

Establishment of a Numerical Model for Sulfate Attacked Concrete Considering Multi-factors

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ABSTRACT

Sulfate attack is one of the major durability problems of concrete structures, which is manifested by expansive cracks and deterioration of cement paste. In this study, a numerical model is proposed to predict the process of ionic diffusion into concrete under external sulfate attack. The chemical reaction and diffusion processes are considered in this model. Furthermore, the influence of calcium leaching, chemical activity of multi-ions, temperature and changes in porosity are also taken into account. The initial porosity and tortuosity are assumed to be homogeneous in concrete, and the chemical potential gradient is regarded as the driving force for ions migrating in pore solution. The modified Davies equation is employed to quantize interaction effect among different ions in solution. A temperature dependent parameter is introduced in the diffusion process of sulfate ion. The dissolution of solid calcium is divided into two stages referring to solid-liquid equilibrium curve of calcium ion. One is the dissolution of the calcium hydroxide, and the other is the decalcification of the calcium silicate hydrate. The influence of calcium leaching on porosity is further considered in diffusion coefficient. Moreover, changes in porosity due to formation of expansive ettringite are also reflected in the diffusion coefficient. Finally, a new numerical model is established and a comparison of the model prediction with the experimental results has been conducted. It is demonstrated that the established diffusion-reaction model can provide a better deterioration assessment of concrete structures exposed to sulfate attack.

Keywords: Sulfate attack, temperature, calcium leaching, multi-ion interaction, numerical model.

1.0 INTRODUCTION

Sulfate attack is a very complicated process in concrete, coupling the effects of ion diffusion, chemical reaction and expansion damage (Yu *et al.*, 2015, Liu *et al.*, 2012). The ingress of sulfate ion leads to the formation of poorly soluble, expansive products like gypsum and ettringite. Concrete is a porous material, then these precipitations could fill in pores resulting in microcracking, expansion even spalling of concrete structures (Clifton and Ponnensheim, 1994; Sun *et al.*, 2013, Zou *et al.*, 2014). With the understanding of mechanism of sulfate attack on concrete (Yokozeki *et al.*, 2004; Ping and Beaudoin, 1992; Bellmann *et al.*, Wang, 2005), studies on the prediction model of concrete degradation under sulfate attack were developed. Samson *et al.* (2005; 2007) studied the reactive diffusion mechanism of sulfate ions with a numerical model considering the electrical coupling between the ions and the chemical activity effects. However, this model did not reflect chemical reaction in solving transport equations and its corresponding effects on diffusion process. Marchand *et al.* (2001; 2002a; 2002b) proposed a diffusion model, named STADIUM, in which the Fick's second law was used to describe the diffusion of ions, the electrical coupling, effects of chemical activity and chemical reaction were also taken into account. Nonetheless, the influence of damage evolution was not considered which can significantly affect the pore

structures and the transport of ions in concrete (Chen *et al.*, 2008). Sarkar *et al.* (2010) developed a numerical methodology based on previous work. Their model included the diffusion of ions described by Fick's second law, chemical reactions considering dissolution and precipitation of solids, and mechanical damage quantized by a continuum damage mechanics approach. Tixier *et al.* (2003a, 2003b) proposed a chemo-mechanical model for the prediction of expansion based on diffusion-reaction approach, and the effects of expansive ettringite were considered by measuring the degraded stiffness of concrete. Ikumi *et al.* (2014) presented a diffusion-reaction model with a new expression for chemical processes and a new approach to calculate expansions in terms of the different filling rates and capacities to accommodate expansive product for each pore size. Cefis and Comi (2017) developed a weakly coupled approach to model the mechanical degradations with considering the chemical and stress-induced damage, which described the actual microcrack formation and the decrease of elastic properties under partially or fully saturated conditions in concrete.

In this paper, a numerical model was developed including diffusion of ions and chemical reaction. The influences of porosity changes, calcium leaching, chemical activity of multi-ions and temperature were considered in this model. The initial porosity and

tortuosity are assumed to be homogeneous in concrete, and the chemical potential gradient is regarded as the driving force for ions migrating in pore solution. The modified Davies equation is employed to quantize interaction effect among different ions in solution. A temperature dependent parameter is introduced in the diffusion process of sulfate ion, and the influence of calcium leaching on porosity is considered in diffusion coefficient. The established diffusion-reaction model was utilized to predict the process of ionic diffusion into concrete under external sulfate attack. A comparison between numerical results and experimental data is provided to validate the proposed models.

