A meso-scale model for analyzing the chloride diffusion of concrete subjected to external stress

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Abstract: This paper proposes a theoretical model to investigate the influence of low stress on the chloride penetration in concrete by modeling concrete at the meso-scale.

At the meso-scale, concrete is modeled as a 3-phase composite material composed of mortar, interfacial transition zone (ITZ) and coarse aggregate. Each phase is further simplified as 2-phase composite material composed of matrix phase (zero porosity) and pore phase (the sum of various scale pores). Chloride permeability of concrete at low deformation is closely related to the porosity of concrete. Low stress changes the porosity of concrete thus influencing the chloride ion diffusion coefficient. Based on the theory of elasticity, an analytical model is developed, and a quantitative relationship is proposed between the external equivalent stress and the diffusion coefficient of the chloride ion as well as current-state porosity of mortar and the ITZ. The good agreement between the proposed model and the available test data illustrates that the proposed model is reliable and accurate. However, as the initial

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assumption was for elastic state, the model is valid for elastic low stress, or the accuracy of model reduces using plastic high stress state.

Keywords: Chloride diffusion; Stress; Mesoscopic scale; Model

1. Introduction

Reinforced concrete structures in chloride salt environments generally suffer from the corrosion of reinforcement steel. Corrosion of steel can reduce the cross-sectional area of rebar (reinforcement steel) and diminish its bonding capability with concrete, which can jeopardize the longevity of the structures [1]. To date, many researchers have focused on the durability problem of concrete caused by chloride ion penetration.

Efforts have been made to explore the chloride diffusivity in concrete from a macro-scale perspective in which concrete is considered as a homogeneous material [2-5]. However, by recognizing the heterogeneity of concrete as an important factor for chloride penetration, scholars have increasingly focused on the chloride penetration of concrete from a meso-scale perspective. For instance, a meso-scale numerical model was developed to investigate the chloride diffusivity in concrete [6]. The study [6] found that both the distribution and the shape of aggregate particles have a negligible influence on the chloride diffusivity in concrete. Branko[7] proposed a three-dimensional lattice model to simulate chloride transport in saturated sound and cracked concrete. In their study, means of computationally determining transport properties of individual phases in heterogeneous concrete (aggregate, mortar, and

interface) are presented and discussed.

However, studies are often performed with no consideration of the chloride penetration of concrete subjected to external stress. The diffusivity of concrete at a stress state may be significantly different from that at a stress-free state[8-10]. The porosity of mortar, interfacial transition zone (ITZ) and coarse aggregate may change under stress, and even formation of cracks within concrete causes changes in the permeability of concrete. Therefore, research on the chloride penetration in concrete subjected to a stress state is essential.

Most of the existing literature focused on the macro empirical model of chloride diffusion coefficient varied with stress level based on the experimental results, for instance, Wang [9] proposed a macro empirical model to predict the chloride diffusion process under different loading conditions. Konin et al.[11]carried out an experiment to investigate the chloride diffusivity of concrete subjected to tensile load. The experimental data showed that the chloride diffusion coefficient increases with the increase in the tension stress and the higher the concrete strength grade, the smaller the chloride ion concentration of penetration. To date, few scholars have investigated the chloride penetration of concrete subjected to external stress from the meso-scale and micro-scale perspectives. Bernard [12] presented a 3D numerical model in order to investigate the influence of ITZ on the compressive strength and on the effective diffusion coefficient when concrete was under uniaxial compressive stress. Du [8] and Jin [10] derived an analytical solution among the diffusion coefficient of the chloride ion, the current porosity of concrete and the external volumetric strain, however, the

selection of parameters is not convenient in the Du [8] and Jin [10] models, the practical engineering tends to be more likely to get external stress, rather than strain. To sum up, there exists very limited documentation on the micro-/meso-scopic model based on the theoretical analysis of the effect of external mechanical stress on chloride diffusivity in concrete. The quantitative relationships based on a micro-scale mechanism among the diffusion coefficient of the chloride ion, the current porosity of concrete and the external equivalent stress have not been fully understood. The objective of this paper is to further clarify those quantitative relationships.

In this study, it is assumed that under the external loadings the concrete is in the elastic stage, namely, before new cracks occur. By modeling concrete at the meso-scale, concrete is simplified as a three-phase sphere composed of mortar, ITZ and coarse aggregate. Based on the theory of elasticity, an analytical model is developed. A quantitative relationship is proposed between the current-state porosity of each phase and the diffusion coefficient of the chloride ion, as well as the external equivalent stress of each phase is evaluated. With the help of finite element method analysis, the model also reveals the meso-scale phenomenon of chloride ion penetration of concrete subjected to external stress.

