditions. According to previous research, the modified diffusion coefficient, D_C , by considering the concrete raw materials, curing time, carbonation, ambient temperature, and relative humidity, can be expressed as

$$D_C = D_{C,0} \cdot f_{C,t}(t_e) \cdot f_{C,\alpha}(\alpha_C) \cdot H_C(T) \cdot H_{CO_2}(\theta) \quad (2)$$

Where $D_{C,0}$ is the reference CO_2 diffusion coefficient of concrete cured under 20 °C, 65% RH for 28 days, which can be approximated based on CEB-FIP(1990) model (Design code 1993)

$$D_{C,0} = 3.6 \times 10^{-0.05(70+f_{cl,k})} \quad (3)$$

Where $f_{cl,k}$ is the compressive strength with standard cylinder specimens (in MPa).

The first modifying expression, $f_{C,t}(t_e)$, considers the aging effects, which is expressed as a function of compressive strength development over time

$$f_{C,t}(t_e) = \frac{10^{0.04 f_{cu28}}}{10^{0.04 f_{cu}(t_e)}} = 10^{0.04(f_{cu28} - f_{cu}(t_e))} \quad (4)$$

$$f_{cu}(t_e) = f_{cu\infty} \cdot \frac{k \cdot t_e}{1 + k \cdot t_e}$$

Where $f_{cu}(t_e)$ is the cubic compressive strength at equivalent age t_e (in MPa); k is the impact factor regarding strength development, which will be elaborated in the following experimental section; f_{cu28} is the cubic compressive strength at 28 days (in MPa); $f_{cu\infty}$ is the cubic compressive strength of mature concrete (in MPa) and can be approximated as $f_{cu\infty} = (1.2 \sim 1.6) \cdot f_{cu28}$. The detail derivation of Eq. (4) is elaborated in the experimental section below.

The second modifying expression, $f_{C,\alpha}(\alpha_C)$, considers the change of pore structure in concrete due to carbonation, since either $CaCO_3$ precipitation or $Ca(OH)_2$ consumption can alter the pore structure. It can be approximately expressed as (Saeki *et al.* 1991)

$$f_{C,\alpha}(\alpha_C) = \phi_C^2 = \begin{cases} \left(1 - \frac{5\alpha_C}{9}\right)^2 & 0 \leq \alpha_C \leq 0.9 \\ 0.5^2 & 0.9 \leq \alpha_C \leq 1.0 \end{cases} \quad (5)$$

Where ϕ_C is the porosity reducing factor and α_C is the degree of carbonation.

The third modifying expression, $H(T)$, considers the temperature effects, which can be approximated using Arrhenius equation (Laidler 1984)

$$H(T) = \exp\left[\frac{E_{a,c}}{R \cdot (273 + T_R)} - \frac{E_{a,c}}{R \cdot (273 + T)}\right] \quad (6)$$

Where T and T_R are the ambient and reference temperature, respectively, $T_R=20$ °C; R is the gas

constant and E_a is the activation energy, $E_a = 35.7$ kJ/mol in this case.

The last modifying expression, $H_{CO_2}(\theta)$, considers the effect of relative humidity $h(\theta)$, which can be expressed as:

$$H_{CO_2}(\theta) = \left[(1 - h(\theta)) / (1 - 0.65) \right]^{2.5} \quad (7)$$

Where θ is the degree of saturation at relative humidity h , in which the correlation between h and water content, i.e. adsorption isotherm, in concrete needs to be clarified. According to the Brunauer–Skalny–Bodor (BSB) model, the adsorption isotherm can be estimated as (Brunauer *et al.* 1969)

$$W_i = \frac{C_T k_s V_m h}{(1 - k_s h) [1 + (C_T - 1) k_s h]}, \quad i = \text{cp, ag} \quad (8)$$

Where W_i is the amount of free water in concrete (g/g) for paste and aggregate; C_T , V_m , and k_s are parameters depending on temperature, water/cement ratio, and the degree of hydration. Based on the research of (Xi 1994)

$$C_T = \exp\left(\frac{855}{T_c + 273}\right) \quad (9)$$

$$V_m = V_{ct} \left(0.068 - \frac{0.22}{t_c} \right) \left(0.85 + 0.45 \cdot \frac{W}{C} \right), t_c > 5 \text{ days}; \quad 0.3 < \frac{W}{C} < 0.7. \quad (10)$$

$$k_s = \frac{C_T \left(1 - \frac{1}{N} \right) - 1}{C_T - 1}, N = N_{ct} \left(2.5 + \frac{15}{t_c} \right) \left(0.33 + 2.2 \frac{W}{C} \right). \quad (11)$$

Where T_c is the curing temperature (in °C); t_c is the curing time and V_{ct} and N_{ct} are constants varying for different types of cement. Considering that $\theta = W_{cp}|_{h=h} / W_{cp}|_{h=100\%}$ if ignoring the moisture absorption in aggregates, θ can be simplified as

$$h = \begin{cases} \frac{CK + \sqrt{CK^2 + 4\theta^2(C_T - 1)k_s^2}}{2\theta(C_T - 1)k_s^2} & 0 < \theta \leq 1. \\ 0 & \theta = 0. \end{cases} \quad (12)$$

Where $CK = (C_T - 1)k_s^2 + (2 - C_T + C_T\theta - 2\theta)k_s - 1$.

