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Predeterminate model of corrosion rate of steel in concrete

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Abstract

The predeterminate model of corrosion rate of steel in concrete, the influence of concrete carbonation exponent and cover thickness to steel corrosion rate, and relationships among steel diameter, cover thickness and exposure time to steel corrosion rate are mainly studied. It is shown that (1) the steel corrosion rate increases when the concrete carbonation exponent increases. (2) The steel corrosion rate decreases when a mild carbon steel with circular diameter in concrete increases. The more the concrete carbonation exponent becomes larger, the more the effect of steel diameter obviously appears. (3) The steel corrosion rate increases when the concrete cover thickness decreases. (4) The steel corrosion rate obviously increases when the exposure time decreases. The results of present studies are discussed in comparison with earlier findings. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Carbonation; Concentration; Corrosion rate; Diffusion; Durability

1. Introduction

The durability of concrete or reinforced concrete (RC) is been considered an important problem by civil engineers today. Since the concrete or RC structure is needed to correspond to design strength, the service life of a concrete or RC structure is also very important. Transportation of aggressive ions in concrete is of an important influence on the durability of concrete [1]. The ingress of carbon dioxide may cause the deterioration of concrete and the corrosion of reinforcement. As a result, the diffusion coefficient of carbon dioxide may be one of the most important parameters for assessing the durability or predicting the service life of a concrete or RC structure [2].

Many methods have been suggested to study the concrete carbonation [3-11] and the corrosion of reinforcement in

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concrete [12-22]. Although many researchers have become interested in the concrete carbonation test, very few workers have recognized the importance of the relationship between steel diameter and exposure time. Accordingly, a not new but very simple approach to determine the diffusivity of aggression ions in concrete, especially for carbon dioxide, has been proposed [22,23]. This approach has also been applied to predict the carbonation depth of concrete, monitor the corrosion rate of steel in concrete and evaluate the service life of the RC structure. The theoretical aspects and applications of this approach are discussed in the present work. The results of this study can be provided as an important reference basis of repair, strengthening or demolition for the existing concrete or RC structures.

2. Corrosion model of steel in concrete

In order to study the corrosion of steel in concrete due to carbonation and establish steel corrosion rate prediction, some basic assumptions should be made as follows: (1) The

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factor of steel occurring corrosion resulted from concrete carbonation is only considered. (2) The diffusion of dioxidation in concrete obeys Fick's first law of diffusion. (3) It needs enough water to build up the corrosion of steel in concrete when the atmospheric relative humidity is higher than the critical relative humidity of steel corrosion. (4) The corrosion of steel embedded in concrete under atmospheric pressure belongs to micro cell corrosion. Both anodic and cathodic electrodes are closely contacted.

According to Faraday's law of electrochemical equivalence [24], the corrosion current density, $i_{\rm corr}$, of steel corrosion cell can be expressed by

$$\frac{i_{\rm corr}(\tau)}{n_{\rm O_2}F} = J_{\rm c}(\tau) \tag{1}$$

where $i_{\rm corr}(\tau)$ is the current density of cathodic electrode at time τ , $J_{\rm c}(\tau)$ is the diffusion flow of ${\rm O_2}$ on the steel surface at time τ , $n_{{\rm O_2}}$ is the obtained electric number of ${\rm O_2}$ molecule participated in chemical reaction, take $n_{{\rm O_2}}$ =4, and F is the Faraday constant, F=96500×10⁴ C/mol.

Based on electrochemistric principle, the diffusion flow of matter A in matter B equals the product of diffusion coefficient of matter A in matter B with the first order derivative of concentration of matter A in the direction of diffusion, i.e.,

$$J_{\rm c}(\tau) = D_{\rm O_2} \frac{\partial C(x)}{\partial x} \tag{2}$$

where D_{O_2} is the diffusion coefficient in $\mathrm{mm}^2/\mathrm{year}$ of O_2 in concrete, C(x) is the concentration distribution of O_2 in concrete and x is the space coordinate in the diffusion direction.