2. Three-phase elasticity model for determining the effective diffusion coefficient

2.1. Mesoscopic model structure of concrete

In a mesoscopic finite element analysis of concrete member, one needs to first establish a reasonable concrete mesoscopic numerical model. At the meso-scale,

concrete is simplified as a composite material of three phases, namely, mortar, ITZ and coarse aggregate. The key to build a mesoscopic numerical model of concrete is appropriately determine the 3-phase composition as shown in Fig. 1.

2.1.1. Mortar

Mortar is a kind of a typical porous composite material that involved cement, water and fine aggregate. The mechanical properties were considered it as a homogeneous elastomer.

2.1.2. Coarse Aggregate

Coarse aggregate is a major component of concrete that occupies approximately half of the volume of concrete[6,13,14]. A key concern in the mesoscopic modeling of concrete is how to model coarse aggregate particles by considering the shape of coarse aggregate particle, volume fraction of coarse aggregate, and the relative positions of different particles within the concrete mass. Wang [15] and Schutter [16] showed that Fuller's gradation curve makes concrete better meet the demand of strength and compactness. Du [6] and Abyaneh [17] revealed that the effect of coarse aggregate shape on the chloride ion diffusion is negligible. Therefore, for simplicity, coarse aggregate particles were modeled as circular solid particles surrounded by mortar, and were simulated for the relative position by the Monte Carlo simulation method.

2.1.3. Interfacial transition zone (ITZ)

Concrete is a multiphase composite material in which aggregate particles are embedded in mortar. Farran [18] observed that the porosity near the surface of

aggregate particles in concrete is greater than the far field mortar and proposed that “Interfacial transition zone (ITZ)” exists in concrete as a zone that is relatively loose, has a low density, and is prone to cracking under external loading. From the formation viewpoint, ITZ is mainly caused by the wall-effect. ITZ as the weakest link in concrete and has a thickness of about $30\sim100\mu m$ around aggregate particles [19,20]. The porosity of ITZ decreases with the increase of distance from the aggregate surface [21]. In the numerical model, however, the ITZ was considered as a uniform region. Although ITZ is relatively small, its effect on the performance of concrete can be substantial. For instance, when the volume fraction of ITZ increased by 50%, the elastic modulus of concrete was reduced by 40% [22]. Ollivier [23] believed that the characteristics of concrete largely depends on the local properties of ITZ. Nilsen [24] founded that the two-phase models of concrete, which do not consider ITZ, cannot predict the concrete properties very well.

Based on literature [9] of the following validation model, the “Series A” was selected. Series A was based on OPC, with a coarse aggregate content of 1116 kg/m^3 and a water/cement ratio of 0.5. According to the test, the volume fraction of coarse aggregate $f_{agg} = 41\%$ of concrete was derived. The mesoscopic structure modeling of concrete was performed as shown in Fig. 2.

2.2. The volumetric stress of the meso-scale components

Multi-phase spherical models have been widely utilized to calculate the apparent diffusion coefficient of concrete [8,25,26]. Based on the theory of the multi-phase spherical model, concrete was modeled as a 3-phase spherical system comprising of

mortar, ITZ and coarse aggregate (Fig. 3). The elastic moduli of mortar, ITZ and coarse aggregate are denoted, respectively, as E_c , E_b and E_a , and their Poisson's ratio are denoted, respectively, as ν_c , ν_b and ν_a .

Fig. 4(b) presents the deformation behavior of concrete when subjected to the prescribed equivalent stress q_c . In Fig. 4, the computational model is assumed to be isotropic, homogeneous and elastic. The initial radii of the three phases in the computational model are a_0 , b_0 and c_0 , respectively. Under the prescribed equivalent stress q_c , the radii become a , b and c respectively.

Based on the theory of elasticity [27,28] and neglecting the body forces. In the x-y plane of polar coordinates, any point can be expressed as $P(\rho, \varphi)$ using the radial coordinate ρ and the circumferential coordinate φ . σ_ρ as the radial stress, σ_φ denotes the circumferential stress, and $\tau_{\rho\varphi}$ and $\tau_{\varphi\rho}$ indicate the shear stresses.