On the other hand, the sink term, $\dot{Q}_{C,s}$, is associated with the chemical reaction between CO_2 and $Ca(OH)_2$, which is also influenced by the RH, CO_2 concentration, carbonation degree, and ambient temperature. It can be expressed as (Saetta *et al.* 1993, Saetta and Vitaliani 2004)

$$\dot{Q}_{c,s}(h, C, \alpha_c, T) = -\alpha_1 \cdot v_c \quad (13)$$

Where α_1 is the influential factor of carbonation, and typically $\alpha_1 = 0.8 \sim 1.0$; v_c is the carbonation velocity, and can be expressed as

$$v_c = v_{c,0} \cdot f_1(h) \cdot f_2(C) \cdot f_3(\alpha_c) \cdot f_4(T) \quad (14)$$

Where $v_{c,0}$ is the carbonation velocity of reference concrete. The first term, $f_1(h)$, considers the influence of RH (Saetta and Vitaliani 2004)

$$f_1(h) = \begin{cases} 0 & 0 \leq h < 0.5 \\ 2.5(h - 0.5) & 0.5 \leq h \leq 0.9 \\ 1 & 0.9 \leq h \leq 1.0 \end{cases} \quad (15)$$

The second term, $f_2(C)$, considers the influence of CO_2 concentration, and can be expressed as (Saetta and Vitaliani 2004)

$$f_2(C) = \frac{C}{C_{\max}} \quad (16)$$

Where C_{\max} is the maximum CO_2 concentration (in kg/m^3 concrete).

The third term, $f_3(\alpha_c)$, considers the influence of carbonation degree α_c , and can be expressed as (Saetta and Vitaliani 2004)

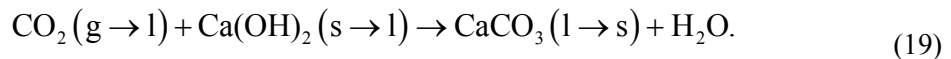
$$f_3(\alpha_c) = 1 - \alpha_c \quad (17)$$

The forth term, $f_4(T)$, considers the influence of temperature, and also can be expressed as Arrhenius equation

$$f_4(T) = \exp\left(\frac{U_c}{T_0 + 273} - \frac{U_c}{T + 273}\right) \quad (18)$$

Where U_c is the ratio of carbonation activation energy and gas constant, $U_c = 4.3 \times 10^3$ K, T_0 is the standard reference temperature, $T_0 = 20^\circ\text{C}$.

As shown before, the accurate calculation of the degree of carbonation is crucial to simulation since it affects both the sink term and diffusion coefficient. According to the carbonation mechanism



Where g, l and s is the physical state of gas, liquid and solid, respectively, and $\text{g} \rightarrow \text{l}$ indicates that the change from gas to liquid. According to the reaction stoichiometry, the

carbonation degree α_c can be expressed using of the consumption of CO_2 instead of $\text{Ca}(\text{OH})_2$

$$\alpha_c = \frac{[\text{CO}_2]}{[\text{CO}_2]_{\max}}. \quad (20)$$

Where $[\text{CO}_2]$ is the accumulated consumption of CO_2 (in kg/m^3 concrete); $[\text{CO}_2]_{\max}$ is the maximum consumption of CO_2 (in kg/m^3 concrete), which can be approximated by

$$[\text{CO}_2]_{\max} = \eta_B \cdot \eta_C \cdot [C] \cdot w_{\text{CaO}} \cdot \frac{M_{\text{CO}_2}}{M_{\text{CaO}}} \quad (21)$$

Where η_B is the reduction factor due to mineral admixture (e.g. slag), since the incorporation of silica-rich admixture can consume $\text{Ca}(\text{OH})_2$ in term of pozzolanic reaction. η_C is the ratio of the CaO (in term of $\text{Ca}(\text{OH})_2$) in cement that can be carrying on carbonation reaction. According to the research of Anna and Renato (2004), $\eta_C = (0.01 \sim 0.1) \cdot P_c$, which is related to porosity; w_{CaO} is the weight of CaO in cement. $[C]$ is the cement amount (in kg/m^3 concrete); M_{CO_2} and M_{CaO} is the molecular weight of CO_2 and CaO , respectively. Furthermore, the CO_2 consumption (in kg/m^3 concrete) can be obtained through the integral of Eq. (13) in the time of $0 \rightarrow t$

$$[\text{CO}_2] = - \int_0^t \dot{Q}_{\text{C},\text{S}} \cdot dt = - \sum_i \left(\dot{Q}_{\text{C},\text{S}}^{i-1} \cdot \Delta t_i \right), \quad i=1, \quad \dot{Q}_{\text{C},\text{S}}^{i-1} = \dot{Q}_{\text{C},\text{S}0}, \quad \Delta t_i = t_i - t_{i-1}. \quad (22)$$

Where $\dot{Q}_{\text{C},\text{S}}^{i-1}$ is the calculated $\dot{Q}_{\text{C},\text{S}}$ value at the time of t_{i-1} ; $\dot{Q}_{\text{C},\text{S}0}$ is the initial $\dot{Q}_{\text{C},\text{S}}$ value. Thus, the carbonation degree of each concrete element at different analysis step can be calculated.