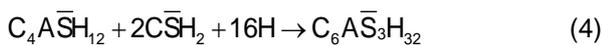
2.0 DESCRIPTION OF THE CHEMO-TRANSPORT MODEL

2.1 Mechanism of sulfate attack

When sulfate ions penetrate into a cement-based material, a series of reactions take place between the hydrated products of cement and the sulfate ions. Assuming the source of sulfate ions to be sodium sulfate, the process is initiated by the reaction:



Then the formation of gypsum ($\text{C}\bar{\text{S}}\text{H}_2$) may react with hydrated and unreacted aluminates led to the formation of ettringite ($\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$) (Tixier *et al.*, 2003a; Idiart *et al.*, 2011; Collepardi, 2003):



As shown in Eqs (2) - (4), three different calcium aluminate phases (i.e. tricalcium aluminate C_3A , tetracalcium aluminate C_4AH_{13} and monosulfate $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$) are considered. In this paper, it is defined that all reactions occur in pore solutions and the pores are generally considered as saturated which means that the above reactions are ionic reaction. These chemical reactions cause the calcium leaching and formation of expansive products (like gypsum, ettringite) resulting in expansion of concrete and formation of microcracks, even macro-cracking and spalling (Cefis, and Comi, 2017). In this work, it is assumed that the expansion is only caused by the ettringite formation, the expansive nature of gypsum formation is not taken into account (Shazali *et al.*, 2006; Planel *et al.*, 2006). Referring to previous researchers' work (Tixier *et al.*, 2003a; Zuo *et al.*, 2012), Eqs. (2) - (4) are lumped in a single expression (i.e. Eq. (5)). It should be noticed that with this simplification, the chemical reaction rate of

sulfate ions will be determined by one single chemical reaction (i.e. Eq. (1)).



where CA refers to the equivalent calcium aluminates, q represents the stoichiometric weighted coefficient of the sulfate phase.

2.2 Diffusion of ions

As concrete is a porous material, it has a large number of pores connected to the interior. However, due to the complex structure of the internal pores, it is difficult to predict the transfer process of the external ions into the concrete. This study assumes that pores are regarded as evenly distributed and only existed in cement mortar. The tortuosity is used to represent influence of porosity on diffusion coefficients of ions in cement mortar. The transport of ions in a saturated porous material can be considered as a regular motion of ions under a concentration gradient as well as under a chemical activity gradient. The diffusion of ions under electrical potential is negligible (Samson and Marchand, 2007; Shen and Chen, 2007). This is expressed as:

$$\text{grad}\mu_i = \text{grad}[R \cdot T (\ln\gamma_i + \ln c_i)] \quad (6)$$

where μ_i is the chemical potential of ion i (J/mol), c_i is the concentration of ion i (mol/m³), γ_i is the chemical activity coefficient of ion i , R is the universal gas constant (8.3143 J/mol/K), T is the temperature (K). The modified Davies equation (Samson *et al.*, 1999) is used to calculate the chemical activity of the ions:

$$\ln\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+a_iB\sqrt{I}} + \frac{(0.2-0.415e^{-5}I)Az_i^2I}{\sqrt{1000}} \quad (7)$$

$$I = \frac{1}{2} \sum z_i^2 c_i \quad (8)$$

$$A = \frac{\sqrt{2}F^2 e_0}{8\pi(\epsilon_k RT)^{\frac{3}{2}}} \quad (9)$$

$$B = \sqrt{\frac{2F^2}{\epsilon_k RT}} \quad (10)$$

$$\epsilon_k = \epsilon_0 \epsilon_r \quad (11)$$

where z_i is the valence of ion i , I is the ionic strength of the solution (mol/m³), a_i is a ionic radius of ion i (assumed to be $3.0e^{-10}$ m), while A and B are temperature dependent parameters, where e_0 is the electrical charge of one electron ($1.602 e^{-19}$ C), F is the Faraday's constant (96488.46 C/mol), ϵ_k is the permittivity of the medium (F/m), ϵ_0 is the permittivity of the vacuum ($8.854e^{-12}$ F/m) and ϵ_r is the dielectric constant of water (80).