According to the basic equations of elasticity (the force/torque balance equations, the compatibility equation of deformation and the constitutive equations), the general solution for the axisymmetric problem can be obtained as[27,28]:

$$\sigma_\rho = \frac{A}{\rho^2} + B(1 + 2 \ln \rho) + 2C \quad (1a)$$

$$\sigma_\varphi = -\frac{A}{\rho^2} + B(3 + 2 \ln \rho) + 2C \quad (1b)$$

$$\tau_{\rho\varphi} = \tau_{\varphi\rho} = 0 \quad (1c)$$

$$u_\rho = \frac{1}{E} \left[-(1 + \nu) \frac{A}{\rho} + 2(1 - \nu) B \rho (\ln \rho - 1) + (1 - 3\nu) B \rho + 2(1 - \nu) C \rho \right] \quad (1d)$$

$$u_\varphi = \frac{4B\rho\varphi}{E} \quad (1e)$$

where u_ρ is the radial displacement and u_φ is the shear displacement. A , B and C are the three parameters to be determined.

For mortar and ITZ, the boundary conditions can be written as:

$$(\tau_{\rho\varphi}^c)_{\rho=b_0} = 0 \quad (2a)$$

$$(\tau_{\rho\varphi}^c)_{\rho=c_0} = 0 \quad (2b)$$

$$(\sigma_\rho^c)_{\rho=b_0} = -q_b \quad (2c)$$

$$(\sigma_\rho^c)_{\rho=c_0} = -q_c \quad (2d)$$

$$(\tau_{\rho\varphi}^b)_{\rho=a_0} = 0 \quad (2e)$$

$$(\tau_{\rho\varphi}^b)_{\rho=b_0} = 0 \quad (2f)$$

$$(\sigma_\rho^b)_{\rho=a_0} = -q_a \quad (2g)$$

$$(\sigma_\rho^b)_{\rho=b_0} = -q_b \quad (2h)$$

We can obtain that

$$A^c = \frac{b_0^2 c_0^2 (q_c - q_b)}{c_0^2 - b_0^2} \quad (3a)$$

$$B^c = 0 \quad (3b)$$

$$C^c = \frac{q_b b_0^2 - q_c c_0^2}{2(c_0^2 - b_0^2)} \quad (3c)$$

$$A^b = \frac{a_0^2 b_0^2 (q_b - q_a)}{b_0^2 - a_0^2} \quad (3d)$$

$$B^b = 0 \quad (3e)$$

$$C^b = \frac{q_a a_0^2 - q_b b_0^2}{2(b_0^2 - a_0^2)} \quad (3f)$$

And thus, the volumetric stress of mortar and ITZ can be obtained as:

$$\sigma_\rho^c = -\frac{\frac{c_0^2}{\rho^2} - 1}{\frac{c_0^2}{b_0^2} - 1} q_b - \frac{1 - \frac{b_0^2}{\rho^2}}{1 - \frac{b_0^2}{c_0^2}} q_c \quad (4a)$$

$$\sigma_{\varphi}^c = -\frac{\frac{c_0^2}{\rho^2} + 1}{\frac{c_0^2}{b_0^2} - 1} q_b - \frac{1 + \frac{b_0^2}{\rho^2}}{1 - \frac{b_0^2}{c_0^2}} q_c \quad (4b)$$

$$\tau_{\rho\varphi}^c = \tau_{\varphi\rho}^c = 0 \quad (4c)$$

$$u_{\rho}^c = \frac{1 + v_c}{E_c(c_0^2 - b_0^2)} \left[-b_0^2 c_0^2 (q_c - q_b) \frac{1}{\rho} - (1 - 2v_c)(q_c c_0^2 - q_b b_0^2) \rho \right] \quad (4d)$$

$$u_{\varphi}^c = 0 \quad (4e)$$

$$\sigma_{\rho}^b = -\frac{\frac{b_0^2}{\rho^2} - 1}{\frac{a_0^2}{a^2} - 1} q_a - \frac{1 - \frac{a_0^2}{\rho^2}}{1 - \frac{a_0^2}{b_0^2}} q_b \quad (4f)$$

$$\sigma_{\varphi}^b = -\frac{\frac{b_0^2}{\rho^2} + 1}{\frac{b_0^2}{a_0^2} - 1} q_a - \frac{1 + \frac{a_0^2}{\rho^2}}{1 - \frac{a_0^2}{b_0^2}} q_b \quad (4g)$$