2.2 Initial and boundary conditions

The CO_2 concentration is assumed to be constant anywhere initially, i.e. $C(x, y, z, 0) = C_0$ with C_0 being the initial CO_2 concentration, and assumed to be zero. In term of boundary conditions, the CO_2 concentration in the boundary is

$$C(t) = \varphi_c(t) \quad (23)$$

Where $\varphi_c(t)$ is the CO_2 concentration in the boundary (in kg/m^3 concrete). The value of φ_c can be translated into volume concentration according to ideal gas state equation and concrete porosity. The equation is as follows

$$\varphi_c = \frac{\varphi_{\text{C}_v}}{100} \cdot \frac{M_{\text{CO}_2}}{22.4} \cdot \frac{273}{273 + T} \cdot \frac{q_{\text{en}}}{q_{\text{S}0}} \cdot P_c. \quad (24)$$

Herein, φ_{C_v} is the volume percentage of CO_2 %; q_{en} and $q_{\text{S}0}$ is environment atmosphere

pressure and standard atmosphere pressure, respectively; P_c is the concrete surface porosity. For the boundary without CO_2 or symmetry boundary, the boundary condition reads

$$\frac{\partial C}{\partial n} = 0 \quad (25)$$

Where n is the normal vector at concrete surface.

2.3 Determine the concrete carbonation depth

In order to quantify the carbonation depth, the relationship between concrete pH value and carbonation degree α_c is given as (Chang and Chen 2006)

$$\text{pH} = \begin{cases} > 11.5 & \alpha_c = 0 \\ 11.5 - 5\alpha_c & 0 < \alpha_c \leq 0.5 \\ 10.5 - 3\alpha_c & 0.5 < \alpha_c \leq 1.0 \\ < 7.5 & \alpha_c = 1.0 \end{cases} \quad (26)$$

It indicates that, the concrete “pH = 9” is corresponding to the carbonation degree of “ $\alpha_c = 0.5$ ”. In this paper, “ $\alpha_c = 0.5$ ” is regarded as the critical value of concrete carbonation, which is further used to compare with experimental results as shown below.

2.4 Coupling of carbonation with moisture fields

According to carbonation reaction, consumption of one CO_2 molecular generates one H_2O molecular. Therefore, consumption one gram CO_2 will accompanied by 0.41 gram water releasing. The carbonation test with concrete grout in literature (Kropp 1983) shows that consumption one gram CO_2 , only 0.17 to 0.23 gram evaporate water was released. Others may be turn into bound water or consumed in the chemical reaction. The moisture change due to carbonation can be expressed as

$$\frac{\partial w_c}{\partial t} = -\eta_{cw} \cdot \frac{M_{\text{H}_2\text{O}}}{M_{\text{CO}_2}} \cdot \dot{Q}_{c,s} \quad (27)$$

Where w_c is the amount of moisture change due to carbonation; η_{cw} is the reduction factor of evaporate water, i.e. $\eta_{cw} = 0.5$; $M_{\text{H}_2\text{O}}$ and M_{CO_2} is the molecular weight of water and CO_2 , respectively. Furthermore, the change of degree of saturation θ_c can be expressed as

$$\frac{\partial \theta_c}{\partial t} = -\eta_{cw} \cdot \frac{M_{\text{H}_2\text{O}}}{M_{\text{CO}_2}} \cdot \frac{\dot{Q}_{c,s}(h, C, \alpha_c, T)}{w_s} \quad (28)$$

Where w_s is the moisture content in the saturated concrete.

3. Numerical solution and algorithm

The numerical analysis can be realized using the temperature filed module in the ANSYS software (Moaveni 2003). For other environmental fields besides temperature field, such as moisture filed, they can also be realized according to the analogs to temperature field. For instance, the CO₂ concentration, CO₂ diffusion coefficient, and CO₂ consumption, are analogous to temperature, heat transfer coefficient, and adiabatic temperature rise, respectively through simple setting setup. In this study, the accelerated carbonation test coupling CO₂ field and moisture field is simulated. The realization of multi-coupling effect is through exchanging the nodes or elements data as embraced in ANSYS. The analysis flow chart is shown in Fig.1.