Now assume that the diffusion of O_2 in concrete obeys Fick's first law of diffusion. This means that the concentration of O_2 with a linear variation in the area of diffusion layer from the maximum value on the concrete surface to the zero value at carbonation front. The thickness of diffusion layer is the complete carbonation depth, D. Thus

$$\frac{\partial C}{\partial x} = \frac{C_{\rm O_2} - C_{\rm st}}{D} \tag{3}$$

where $C_{\rm O_2}$ is the concentration of $\rm O_2$ on the concrete surface. Take $C_{\rm O_2}$ =8.93×10⁻⁹ mol/mm³. (The density and atomic weight of $\rm O_2$ are 0.28576 g/l and 32 g/mol, respectively. $C_{\rm O_2}$ is the ratio of density to atomic weight of $\rm O_2$.) $C_{\rm st}$ is the concentration in mol/mm³ of $\rm O_2$ on the steel surface and D is the completely carbonated depth in mm.

Since the steel corrosion is assumed to be controlled by the O_2 reacted with O_2 and pore water in concrete, i.e., $C_{\rm st}$ in Eq. (3) can be taken with zero value, Eq. (3) is changed as

$$\frac{\partial C}{\partial x} = \frac{C_{\text{O}_2}}{D} \tag{4}$$

The substitution of Eqs. (2) and (4) into Eq. (1) yields

$$i_{c}(\tau) = \frac{n_{O_2} F D_{O_2} C_{O_2}}{D} \tag{5}$$

On the authority of Faraday's law, the product of steel corrosion in the range of time $\tau \sim \tau + d\tau$ can be written out. Meanwhile, the diffusion of O_2 at cathode controls the reaction process. Therefore, the anodic current certainly equals cathodic current, i.e.,

$$dW_{\tau} = \frac{i_{\text{corr}}(\tau)}{n_{\circ}F} M A_{\text{a}} d\tau \tag{6}$$

where $\mathrm{d}W_{\tau}$ is the product in g of steel corrosion during time $\mathrm{d}\tau$, A_{a} is the corrosion surface area of steel in concrete at time τ , M is the atomic weight of Fe in 55.85 g/mol and n_{a} is the electric charge of iron ion. In fact, the value of n_{a} is obtained by the weight of product ratio Fe₂O₃ and Fe₂O₄. Herein, the molars of their product are same. Through calculation, one has n_{a} =2.8.

When calculate the value of A_a , one takes 1 mm unit length. One obtains

$$A_{\rm a} = 2r \arccos \frac{r + c - D}{r} = d \arccos \frac{d + 2c - 2D}{d} \tag{7}$$

where r is the radius in mm of steel, d is the diameter in mm of steel, c is the cover thickness in mm of concrete and D is the carbonation depth in mm of concrete.

Based on experimental data, the relationship between carbonation depth and exposure time [21,25] is

$$D = \alpha \tau^{\lambda} \tag{8}$$

where α is the coefficient of carbonation velocity, λ is the carbonation exponent and τ is the exposure time of concrete or RC structure. The constants of α and λ are determined by the least-squares fitting method.

The parameter of D_{O_2} in Eq. (5) can be expressed as [22]

$$D_{O_2} = 3.1536 \times 10^5 \left(\frac{32.15}{f'_{cu}} - 0.44 \right) \text{ (mm}^2/\text{year)}$$
$$= 0.01 \left(\frac{32.15}{f'_{cu}} - 0.44 \right) \text{ (mm}^2/\text{s)}$$
(9)

where f'_{cu} is the cube compressive strength in (N/mm^2) of concrete. It is worth noting that $f'_{c}(cylinder)=0.85f'_{c}(cube)=1.10f'_{c}(prism)$ [26].