$$\tau_{\rho\varphi}^b = \tau_{\varphi\rho}^b = 0 \quad (4h)$$

$$u_{\rho}^b = \frac{1 + v_b}{E_b(b_0^2 - a_0^2)} \left[-a_0^2 b_0^2 (q_b - q_a) \frac{1}{\rho} - (1 - 2v_b)(q_b b_0^2 - q_a a_0^2) \rho \right] \quad (4i)$$

$$u_{\varphi}^b = 0 \quad (4j)$$

152 For coarse aggregate, the boundary conditions can be written as:

$$(\sigma_{\rho}^a)_{\rho=a_0} = -q_a \quad (5a)$$

$$\lim_{\rho \rightarrow 0} u_{\rho}^a = 0 \quad (5b)$$

153 Substituting Eq. (4) into Eq. (8), one can get:

$$A^a = 0 \quad (6a)$$

$$B^a = 0 \quad (6b)$$

$$C^a = -\frac{q_a}{2} \quad (6c)$$

154 The radial displacement at $\rho = a$ can be obtained as:

$$u_{\rho}^a = -\frac{(1 + v_a)(1 - 2v_a)}{E_a} q_a a \quad (7)$$

155 Since the displacement of the contact surface is continuous, the boundary

156 conditions can be written as:

$$(u_\rho^a)_{\rho=a_0} = (u_\rho^b)_{\rho=a_0} \quad (8a)$$

$$(u_\rho^b)_{\rho=b_0} = (u_\rho^c)_{\rho=b_0} \quad (8b)$$

157 The relationship among q_a , q_b and q_c can be determined easily as:

$$q_a = \frac{\beta_1}{\beta_3 - \beta_2} q_b \quad (9a)$$

$$q_b = \frac{\beta_6}{\left(\beta_4 - \beta_7 + \frac{\beta_5\beta_1}{\beta_3 - \beta_2}\right)} q_c \quad (9b)$$

158 where,

$$\beta_1 = \frac{-a_0 b_0^2 (1 + v_b) (2 - 2v_b)}{E_b (b_0^2 - a_0^2)} \quad (10a)$$

$$\beta_2 = \frac{a_0 (1 + v_b) [b^2 + a_0^2 (1 - 2v_b)]}{E_b (b_0^2 - a_0^2)} \quad (10b)$$

$$\beta_3 = \frac{a_0 (1 + v_a) (1 - 2v_a)}{E_a} \quad (10c)$$

$$\beta_4 = \frac{-b_0 (1 + v_b) [a_0^2 + b_0^2 (1 - 2v_b)]}{E_b (b_0^2 - a_0^2)} \quad (10d)$$

$$\beta_5 = \frac{a_0^2 b_0 (1 + v_b) (2 - 2v_b)}{E_b (b_0^2 - a_0^2)} \quad (10e)$$

$$\beta_6 = \frac{-b_0 c_0^2 (1 + v_c) (2 - 2v_c)}{E_c (c_0^2 - b_0^2)} \quad (10f)$$

$$\beta_7 = \frac{b_0 (1 + v_c) [c_0^2 + b_0^2 (1 - 2v_c)]}{E_c (c_0^2 - b_0^2)} \quad (10g)$$

159 Fig. 5 shows the relationship between the stress of the meso-components and the
 160 external equivalent stress q_c . Other physical and mechanical parameters of materials
 161 are taken from Table 1. From Fig. 5, one can easily find that with an increase in the
 162 equivalent stress q_c , the volumetric stress of the meso-components increases, and
 163 also the volumetric stress of the coarse aggregate phase is larger than those of the

mortar and the ITZ phases. These results are consistent with those in a previous study [10]. The main reason is attributed to the elastic modulus E , Poisson's ratio ν and volume fraction f of each phase.

2.3. Quantitative relationship between the current state porosity, the external equivalent stress and the initial state porosity for mortar or ITZ

Based on the 3-phase sphere model as derived above, at the micro-scale, saturated mortar or saturated ITZ was simplified as a 2-phase sphere model comprised of matrix phase (zero porosity) and pore phase (the sum of various scales pores). The details of the 2-phase model for the ITZ are presented hereunder, similar modeling applies to mortar. Fig.6(a) presents the simplified model for the ITZ for porosity variation when subjected to the equivalent stresses q_b and q_a . Upon simplification, the porosity variation of ITZ in Fig.6(a) can be approximated as in Fig.6 (b). **Notice that in Fig.6 dash lines indicate the deformation of 3-phase sphere model before equivalent stress acting, solid lines indicate the deformation of 3-phase sphere model subjected to the equivalent stress.**