Implementing explicitly algorithm scheme, the calculate solution at the time t_{i-1} is put into the analysis step ($t_{i-1} \rightarrow t_i$), to get the calculate solution at time of t_i , which can avoid tedious iteration analysis, with convergence criterion of $\left(\sum R_{\theta i}^2\right)^{1/2} < 0.5\% \cdot \left(\sum \bar{\theta}^2\right)^{1/2}$. In addition, in order to get stable analysis solution, the interval should be small enough by satisfying $\left|\dot{Q}_{C,S}^k(h_{i-1}^k, C_{i-1}^k, \alpha_{C,i-1}^k, T) \cdot \Delta t_i\right| \leq C_{i-1}^k$, ($C_{i-1}^k \neq 0$ and $h_{i-1}^k > 0.5$), where i and k is the time step and node number. The Eq. (29) indicates that, the CO₂ consumption in each node at the step $t_{i-1} \rightarrow t_i$ will not exceed the CO₂ content in node t_{i-1} . Considering Eq. (13), the interval at every analysis step can be given

$$\Delta t_i = \frac{\alpha_{tm}}{\alpha_1 \cdot [1 - \min(\alpha_{C,i-1}^k)] f_1(h_{i-1})} \cdot \frac{C_{\max}}{v_{C,0}}. \quad (29)$$

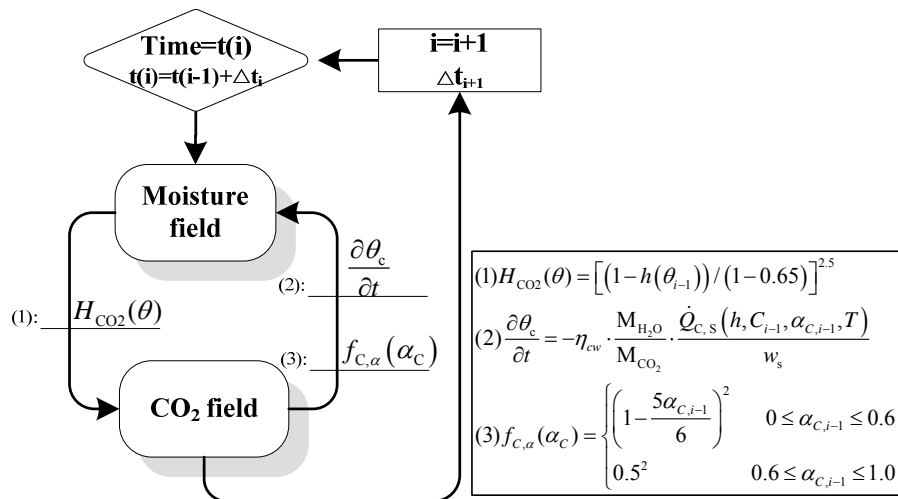


Fig. 1 Basic analysis of flow chart

Where $\min(\alpha_{C,i-1}^k)$ is the minimum value of the carbonation degree in the nodes; $\alpha_{C,0}^k$ is the initial carbonation degree of the nodes; $f_1(h_{i-1})$ is the influence factor of RH; h_0 is initial RH; α_{tm} is the time reduction factor ($0 < \alpha_{tm} < 1$), replace the “<” of Eq. (28); C_{max} is the maximum CO₂ concentration (φ_c).

4. Experimental programs

4.1 Materials and mixing proportions

In order to experimentally investigate the carbonation resistance of SCC compared with CVC with comparable comprehensive strength, both SCC and CVC were prepared. The binder materials used in the present SCC is comprised of ordinary portland cement, fly ash and blast furnace slag. The cement with P.II 42.5 with a density of 3140 kg/m³, and the chemical, physical and mechanical properties are listed in Table 1. Class II fly ash (according to Chinese standard) with a density of 2210 kg/m³ were used, and its properties are listed in Table 2. Slag with a density of 2880 kg/m³ were used, and its properties are shown in Table 3. The sand with a fineness modulus (FM) of 2.75 was used, and its apparent density and packing density were measured to be 2610 kg/m³ and 1710 kg/m³, respectively, according to Chinese standard (JGJ52-2006) (Chinese Standard 2006). The coarsen aggregate with a continuous grading from 5 mm~16 mm obtained from crushed stone was used. The apparent density and packing density were measured to be 2650 kg/m³ and 1330 kg/m³, respectively, according to Chinese standard (JGJ52-2006). The admixture specifically used in SCC, OPC in this study was high performance polycarboxylic superplasticizers and ZWL-A-II pumping admixture, respectively.

Two types of comprehensive strength, i.e. C30 and C50, were prepared for SCC and CVC. As shown in Table 4, the W/C ratio for SCC and CVC with comparable compressive strength is similar. The detail test properties of SCC are listed in Table 5. The measured comprehensive strength for the mixtures in Table 4 has been published but shown in Fig. 2. As mentioned in Eq. (4), the aging effect can be approximated using the evolution of compressive strength. By regressing the development using formula $f_{cu} = f_{cu\infty} \cdot [1 - (1 - k \cdot t(1 - n))^{\frac{1}{1-n}}]$ (Bernhardt 1956), which establishes the correlation between aging effect and comprehensive development, Eq. (4) can be obtained after regression by selecting $n=2$. On the other hand, as shown in Fig. 3, the slump test demonstrated that the mixture for SCC can prepare specimens with remarkable workability, as compared with CVC with comparable compressive strength.