Substituting Eqs. (5), (7) and (8) into Eq. (6), one obtains

$$\mathrm{d}W_{\mathrm{\tau}} = 7.118 \times 10^{-7} \frac{D_{\mathrm{O}_2} d}{\alpha \tau^{\lambda}} \arccos \frac{d + 2c - 2\alpha \tau^{\lambda}}{d} \mathrm{d}\tau \qquad (10)$$

Taking integral of Eq. (10) with respect to time, one has

$$W_t = SP_{\rm RH} \int_{t_0}^t \mathrm{d}W_{\tau} \tag{11}$$

where $P_{\rm RH}$ is the correction factor of steel corrosion occurred with probability 60% when the consideration of atmospheric relative humidity is larger than the critical relative humidity of steel corrosion [21], and S is the correction factor only considered the solution of O_2 in water

when react with steel rust. The solubility of O_2 in water is 0.028 [23].

It is needed to illustrate Eq. (11) that is under the condition of $t_0 \le t \le t_1$, where $t_0 = (\frac{c}{\alpha})^{\frac{1}{2}}$ is the time in years of steel occurred corrosion, t is the predicted time in years of steel corrosion and $t_1 = (\frac{c+d}{\alpha})^{\frac{1}{2}}$ is the start time in years of the whole corrosion of steel surface. When $t \ge t_1$, $A_a = \pi d$ and D = c + d, Eq. (11) is changed as

$$W_{t} = SP_{RH} \left(\int_{t_{0}}^{t_{1}} dW_{\tau} + \int_{t_{1}}^{t_{2}} dW_{\tau}' \right)$$
 (12)

where $dW'_{\tau} = 7.118 \times 10^{-7} (\pi D_{O_{\tau}} d/c + d) d\tau$.

Usually, the measurement of the degree of steel corrosion is adopted the steel corrosion rate, $\rho = (W_{\rm f}/W_0) \times 100\%$, where W_0 is the theoretical weight of steel. If takes a unit length 1 mm of steel, then $W_0 = 1/4\pi d^2 \times 7.8 \times 10^{-3}$ g. Thus, the representation of ρ becomes

$$\rho = 0 t < t_0 (13a)$$

$$\rho = 3.254 \times 10^{-4} \frac{SD_{O_2}P_{RH}}{\alpha d} \int_{t_0}^{t} \frac{\arccos \frac{d + 2c - 2\alpha \tau^{\lambda}}{d}}{\tau^{\lambda}} d\tau$$

$$t_0 \le t \le t_1 (13b)$$

$$\rho = 3.254 \times 10^{-4} \frac{SD_{O_2}P_{RH}}{d}$$

$$= 3.254 \times 10^{-1} \frac{1}{d} \times \left[\frac{\pi(t - t_1)}{c + d} + \int_{t_0}^{t_1} \frac{\arccos \frac{d + 2c - 2\alpha \tau^{\lambda}}{d}}{\alpha \tau^{\lambda}} d\tau \right] t \ge t_1$$
(13c)

If we assume λ =0.5 [7,10,21,25–29], taking integral to Eqs. (13a)–(13c), one obtains

$$\rho = 0 \qquad t < t_0 \tag{14a}$$

$$\rho = 3.254 \times 10^{-4} \frac{SD_{O_2}P_{\rm RH}}{\mathrm{d}\alpha^2} \left[\sqrt{d^2 - \left(d + 2c - 2\alpha\sqrt{t}\right)^2} - \left(d + 2c - 2\alpha\sqrt{t}\right) \arccos\frac{d + 2c - 2\alpha\sqrt{t}}{d} \right] \qquad t_0 \le t \le t_1$$
(14b)

$$\rho = 3.254 \times 10^{-4} \frac{SD_{O_2} P_{RH}}{d} \left[\frac{\pi (t - t_1)}{c + d} + \frac{\pi d}{\alpha^2} \right] \qquad t \ge t_1$$
(14c)

When using Eqs. (14a)–(14c) to calculate the steel corrosion rate, it is not convenient for solution due to the complicated calculation process. Accordingly, a numerical technique is employed to represent the integral of Eqs. (13b) and (13c) as a power function of τ [21], i.e.,

$$f(\tau) = \frac{\arccos\left(\frac{d + 2c - 2\alpha\tau^{\lambda}}{d}\right)}{\tau^{\lambda}} = a(\tau - t_0)^b$$
 (15)

where a and b are to be determined coefficients and are the function of parameters t, r, c, α and λ .