As shown in Fig.6 (b), the current-state porosity of the ITZ p_{itz} can be expressed as:

$$p_{itz} = \frac{a^2}{b^2} = \frac{\left[a_0 - (u_\rho)_{\rho=a_0} \right]^2}{\left[b_0 - (u_\rho)_{\rho=b_0} \right]^2}$$

$$= \frac{\left[a_0 - \frac{1 + \nu_b^2}{E_b(b_0^2 - a_0^2)} [-a_0 b_0^2 (q_b - q_a) - (1 - 2\nu_b)(q_b - q_a) b_0^2 a_0] \right]^2}{\left[b_0 - \frac{1 + \nu_b^2}{E_b(b_0^2 - a_0^2)} [-a_0^2 b_0 (q_b - q_a) - (1 - 2\nu_b)(q_b - q_a) b_0^3] \right]^2}$$

$$\begin{aligned}
&= \frac{\left[a_0 + \frac{a_0}{E_b(1 - a_0^2/b_0^2)} [(1 + v_b^2)(2 - 2v_b)(q_b - q_a)] \right]^2}{\left[b_0 + \frac{b_0(1 + v_b^2)}{E_b(1 - a_0^2/b_0^2)} [(1 - 2v_b + a_0^2/b_0^2)(q_b - q_a)] \right]^2} \\
&= p_0^{itz} \left(\frac{E_b(1 - p_0^{itz}) + (1 + v_c^2)(2 - 2v_c)(q_c - q_b)}{E_b(1 - p_0^{itz}) + (1 + v_c^2)(1 - 2v_c + p_0^{itz})(q_c - q_b)} \right)^2 \quad (11)
\end{aligned}$$

181 in which p_0^{itz} indicates the initial state porosity of the ITZ.

182 Similarly, the current state porosity of mortar p_{cp} can be written as:

$$p_{cp} = p_0^{cp} \left(\frac{E_b(1 - p_0^{cp}) + (1 + v_c^2)(2 - 2v_c)(q_c - q_b)}{E_b(1 - p_0^{cp}) + (1 + v_c^2)(1 - 2v_c + p_0^{cp})(q_c - q_b)} \right)^2 \quad (12)$$

183 where p_0^{cp} indicates the initial state porosity of mortar.

184 From the above derived formula, taking an example of ITZ, the same calculation
185 is also applicable for mortar. For the elastic moduli E_b and the Poisson's ratio v_b
186 taken from Table 1, the relationship between the current state porosity p_{itz} and the
187 external equivalent stress $q_b - q_a$ is plotted in Fig.7. Similarly, the relationship
188 between the current state porosity p_{itz} and the initial state porosity p_0^{itz} is plotted in
189 Fig.8. It can be seen that the current state porosity p_{itz} decreases with an increase in
190 the external compressive equivalent stress $q_b - q_a$ and increases with an increase in
191 the external tensile equivalent stress $q_b - q_a$. Furthermore, the current state porosity
192 p_{itz} decrease with an decrease in the initial state porosity p_0^{itz} and increase with an
193 increase in the initial state porosity p_0^{itz} . Obviously, the degree of influence of the
194 initial state porosity p_0^{itz} is greater than that of the equivalent stress $q_b - q_a$. And
195 thus, we inferred that initial state porosity is a dominated factor in the aspect of
196 porosity change when concrete under low deformation levels.

2.4. Chloride diffusion coefficients of the three meso-components

2.4.1. Prediction of the effective diffusion coefficient of mortar

At the micro-scale, mortar was simplified into a 2-phase composite material comprised of a matrix phase (zero porosity) and pore-water phase (the sum of various scales pores). Many scholars, such as [29,30], have done extensive work on this approach. For simplicity, in this paper, the porosity has been used synonymously to the chloride ion penetration capability of concrete. According to an analytical solution [31], the chloride ion diffusivity is given as:

$$D_{cp} = \frac{2p_{cp}^{2.75}D_p}{p_{cp}^{1.75}(3 - p_{cp}) + n(1 - p_{cp})^{2.75}} \quad (13)$$

where D_p means the chloride ion diffusivity in the pore solution taken as $D_p = 1.07 \times 10^{-10} \text{ m}^2/\text{s}$ [32]; n is an optimized parameter based on Tang [33] experiment taken as $n = 14.44$, and p_{cp} is the current state porosity of mortar.