4.2 Specimens

The dimension of specimens was selected to be 100 mm × 100 mm × 400 mm according to the Chinese standard of long-term performance and durability experimental methods (Chinese Standard 2009). The specimens were demolded at 24 hours after casting and cured in standard moisture (99% RH and $20 \pm 5^\circ\text{C}$) room for 26 days. Before putting them into the carbonation chamber, all specimens are initially dried at 50°C for 48 h and then waxed by leaving two

opposite surfaces unwaxed for the purpose of exposing to atmosphere. The carbonation chamber controls the carbon dioxide concentration, relative humidity and temperature to be $20 \pm 3 \%$, $70 \pm 5 \%$ RH, and $20 \pm 5^\circ\text{C}$, respectively.

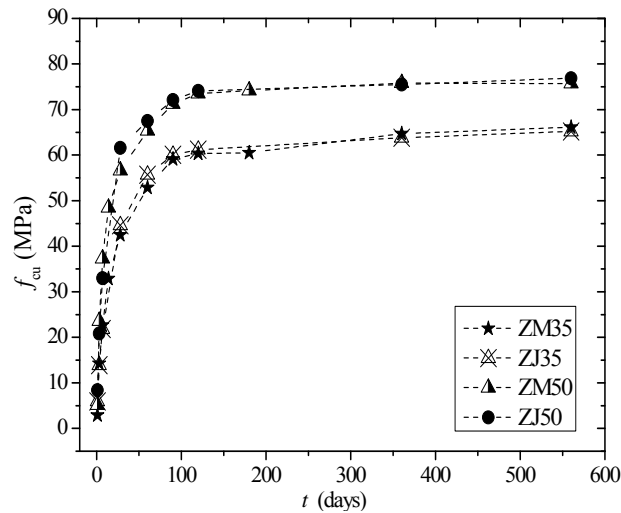


Fig. 2 The cubic compressive strength development of all mixtures over time (Fu *et al.* 2011)



Fig. 3 Comparison of slump between SCC and CVC used in Table 4

Table 1 Chemical, physical and mechanical properties of cement

Items	Loss of Ignition (%)	MgO (%)	SO ₃ (%)	Fineness 80μm sieve	Alkali (%)	Bending strength (MPa)		Compressive strength (MPa)	
						3 d	28 d	3 d	28 d
Standard	--	--	--	≤ 10.0 %	--	≥ 3.5	≥ 6.5	≥ 17.0	≥ 42.5
Measured	0.82	2.21	1.74	1.7%	0.42	5.3	8.1	24.7	52.7

Table 2 Chemical and physical properties of fly ash

Items	Loss of Ignition (%)	Fineness 45 μ m sieve	Demanded water (%)	SO ₃ (%)	Moisture content (%)	Reactivity (%)	
						7 d	28 d
Standard	≤ 8.0	$\leq 10.0\%$	≤ 105	≤ 3.0	≤ 1.0	≥ 50	≥ 70
Measured	3.46	3.8%	101	0.52	0.20	70	74

Table 3 Chemical and physical properties of slag

Items	Loss of Ignition (%)	MgO (%)	SO ₃ (%)	Demanded water (%)	Moisture content (%)	Reactivity (%)		
						3 d	7 d	28 d
Standard	≤ 3.0	--	--	≤ 100	≤ 1.0	≥ 55	≥ 75	≥ 104
Measured	0.72	7.45	2.85	100	0.54	67	85	104

Table 4 Mix proportions for testing (kg/m³)

Mixtures	Cement	FA	Slag	sand	Aggregate	water	admixtures	W/C
ZM35	312	121	48	782	865	194	4.81	0.62
JZ35	355	93	0	678	1067	215	6.05	0.61
ZM50	400	90	30	782	865	187	5.72	0.47
JZ50	436	67	0	565	1113	200	6.79	0.46

Notes: ZM35 and ZM50 is the C35 and C50 SCC respectively; JZ35 and JZ50 are the C35 and C50 vibrated concrete respectively. They had been used in the nuclear power station in China.

Table 5 Testing results of SCC properties

Mixtures	Workability (mm)		Compressive strength (MPa)					Permeability
	Workability	U-shape test	1 d	3 d	7 d	14 d	28 d	Level
ZM35	710	0 ~ 10	2.9	14.3	22.6	32.9	42.5	P16
ZM50	700	10	5.2	23.6	37.3	48.5	56.6	P20

4.3 Measuring the carbonation depth

The carbonation depth was measured at 3d, 7d, 14d, 21d, 28d, 60d and 120d after putting specimens in the carbonation chambers. The measuring surface was selected in the middle of the specimens by cracking the sample using pressure testing machine. After cracking the surface each time, the newly-exposed surfaces were waxed again and put back to carbonation chamber till next measuring age. The other parts of cracked samples were used to determine the carbonation depth by using 1.0% phenolphthalein. The carbonation depths were measured at both opposite sides based on the pre-drawn grids with an interval of 10mm after 30 seconds. If the measurement encountered with an aggregate, the averaged carbonation depth was picked to the carbonation depth for that particular point.