Substituting Eq. (15) into Eqs. (13a)–(13c), one obtains a simple prediction model of steel corrosion rate

$$\rho = 0 \qquad t < t_0 \tag{16a}$$

$$\rho = 3.254 \times 10^{-4} \frac{SD_{O_2}P_{RH}}{\alpha d} \times \frac{\alpha (t - t_0)^{b+1}}{b+1} \qquad t_0 \le t \le t_1$$
(16b)

$$\rho = 3.254 \times 10^{-4} \frac{SD_{O_2} P_{RH}}{d} \left[\frac{\pi (t - t_1)}{c + d} + \frac{a(t_1 - t_0)^{b+1}}{\alpha (b+1)} \right]$$

$$t \ge t_1$$
(16c)

Many parameters influence the values of a and b. Moreover, the influence of each parameter is not neglected. Thereafter, the calculation process is too complicated to use. It is noteworthy to point out that the error of b to the influence of calculated results is very obvious due to parameter b positioned at exponent. Accordingly, using table is not only simple but also practical way. The corresponding values of a and b are herein not listed in present work [30].

3. Verification and analytical results

3.1. Rationality of the simplified prediction model

Through some examples for calculation and comparison, the rationality of Eqs. (16a)–(16c) with a simplified prediction model can be verified. For convenience, one recognizes ρ_0 and ρ_1 obtained from the ρ of Eqs. (13a)–(13c) and (16a)–(16c), respectively. Taking $P_{\rm RH}$ =0.50 and S=0.028, the calculated results are listed in Table 1. From Table 1, it is obvious that the results calculated by Eqs. (13a)–(13c) and (16a)–(16c) are very close. The maximum error is 5.19%. The other errors are very small. On this account, it is reasonable to use Eqs. (16a)–(16c) to predict the corrosion rate of steel in concrete.

Table 1 Comparison of ρ_0 with ρ

Comparison of ρ_0 with ρ_1								
Order	с	r	α	λ	t	ρ_0	ρ_1	$(\rho_0 - \rho_1 /\rho_0)$ ×100/100%
1	25	8	5	0.5	30	0.320	0.325	1.56
2	25	8	5	0.5	50	3.091	3.094	0.10
3	25	8	7	0.5	30	2.389	2.421	1.34
4	25	8	7	0.5	50	6.788	7.140	5.19
5	25	8	5	0.48	50	2.333	2.336	0.13
6	25	8	5	0.56	50	5.486	5.453	0.60
7	25	10	5	0.5	50	2.168	2.171	0.14
8	25	8	5	0.5	50	3.091	3.094	0.10

Remark: c=cover thickness (mm), r=steel radius (mm), α =coefficient of carbonation velocity, λ =carbonation exponent, t=the time predicted steel corrosion quantity (years), ρ_0 =the value of steel corrosion rate ρ calculated from Eqs. (13a)–(13c) is referred as ρ_0 , ρ_1 =the value of steel corrosion rate ρ calculated from Eq. (16a)–(16c) is referred as ρ_1 .

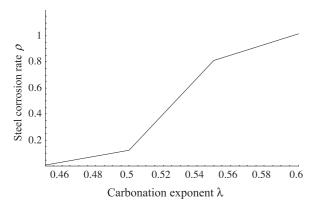


Fig. 1. Calculated relationship between steel corrosion rate and carbonation exponent.