The initial state porosity p_0 of a porous material is made up of the porosities of the capillary and the gel pores as:

$$p_0 = p_{cap}^0 + p_{gel}^0 \quad (14)$$

where p_{cap}^0 and p_{gel}^0 are the porosities of the capillary and the gel pores, respectively. Powers [34] assumed the parameters of the porosities of the capillary and the gel pores in Eq. (17) can be calculated as follows:

$$p_{cap}^0 = \frac{0.19\alpha}{w/c + 0.32} \quad (15a)$$

$$p_{gel}^0 = \frac{w/c - 0.36\alpha}{w/c + 0.32} \quad (15b)$$

So, the total initial state porosity p_0 can be obtained by substituting Eq. (15) into (14) as follows:

$$p_0^{cp} = \frac{w/c - 0.17\alpha}{w/c + 0.32} \quad (16)$$

where w/c is water to cement ratio ($0.4 < w/c < 0.7$ [35]) and α is the degree of hydration ($0.3 < w/c < 0.9$). Corresponding to these values, one can get the initial state porosity p_0 to vary from 0.2 to 0.6.

2.4.2. Prediction of the effective diffusion coefficient of the ITZ

ITZ has a higher water-to-cement ratio and thus a larger porosity than of the mortar. Lutz [21] found that the porosity of the ITZ decreases with an increase in distance from the aggregate surface. However, in this numerical study, the ITZ was modeled as a uniform region.

Based on this assumption, the relative diffusivity of ITZ as proposed by Garboczi [36] was adopted in this study as:

$$D_{itz} = D_0(0.001 + 0.07p_{itz}^2 + 1.8 \cdot H(p_{itz} - \varphi_{cri}) \cdot (p_{itz} - \varphi_{cri})^2) \quad (17)$$

where $D_0 = 2.03 \times 10^{-9}(m^2/s)$ is the diffusion coefficient in bulk water at 25°C, p_{itz} is the average porosity of the ITZ, H is the Heaviside function (if $x > 0, H(x) = 1$, and otherwise, $H(x) = 0$), and $\varphi_{cri} = 0.18$ is the critical porosity at which the capillary pore space is disconnected.

2.4.3. Prediction of the effective diffusion coefficient D_{eff} of concrete

As shown in Fig.9, Phase 1 constitutes the central core and Phase(i) lies within the shell limited by the two concentric spheres with the radii R_{i-1} and R_i , respectively. Based on the generalized self-consistent theory, the analytic solution for composite spheres assemblage model has been given by Herve [37] as:

$$D_{(i)}^{eff} = D_i + \frac{D_i(R_{i-1}^3/R_i^3)}{\left[D_i \left(D_{(i-1)}^{eff} - D_i\right)\right] + (1/3)[(R_i^3 - R_{i-1}^3)/R_i^3]} \quad (18)$$

where D_i is effective diffusivity coefficient of the i^{th} phase, $D_{(i)}^{eff}$ is effective diffusivity coefficient of the composite spheres made up of the first phase to the i^{th} phase.

To obtain the effective diffusion coefficient of concrete, the diffusion coefficient of the coarse aggregate was assumed as zero ($D_{agg} = 0$). Defining the coarse aggregate volume fraction as V_a and the ITZ volume fraction as V_i , the diffusion coefficient of the mortar was obtained as D_{cp} and the diffusion coefficient of the ITZ was obtained as D_i .

Finally, the effective diffusion coefficient of concrete can be expressed as:

$$D_{eff} = D_{cp} \frac{6D_{cp}(1 - V_a)(V_a + V_i) + 2V_i(D_i - D_{cp})(1 + 2V_a + 2V_i)}{3D_{cp}(2 + V_a)(V_a + V_i) + 2V_i(1 - V_a - V_i)(D_i - D_{cp})} \quad (19)$$

3. Model verification and parametric studies

3.1. Input parameters and calculation flow

In order to verify the model proposed in this study with the test data, a number of parameters and steps are involved. By comparing the parameters of the three-sphere model to the original cross-sectional dimension, the radii a , b and c of the three spheres and the volume fraction of the ITZ f_{itz} were obtained. However, it is to be noted that the physical and mechanical parameters were still not complete for predicting the diffusivity of concrete. In the computations in this study, some physical parameters were thus assumed. For example, the initial mortar porosity p_0^{cp} was assumed to be 40% ($30\% < p_0^{cp} < 60\%$); the ITZ average porosity p_0^{itz} was assumed to

be 63% (about $1.5p_0^{cp}$ [12]). The other physical and mechanical parameters of materials were assumed as listed in Table 1. A flowchart for the prediction of the diffusion coefficient of chloride ions into saturated concrete under the external equivalent stress is depicted in Fig.10.