4.4 Experimental results and discussion

Fig. 4 shows the evolution of carbonation depths for all four mixtures as a function of carbonation time. It can be seen that ZM35 has considerable higher carbonation resistance than that of JZ35, where ZM50 merely shows slight higher carbonation resistance than that of JZ50. Based on the change of slope as a function of time as shown in Fig. 2, it can be seen that the carbonation occurs faster at early 7 days, but slower down at later age, regardless of the mixture proportion or the comprehensive strength. However, it demonstrates that the specimens with higher comprehensive strength have significant higher carbonation resistance, which is more obvious at early age.

As introduced before, one of the controlling parameters affecting the carbonation resistance of concrete is the diffusion rate of carbon dioxide in concrete, which is inherently determined by the network of pore structure in concrete. Since all the environmental conditions were keep the same for these four mixtures, the distinct performance is related to the mixtures. As a decrease in W/C ratio, the pore structure tends to become finer, which is consistent with this study showing that ZM50 and JZ50 have higher carbonation resistance than ZM35 and JZ35, respectively. With similar comprehensive strength, SCC has slight high water-to-binder ratio, but high carbonation resistance, probably due to effects of slag, fly ash or superplasticizers. According to previous findings, the incorporation of slag can considerable refine the pore structure of concrete, and hence reduce gas diffusivity. Also, the applied superplasticizers in this study have the properties of introducing entrained air in concrete, which can potentially also modify the pore structure and increase its carbonation capability.

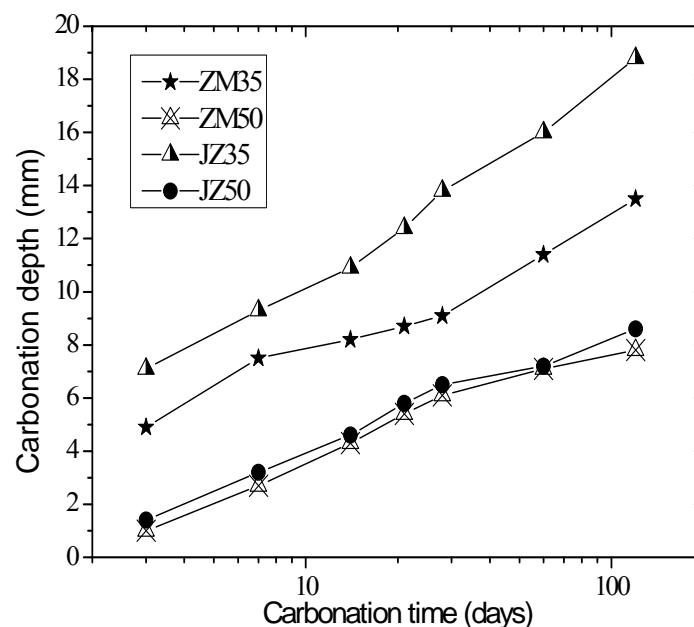
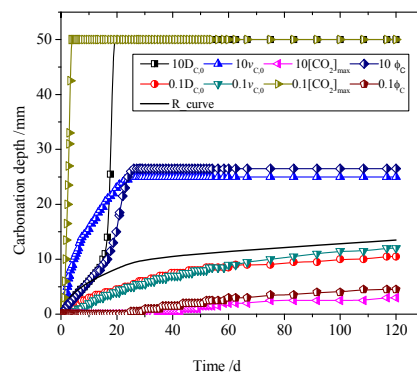


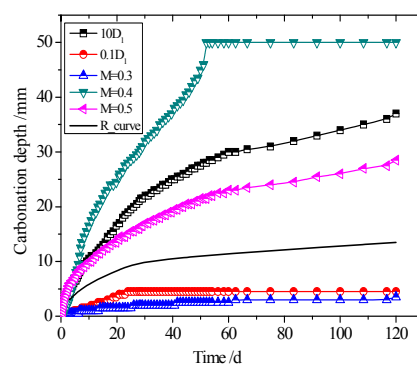
Fig. 4 The evolution of carbonation depth in all mixtures

5. Numerical results and comparison with experimental results

Based on the reaction-diffusion model proposed before, there are mainly four parameters in the CO_2 distribution model, i.e. $D_{\text{C},0}$, ϕ_{C} , $\nu_{\text{C},0}$ and $[\text{CO}_2]_{\text{max}}$. All four parameters can affect the numerical solution considerably based on the parameters sensitivity analysis. As shown in Fig. 5 (a), taking ZM35 for example, simply changing one parameter can dramatically affect the predicted carbonation depth. After the sensitivity analysis, it is found that $[\text{CO}_2]_{\text{max}}$ maximally impacts the simulation results. In particular, the CO_2 diffusion is accelerated with reducing $[\text{CO}_2]_{\text{max}}$ value, since $[\text{CO}_2]_{\text{max}}$ reflects the capability of CO_2 consumption, which is related to the mixing proportion and material properties. Furthermore, moisture field also have a large impact on the carbonation depth, as shown in Fig. 5(b). With the change of moisture diffusion coefficient within reasonable range, the carbonation depth alerts. For example, increasing the RH from 30% to 40%, the carbonation is accelerated greatly. However, the carbonation slow down when the RH increasing from 40% to 50%. The main reason is that the high RH retains the CO_2 entering into the concrete, and the low RH limit the supply of enough water in the carbonation reaction.