3.2. Influence factors of the simplified prediction model

Now assume that a RC member has d=16 mm and c=25mm. The carbonation depth of the member has D=20 mm after using t=30 years. Fig. 1 indicates the relationship between steel corrosion rate and carbonation exponent at t=50 years using $P_{RH}=0.5$ and S=0.028. It is clearly seen that the steel corrosion rate has a significant variation in the range of λ =0.50–0.55. The steel corrosion rate increases when the carbonation exponent, λ , or the coefficient of carbonation velocity, α , increases. Using the same parameters values, Fig. 2 shows the relationship between steel corrosion rate and steel diameter at different values of λ . It is understandable that the steel corrosion rate decreases when the steel diameter increases. Furthermore, the more the carbonation exponent increases, the more the influence of steel diameter is noteworthy. As a consequence, the bigger diameter of steel is chosen to protect corrosion for a RC structure in corrosive environment. Based on the same parameter values, Fig. 3 displays the relationship between steel corrosion rate and cover thickness of concrete. It was found that the steel corrosion rate is significantly increased when the cover thickness decreases. It is also worthy to point out that the steel corrosion rate with c=10 mm has 2.81 times c=20 mm does. This means that the RC structure will increase corrosion damage when the cover thickness is

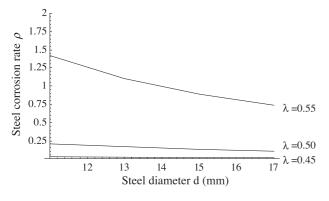


Fig. 2. Relationship between calculated steel corrosion rate and steel diameter.

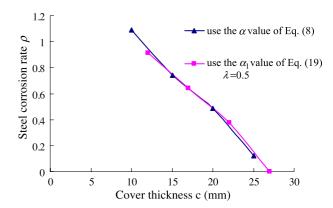


Fig. 3. Relationship between steel corrosion rate and cover thickness.

not satisfied by the design requirement. Therefore, the cover thickness of concrete has a great deal of influence to the durability of RC structures. Keeping the invariable values of parameters, Fig. 4 reveals the relationship between the steel corrosion rate and the exposure time. It is obvious that the steel corrosion rate increases when the exposure time increases.

4. Discussion

The major carbonation reaction [31] of RC structures can be expressed as

$$H_2O + CO_2 \leftrightarrow 2H^+ + CO_3^{2-}$$

 $H_2O + CO_2 \leftrightarrow HCO_3^- + H^+$
 $HCO_3^- \leftrightarrow CO_3^{2-} + H^+$
 $Ca(OH)_2 + 2H^+ + CO_3^{2-} \rightarrow CaCO_3 + 2H_2O_3^-$

The values of pH of concrete change from 13 to 14 to below 9 due to the above chemical reaction. Distinctly, the study of carbonation depth is very important to the corrosion time of calculating RC structures. One defines the time of O_2 reached on the steel surface as the occurring corrosion time of steel in concrete. Thus, one may employ Fick's second law of diffusion to predict the carbonation depth.

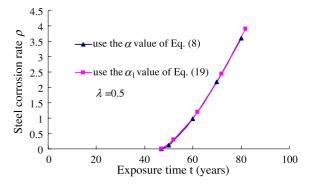


Fig. 4. Relationship between steel corrosion rate and exposure time.

The Fick second law of diffusion can be described as a onedimensional diffusion equation with initial and boundary conditions [32]

$$\frac{\partial C}{\partial t} = D_{0_2} \frac{\partial^2 C}{\partial x^2} \tag{17a}$$

$$C(x,0) = C_i (17b)$$

$$C(0,t) = C_{st}, C(c,t) = C_i$$
 (17c)

where C(x,t) is the O_2 concentration at depth x at time t, C_i is the initial O_2 concentration of the steel, C_{st} is the O_2 concentration on the steel surface and D_{O_2} is the diffusion coefficient of O_2 of steel in concrete.

Applying the Laplace transform to Eqs. (17a)–(17c), the particular solution [32] is

$$C(x,t) = C_{\rm i} + (C_{\rm st} - C_{\rm i}) \operatorname{erfc}\left(\frac{x}{\sqrt{4tD_{\rm O_2}}}\right)$$
 (18)

where erfc is the error function complement.

Tuutti [33], Guirguis [34] and Mallett [35] pointed out that a general expression for the carbonation depth of carbonation, D, to the concrete quality and exposure time, t, can be given in the from

$$x = D = \alpha_1 \sqrt{t} \tag{19}$$

where α_1 is related to the rate of carbonation and is dependent upon the properties of the concrete. Eq. (18) may be written as Eq. (19) with x=D and $\alpha_1 = \sqrt{4D_{\rm O_2}}erfc^{-1}\left(\frac{C-C_{\rm i}}{C_{\rm st}-C_{\rm i}}\right)$.