3.2. Model verification

In this section, the experimental observations of Wang [9] are selected to verify the accuracy and rationality of the numerical model proposed in this paper. In their tests, the “Series A” was selected. Series A was based on OPC, with a coarse aggregate content of 1116 kg/m^3 and a water/cement ratio of 0.5. During the permeability tests, the concrete specimens were exposed to the salt fog for two months under the sustained compress loading conditions, and then chloride concentration of the concrete samples at different depths were obtained. To analyze the impact of external compressive stress on the chloride ion penetration of concrete, an index stress level was defined as λ_σ such that $\lambda_\sigma = \frac{\sigma_c}{f_c}$ where σ_c is the applied compressive stress and f_c is the compressive strength of concrete. For the sake of simplicity, concrete which is subjected to uniaxial compression σ_c is equivalent to three-phase phase model which is only considering radial stress q_c . The processing way is consistent with that in the work of [10]. The theoretical results were compared to the experimental observations, and the relationships were plotted as shown in Fig.11. Fig.11 shows that, for an ideal ratio of 1, the ratios of the theoretical and the experimental values corresponding to points F, G, H and I are 0.99, 0.99, 0.95 and 0.91, respectively. These values demonstrate the reliability and accuracy of the

proposed model.

The reason for the slight discrepancies in Fig.11 between the analytical results and the available test data is that the analytical results were obtained from an elastic model in which the constitutive relationship for concrete subjected to uniaxial compression σ_c before reaching the compressive strength was assumed linear. Reasons for discrepancies are discussed in details in the following section.

In fact, the initial pores and the initial cracks existed in concrete from the initial state. The deformation was mainly elastic deformation of mortar, ITZ and aggregates. New cracks were not formed until the uniaxial compression σ_c was 30% of the compressive strength f_c . In this stage, the initial volume of cracks V_{icr} in the concrete remained constant and the initial volume of pores V_{ip} in the concrete decreased with an increase in compressive stress. Therefore, the total volume of the chloride diffusion V_t decreased, and thus the curves of both the analytical results and the available test data of the chloride diffusion coefficient of concrete subjected to compressive stress showed a decrease in the chloride diffusivity.

When compressive stress σ_c was such that $0.3f_c < \sigma_c \leq 0.8f_c$, the constitutive relationship curve became non-linear, indicating the formation of a large number of cracks. In this stage, the total volume of cracks V_{cr} in concrete increased and the initial volume of pores V_{ip} in concrete decreased with an increase in compressive stress σ_c . The degree of reduction in the initial volume of the pores V_{ip} in the concrete was greater than the degree of increment of the total volume of cracks V_{cr} in concrete. Therefore, the total volume of the chloride diffusion V_t decreased, and thus the curves

of the analytical results and the available test data showed a reduction in the chloride diffusivity.

The obtained analytical results were slightly greater than the available test data. This is mainly because the analytical results were obtained from an elastic model in which the constitutive relationship was linear. However, for the test data from the elastic-plastic model, in which the constitutive relationship curve becomes non-linear, the decrease in the degree of the total volume of the chloride diffusion V_t of the test data is larger than the decrease in the degree of the total volume of the chloride diffusion V_t of the obtained analytical results.

In summary, the proposed model is relatively more suitable for low deformation levels **before the concrete passes its elastic state**, namely, before new cracks occur ($\sigma_c \leq 0.3f_c$).

3.3. Parametric studies

To investigate the influence of the three meso-components to the chloride penetration of concrete subjected to stress, the chlorine ion penetrated into saturated concrete was assumed as one-dimensional, which penetrated into concrete from the bottom edge, and the other three edges had no flux as shown in Fig.12. Chloride ion diffusion in saturated concrete were explored based on the Fick's second law [38] as:

$$\frac{\partial C(x, t)}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C(x, t)}{\partial x} \right) \quad (20)$$

where D is the chloride diffusion coefficient and t is the exposure time.