(a) Parameters analysis of CO_2 distribution field



(b) Parameters analysis of moisture field

(Notes: The curves named “R_curve” are the carbonation depth of ZM35 (Initial relative humidity $M=0.39$), which are based on the data in Table 2. $10D_{\text{C},0}$ and $0.1D_{\text{C},0}$ is the ten times and one-tenth of the $D_{\text{C},0}$, other and so on.)

Fig. 5 Effect of each factor on simulating carbonation depth

Table 6 shows the main parameters used in the simulations for all the four mixtures. The selection of parameters values in Table 6 is based on test results of accelerated carbonation in this study. Increasing the $D_{C,0}$ and ϕ_C value is equivalent to increasing the supply of CO_2 , hence carbonation is accelerated. The early stage carbonation is also accelerated with increasing of carbonation reaction velocity, $v_{C,0}$, but restrains the later carbonation velocity, since carbonation in early stage can reduce the concrete porosity.

According to the experimental study, CO_2 and moisture diffusion can be reduced to one-dimensional diffusion problem. Two-dimensional temperature unit PLANE55 (Moaveni 2003) was used in the numerical simulation. The FE model, boundary condition and initial condition are shown in Fig. 6. The initial CO_2 concentration and initial carbonation degree is zero; the initial RH is 0.35 to 0.45 ; The model and element dimension is 50 mm×2 mm and 0.5 mm×0.5 mm, respectively; there are 400 elements and 505 nodes.

Fig. 7 shows the numerical solution of CO_2 diffusion and the comparison between numerical modeling and experimental results. It can be seen that the numerical simulation match reasonable with the experimental results. At early age of carbonation process, the predicted values for C35 SCC and CVC are generally smaller than the measured values, indicating that initially carbonation may not delay much on the carbonation rate until reaching a critical point. However, the prediction values for C50 is much consistently with the measured value at early age, probably because of the initial finer pore structure, which makes its much sensitive to the carbonation, resulting a decrease of CO_2 diffusion coefficient.

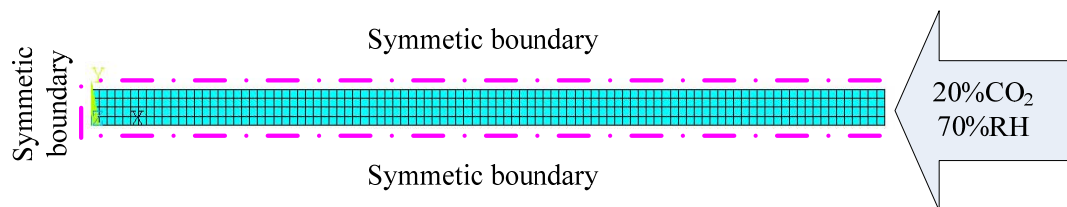
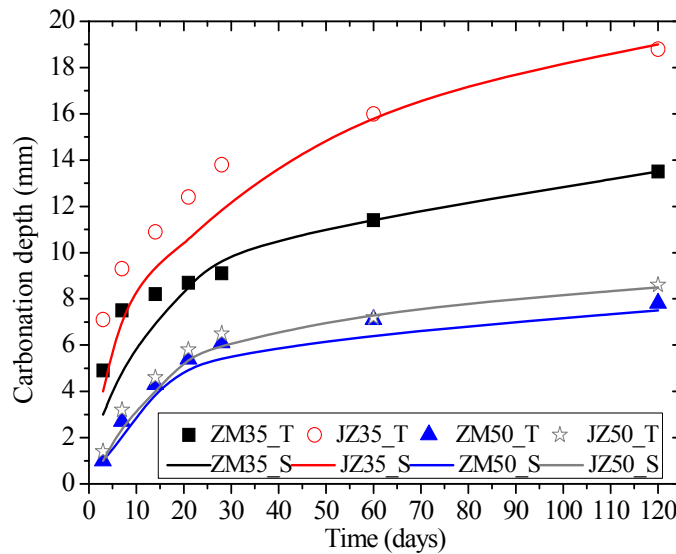
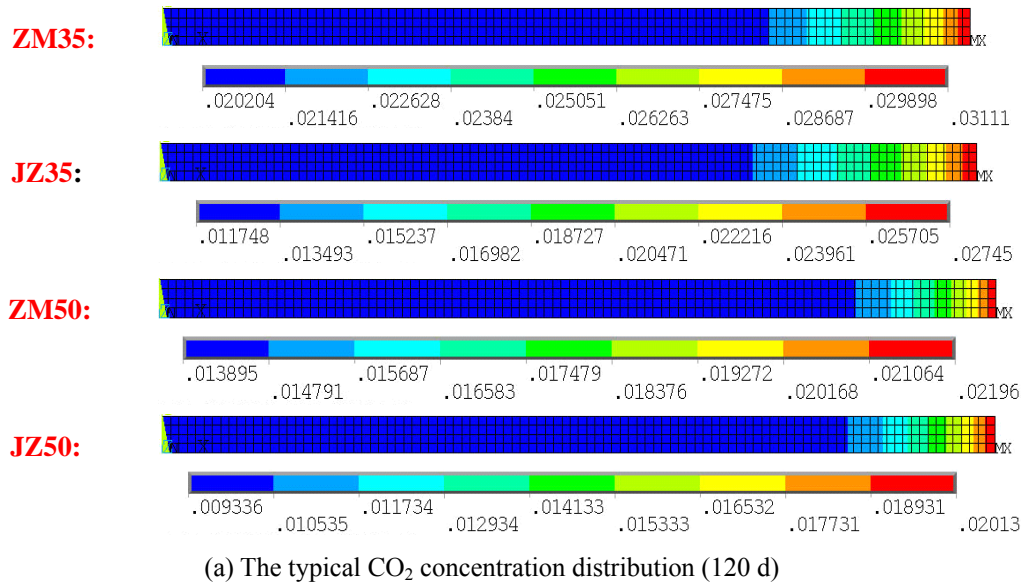