2.3 Diffusion–reaction model

In this work, diffusion flux is defined as approximately unidirectional in one dimensional. The diffusion of sulfate ions under a concentration gradient and its depletion due to gypsum formation are taken into account. By introducing the lumped reaction (Eq (5)), the equations describing the diffusion–reaction process are expressed as:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[\frac{D_{SO_4^{2-}}}{RT} c_{SO_4^{2-}} \frac{\partial \mu_{SO_4^{2-}}}{\partial x} \right] - \frac{\partial c_d}{\partial t} \quad (12)$$

$$\frac{\partial c_d}{\partial t} = k \cdot \{Ca\} \cdot \{SO_4\} \quad (13)$$

where c is the concentration of sulfate ions (mol/m^3), D is the diffusion coefficient of sulfate ions (m^2/s), x is the depth from the surface (m), t is the time (s), $\partial c_d / \partial t$ is the depletion rate of sulfate ions caused by chemical reactions, k represents the rate of take-up of sulfates (s^{-1}), $\{Ca\}$, $\{SO_4\}$ represents the calcium ion activity of calcium and sulfates (mol/m^3), respectively.

The sulfate attack is usually in accompany with calcium leaching including dissolution of the calcium hydroxide (CH) and sophisticated decalcification of the calcium silicate hydrate (C–S–H) (Wang, 1994). Its consumptions cause reductions in strength and stiffness, and increases in porosity facilitating the migration of aggressive species inside the material and formation of microcracks in concrete. As proposed by Berner (1988), a solid-liquid equilibrium model was adopted to further refine this process.

$$Cas(x, t) = \begin{cases} \left[\frac{-2}{x_1^3} C^3(x, t) + \frac{3}{x_1^2} C^2(x, t) \right] \left\{ C_{CSH} \left[\frac{C(x, t)}{C_{sat}} \right]^{1/3} \right\} \\ \left\{ C_{CSH} \left[\frac{C(x, t)}{C_{sat}} \right]^{1/3} \right\} \\ \left\{ C_{CSH} \left[\frac{C(x, t)}{C_{sat}} \right]^{1/3} \right\} + \frac{C_{CH}}{(satC - x_2)^3} [C(x, t) - x_2]^3 \end{cases} \quad (14)$$

where $Cas(x, t)$ is the calcium ion concentration in solid phase (mol/m^3), $C(x, t)$, is the concentration of calcium ion in pore solution (mol/m^3), C_{sat} is the saturated liquid phase calcium ion concentration (mol/m^3), C_{CSH} is the amount of calcium in the solid phase of the C-S-H gel (mol/m^3), C_{CH} is the amount of calcium in the solid phase of the calcium hydroxide (mol/m^3), x_1 is the liquid phase calcium ion concentration when the rapid transition of C-S-H gel into silica gel begins (mol/m^3), x_2 , is the liquid phase calcium ion concentration when the calcium hydroxide has completely dissolved and the dissolution of C-S-H gel begins (mol/m^3).

2.4 Diffusion coefficient of sulfate ions

The diffusion coefficient of sulfate ions is highly dependent on the stage of the degradation process

with chemical reactions. In this paper, changes in porosity due to formation of expansive ettringite and calcium leaching are considered and reflected in the diffusion coefficient. The influence of temperature on diffusion coefficient is also taken into account. In this way, three effects are considered for the calculation of the effective diffusion coefficient at the same time.

Changes in porosity resulting from ettringite formation and calcium leaching

The effective diffusivity of sulfate ions is decreased by the precipitation of ettringite in the pore system, and increased with expanding micro-cracks when the stress produced by the expansions reaches the tensile strength of concrete (Ikumi, *et al.*, 2014). As described in section 2.3, the dissolution of calcium hydroxide and calcium silicate hydrate gel may cause an increase in porosity (Cefis and Comi, 2017). In the present study, the filling effect in pores has been considered and the changes in porosity can be calculated as (Sarkar *et al.*, 2012):

$$\varphi = \varphi_0 - \frac{\Delta V}{V} \quad (15)$$

where V is volume of the representative volume element (m^3), ΔV is the change in corresponding solid volume element (m^3), φ_0 is the initial porosity, φ is the current porosity value. A Kozeny-Carman model (Xu *et al.*, 2006) is adopted to describe the changes in porosity on diffusion coefficient. The diffusion coefficient is calculated as:

$$D_{Ett} = f(\varphi_{Ett}) \cdot f(\varphi_{Ca}) \cdot D_0 \quad (16)$$

$$f(\varphi_{Ett}) = \left(\frac{\varphi_{Ett}}{\varphi_0} \right)^3 \left(\frac{1 - \varphi_0}{1 - \varphi_{Ett}} \right)^2 \quad (17)$$

$$f(\varphi_{Ca}) = \left(\frac{\varphi_{Ca}}{\varphi_0} \right)^3 \left(\frac{1 - \varphi_0}{1 - \varphi_{Ca}} \right)^2 \quad (18)$$

where D_0 is the initial diffusion coefficient, $f(\varphi_{Ett})$, $f(\varphi_{Ca})$ are the influence of porosity caused by formation of ettringite and calcium leaching respectively, φ_0 is the initial porosity, φ_{Ett} , φ_{Ca} represent the updated porosity value with formation of ettringite and calcium leaching respectively.

Temperature effects

This paper argues that during the movement of the sulfate ion, other particles are assumed to be stationary. Under a chemical potential gradient, sulfate ion needs to overcome some obstacles in the transmission process such as the intermolecular force and friction between other particles. Based on the theory of solid diffusion, these effects consume a part of energy, which is defined as diffusion activation energy E_D . In this paper, it is assumed that E_D remains a constant when temperature is increased, and accepted that the influence of temperature on the diffusion process of sulfate ions is relatively close to the Arrhenius model. The diffusion coefficient is calculated as:

$$D = D_{ref} \cdot f(T) \tag{19}$$

$$f(T) = \exp \left[\frac{E_D}{R} \cdot \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \tag{20}$$

where $f(T)$ is the influence of temperature on diffusivity; T is the reference temperature and taken as 298K; D_{ref} is the diffusion coefficient at the reference temperature, and is equal to $1.07 \times 10^{-9} \text{m}^2/\text{s}$ referring to Li and Gregory (1974); R is the universal gas constant (8.3143 J/mol/K).

3.0 VERIFICATION

3.1 Experiment

The proposed model was verified by comparing with experimental results. 100 mm × 100 mm × 400 mm concrete specimens were cast with commercial concrete. Ordinary Portland cement of type 42.5 N was used and its chemical oxide compositions are shown in Table 1. Concrete mix proportion (by mass) was 1: 0.48: 1.98: 2.94 (binder: water: sand: gravel), and the cement was replaced by fly ash with a ratio of 0.3. After demoulded, the specimens were cured for 28 days in which the temperature and relative humidity were kept at 298 K and 90%, respectively. Then, each specimen was sealed on four sides with two opposite sides (100 mm × 400 mm cross section) left for diffusion, so that sulfate ion transferring can be simplified as a one-dimensional diffusion. All samples were fully immersed in 30L concentration of 5% sodium sulfate solution, the initial value of PH was 7.0, the experimental temperature was kept at 298K. The sulfate concentrations at different depths in the specimens were obtained referring to “General test method in salt industry—Determination of sulfate” (GB/T 13025.8, 2012). The first measurement concentration was taken after immersed for 60 days and then it was measured every 30 days.

3.2 Model validation

In this paper, COMSOL software was used to analyze the distribution of sulfate ions at different depths under different attack times. The initial porosities were determined through the mass difference between at water saturation state and dry state, and the average value is 0.1486 of three specimens. The solid-liquid equilibrium curve was calculated according to the formulas presented in section 2.3, cement chemical compositions (as shown in Table 1) and mix proportion of concrete specimens. The obtained curve is shown in Fig. 1. These parameters were used to solve the proposed model. A two-dimensional polygonal random aggregate geometry is generated. It was meshed in COMSOL software and the mesh is refined near the edges where exposed to sulfate attack, as presented in Fig. 2.