The boundary conditions and the initial condition satisfy the following equations:

The bottom edge: $C(x, t) = C_s, x = 0$ (21a)

The other three edges: $C(x, t) = 0, x \geq 0$ (21b)

The initial condition: $C(x, t) = 0, t = 0$ (21c)

in which C_s is the boundary chloride concentration and was assumed equal to 0.5 (% concrete weight). Notice that the other physical and mechanical parameters of materials in the following calculations are taken from Table 1.

3.3.1. Relationship between the diffusivity properties and the external equivalent

stress q_c

Fig.13 illustrates the relationships between the diffusivity properties and the external equivalent stress q_c when $t = 5a$. The chloride diffusion content of concrete decreased with an increase in compressive stress, and it increased with an increase in tensile stress. However, the influence degree of the external equivalent stress q_c on the chloride ion concentration is not obvious.

3.3.2. Effect of diffusivity properties of the ITZ

In order to explore the role of ITZ on the chloride ion diffusion performance of concrete, the influence of different p_0^{itz}/p_0^{cp} ratios were considered. The distribution profiles of chloride ions when $t = 5a$ and $q_c = -4.79Mpa$ are shown in Fig. 14. Moreover, Fig. 15 plots the relationships between the chloride concentrations and the depth of concrete from the surface. One can find from Fig. 14 and Fig. 15 that, with an increase in p_0^{itz}/p_0^{cp} ratio, the chloride diffusivity increased slightly. Therefore, the ITZ of concrete should be considered in the study of the chloride ion penetration.

3.3.3. Effect of diffusivity properties of coarse aggregate

Coarse aggregates in the concrete imparts blocking and redirecting effects while the ITZ imparts percolation effects. To investigate the effect of coarse aggregate volume fraction on the chloride diffusivity in concrete, this section discusses the effect of coarse aggregate on the effective diffusivity properties D_{eff} of a heterogeneous concrete sample at a stress-free state. Fig.16 presents the relationship curves of a heterogeneous concrete sample at different D_{eff}/D_{cp} values for a stress-free state. Notice that D_{cp} is diffusivity coefficient of a homogeneous mortar sample without considering ITZ and Coarse aggregates.

1) When $D_{itz}/D_{cp} < 14$, the overall chloride diffusivity in the heterogeneous concrete was lower than that in the pure mortar. Both the effect of aggregate and of the ITZ hindered the chloride ion diffusion. Chloride ion diffusivity properties decreased with an increase in the coarse aggregate volume fraction.

2) When $D_{itz}/D_{cp} = 14$, the overall chloride diffusivity in the heterogeneous concrete equaled that in the pure mortar. The effect of coarse aggregate and of the ITZ in the chloride ion diffusion almost compensated each other. Chlorine ion diffusivity properties were independent of the coarse aggregate volume fraction.

3) When $D_{itz}/D_{cp} > 14$, the overall chloride diffusivity in the heterogeneous concrete was greater than that in the pure mortar. Both the effect of coarse aggregate and of the ITZ accelerated the chloride ion diffusion. Chloride ion diffusivity properties increased with an increase in the coarse aggregate

volume fraction.

4. Conclusions

This paper proposed a meso-scale concrete model for predicting the chloride diffusivity of concrete subjected to external equivalent stress based on a 3-phase sphere model. The volumetric stress and the current-state porosities of each meso-components (mortar, ITZ and coarse aggregate) were derived when subjected to the external equivalent stress. The following are the main conclusions:

1) The chloride diffusion coefficient of concrete at low deformation levels decreased with an increase in compressive stress and increased with an increase in tensile stress. However, the initial state porosity of concrete is still the primary factor influencing the chloride ion diffusion.

2) The ITZ and the coarse aggregate of concrete play an important role in the chloride ion penetration, and hence, cannot be ignored. With an increase in p_0^{itz}/p_0^{cp} ratio, the chloride diffusivity properties increased. The chloride diffusion coefficient of concrete at low deformation levels decreased with an increase in compressive stress and increased with an increase in tensile stress. However, the initial state porosity of concrete is still the primary factor influencing the chloride ion diffusion.

3) The proposed model is relatively more suitable for low deformation levels before the concrete passes its elastic state, namely, the accuracy of model reduces using plastic state.

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materials	Young's modulus, $E(Gpa)$	Poission's ratio, ν	The volume fraction $f, \%$
Mortar matrix	30.1	0.28	53.4
ITZ matrix	21	0.28	5.6
Coarse aggregate	86.7	0.17	41