Fig. 6 Finite element model and boundary, initial conditions

Table 6 Basic parameters table of CO_2 distribution field

Mixture	ZM35	JZ35	ZM50	JZ50
Parameters				
$D_{C,0}$ (m^2/h)	2.271×10^{-5}	1.872×10^{-5}	6.256×10^{-6}	3.911×10^{-6}
$v_{C,0}$ ($kg/(h \cdot m^3)$)	0.068	0.075	0.030	0.044
$[CO_2]_{max}$ (kg/m^3)	0.375	0.463	0.389	0.475
ϕ_C (kg/m^3)	3.111×10^{-2}	2.745×10^{-2}	2.196×10^{-2}	2.013×10^{-2}



(b) Carbonation depth of simulation results and test results

Fig. 7 Numerical simulation results of CO₂ diffusion

(Notes: ZM35_T is the test results of ZM35 concrete; ZM35_S is the simulation results of carbonation depth.)

6. Conclusions

In this paper, a reaction-diffusion model of carbonation process in self-compacting concrete

(SCC) is realized with the consideration of multi-field couplings. The governing equation of carbon dioxide diffusion in porous materials is expressed according to the Fick's second law and mass conservation principle. The numerical calculation framework used to simulate the multi-field coupling conditions was proposed by ANSYS. In addition, experimental investigation was also performed to compare the carbon resistance capability of SCC with CVC. Following conclusions can be drawn from the present study:

- SCC has a higher carbonation resistance than ordinary vibrated concrete with a comparable compressive strength.
- It is an effective way to modify the conventional carbonation model by comprehensively combining the parameters from concrete properties, temperature field, moisture field and CO₂ consumption, which basically improves the precision of simulation.

The parameters analysis indicates that the CO₂ and moisture fields affect the carbonation process of SCC significantly. The numerical solution analysis agrees well with the test results.

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Notations

C = CO₂ concentration (in kg/m³ concrete).

D_{Ci} = CO₂ diffusion coefficient in the direction $i(x,y,z)$.

$\dot{Q}_{C,s}$ = sink term due to carbonation (in g/(m³·h)).

D_C = modified diffusion coefficient (in m²/h).

$D_{C,0}$ = referenced CO₂ diffusion coefficient of concrete cured under 20 °C, 65% RH for 28 days (in m²/h).

$f_{cl,k}$ = compressive strength with standard cylinder specimens (in MPa).

$f_{C,t}(t_e)$ = modifying expression of CO₂ diffusion coefficient, in which the aging effect is considered.

$f_{C,\alpha}(\alpha_C)$ = modifying expression of CO₂ diffusion coefficient, in which the change of pore structure in concrete due to carbonation is considered.

$H(T)$ = modifying expression of CO₂ diffusion coefficient, in which the temperature effect is considered.

$H_{CO_2}(\theta)$ = modifying expression of CO₂ diffusion coefficient, in which the relative humidity $h(\theta)$ is considered.

$f_{cu}(t_e)$ = cubic compressive strength at equivalent age t_e (in MPa).

ϕ_C = porosity reducing factor.

α_C = degree of carbonation.

θ = degree of saturation at relative humidity h .

W_i = amount of free water in concrete (g/g) for paste and aggregate.

v_C = carbonation velocity.

$f_1(h)$ = modifying coefficient of carbonation velocity, in which the RH is considered.

$f_2(C)$ = modifying coefficient of carbonation velocity, in which the CO₂ concentration is considered.

$f_3(\alpha_C)$ = modifying coefficient of carbonation velocity, in which the carbonation degree α_C is considered.

$f_4(T)$ = modifying coefficient of carbonation velocity, in which the temperature is considered.

$[CO_2]$ = accumulated consumption of CO₂ (in kg/m³ concrete).

η_B = reduction factor due to mineral admixture.

η_C = ratio of the CaO (in term of Ca(OH)₂) in cement that can be carrying on carbonation reaction.

$\varphi_C(t)$ = CO₂ concentration in the boundary (in kg/m³ concrete).

w_c = amount of moisture change due to carbonation.

θ_c = change degree of saturation.