Table 1. Chemical oxide compositions of cement materials

Chemical compositions	Mass (%)
SiO ₂	20.60
Al ₂ O ₃	5.03
CaO	65.06
MgO	0.55
SO ₃	2.24
Fe ₂ O ₃	4.38
others	2.14

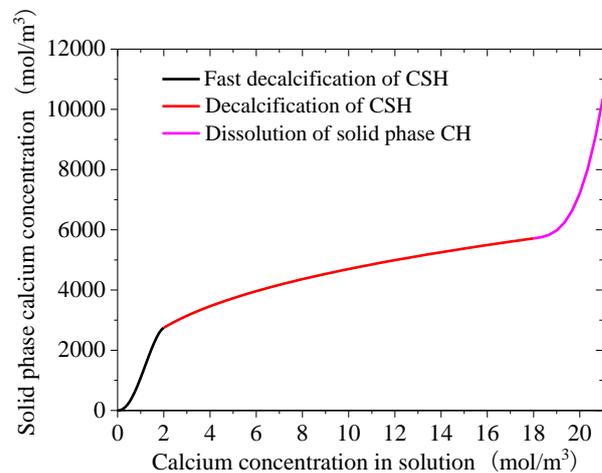


Fig. 1. The solid-liquid equilibrium curve of concrete.

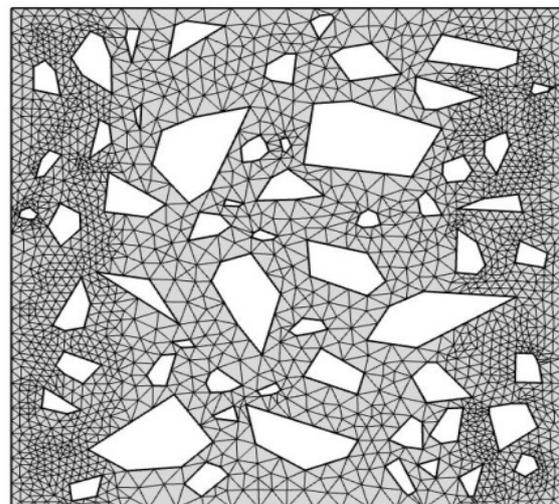


Fig. 2. Finite element model of a polygonal aggregate geometry at the meso-scale.

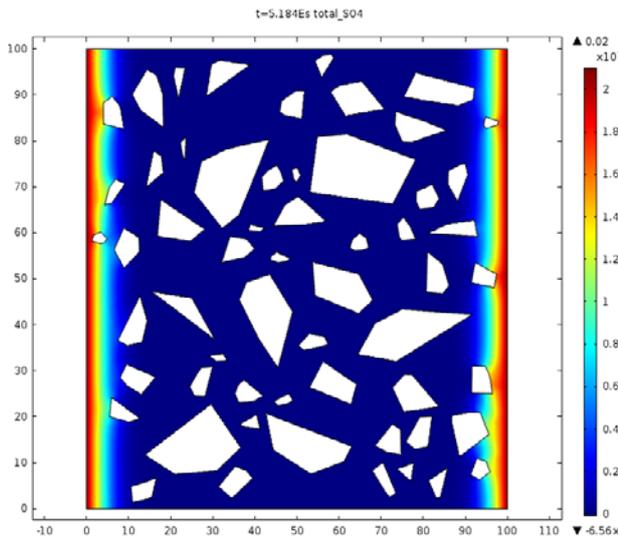


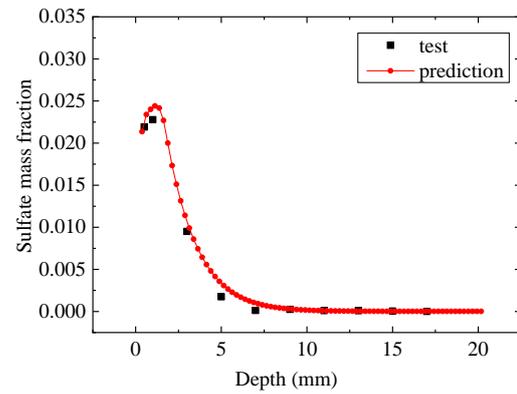
Fig. 3. The predicted sulfate diffusion profiles after immersing 60 days in numerical model

Fig. 3 depicts the predicted sulfate concentration profiles in the specimens exposed to a 5% sodium sulfate solution after immersing 60 days. The total sulfate ion concentration is divided into the sulfate ions in the solution and the sulfate products in the solid phase after chemical reaction. The sulfate concentration of solid phase over time can be calculated as:

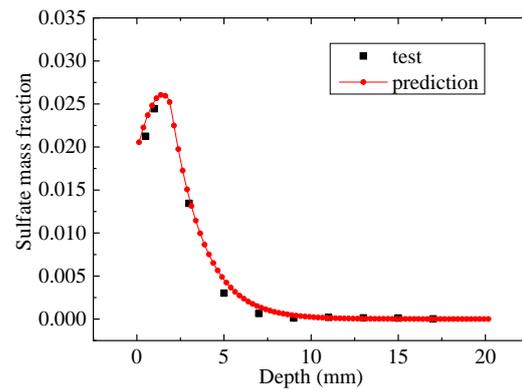
$$C_{S(SO_4)} = \int_0^t [k \cdot \{Ca\} \cdot \{SO_4\}] dt \quad (21)$$

where k represents the rate of take-up of sulfates (s^{-1}), $\{Ca\}$, $\{SO_4\}$ represents the calcium ion activity of calcium and sulfates (mol/m^3), respectively. Then the distribution of sulfate mass fraction under different immersing time was obtained and compared with the experimental results.

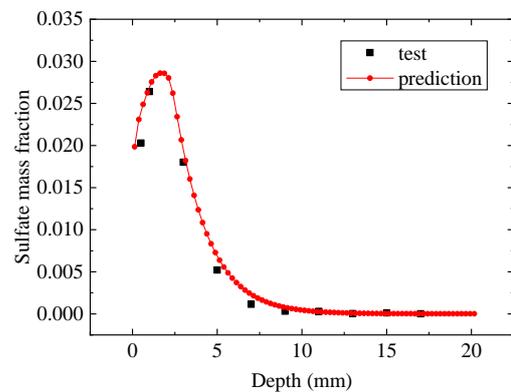
As shown in Fig. 4, it is seen that the numerical results are close to the test results, and the tendency of boundary value, peak value and the penetration depth with immersion time is almost consistent with the test results. Due to the precipitation of solid phase sulfate (like ettringite, gypsum) coming from chemical reactions between liquid sulfate ions and hydrate products, there is a peak value of sulfate ions at a certain depth during the diffusion process (Yu *et al.*, 2015; Sarkar *et al.*, 2010). As immersion time increased, more sulfate ions penetrated and diffused to the inside of concrete, the peak value of fraction increases and moves deeper inside of concrete both in theoretical model and experimental results. Whereas, because of that and the sulfate solution was not renewed every month, the boundary concentrations of sulfate ions are decreased with increasing of immersion time. It is also noted that the penetration depth increased with diffusion of sulfate ions. These results can be indicated that the proposed model is in a good agreement with the experimental results.



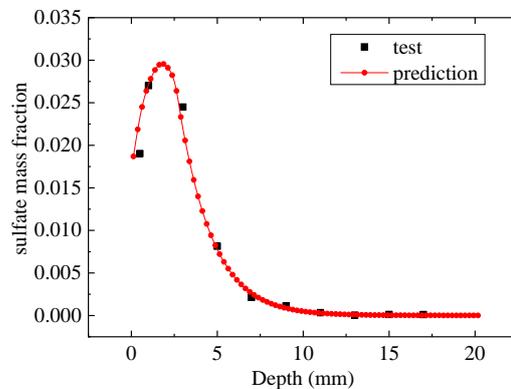
(a) 60 days



(b) 90 days



(c) 120 days



(d) 150 days

Fig. 4. Comparison of experimental and model results under different immersing time

4.0 CONCLUSIONS

This paper proposed a numerical model considering the chemical reaction and diffusion processes under sulfate attack on concrete. The influences of chemical reaction, precipitations of ettringite, calcium leaching and temperature on diffusion coefficient of sulfate ion were taken into account. Finally, a numerical model was established to describe the penetration of sulfate ions in concrete. The comparison of the model prediction with the experimental results has demonstrated the reliability of the diffusion model developed.

Acknowledgement

The present study was sponsored by the National Nature Science Foundation of China (Grant Nos.51678205, 51678200), Program of Shenzhen Science and Technology Plan (Grant No. JCYJ20170307150200952), Guangdong Provincial Natural Science Foundation of China (Grant No. 2017A030313259), and Project (GDDCE 16-09) supported by Guangdong Provincial Key Laboratory of Durability for Civil Engineering, Shenzhen University.

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