The concrete carbonation problem is described as a result of a chemical diffusion process due to O_2 penetrating into concrete. The O_2 concentration can be predicted by means of a linear diffusion equation. Consider the one-dimensional diffusion equation [32] with initial and boundary conditions [2,10,29]

$$\frac{\partial C}{\partial t} = D_{\rm O_2} \frac{\partial^2 C}{\partial x^2} - K_{\rm T} C \tag{20a}$$

$$C(x,0) = C_{i} \tag{20b}$$

$$C(0,t) = C_{\rm st}, C(c,t) = C_{\rm f} = C_{\rm i}$$
 (20c)

where $K_{\rm T}$ is a constant.

Putting $C = \bar{C}e^{-K_T t}$ [36], where \bar{C} is a new O₂ concentration variable and employing the Laplace transform method to Eqs. (20a)–(20c), one obtains an analytical solution [2,10,29]

$$C(x,t) = \left[C_{i} + \left(C_{st}e^{K_{T}t} - C_{i}\right)erfc\left(\frac{x}{\sqrt{4D_{O_{2}}t}}\right)\right]e^{-K_{T}t}$$
(21)

At a given time, the O_2 concentration at the depth of the carbonation $x=x_0$ ($x_0>c$) is equal to the value $C=C_0$. In this

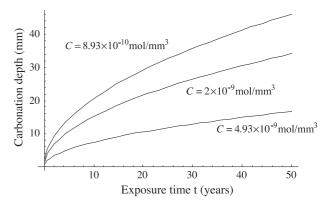


Fig. 5. Relationship between carbonation depth and exposure time using Eqs. (18) and (21).

situation, Eq. (21) can be written as Eq. (19) with $\alpha_2 = \sqrt{4D_{O_2}erfc^{-1}\left(\frac{Ce^{K_{T'}}-C_i}{Cst^{K_{T'}}-C_i}\right)}$.

It is very obvious that the values of α_1 and α_2 are equal if $C_i=0$.

In order to use Eq. (21), the first task is to determine the value of $e^{K_T t}$. If the chemical reaction is assumed to be a first-order reaction [37–39], one may write out

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -K_{\mathrm{T}}C\tag{22}$$

where C is the concentration of reactant.

A first-order reaction may be of the type [37]

$$X \rightarrow Y$$
 (23)

Assume that at the beginning of the reaction (t=0) the concentration of X is x_0 and that of Y is zero. If after time t the concentration of Y is y, that of X is x_0 –y. The rate of change of the concentration of Y is dy/dt, and thus for a first-order reaction

$$\frac{\mathrm{d}y}{\mathrm{d}t} = K_{\mathrm{T}}(x_0 - y) \tag{24}$$

Separation of the variables gives

$$\frac{\mathrm{d}y}{x_0 - y} = K_{\mathrm{T}} \mathrm{d}t \tag{25}$$

and integration gives

$$-\ln(x_0 - y) = K_{\rm T}t + Q \tag{26}$$

where Q is the constant of integration. This constant may be evaluated using the initial condition that y=0 when t=0; hence

$$-\ln x_0 = Q \tag{27}$$

The substitution of Eq. (27) into Eq. (26) yields

$$\ln \frac{x_0}{x_0 - y} = K_{\mathrm{T}}t$$
(28)

Eq. (28) can be written as

$$y = x_0 (1 - e^{-K_T t}) (29)$$

and as

$$e^{K_{\rm T}t} = \frac{x_0}{x_0 - y} \tag{30}$$

Eq. (30) shows that the concentration of reactant, x_0-y , decreases exponentially with time, from an initial value of x_0 to a final value of zero.

Suppose that C_i =0 mol/mm³ and C_s =8.93×10⁻¹⁰ mol/mm³. Fig. 5 shows the relationship between carbonation depth and exposure time using Eqs. (18) and (21). From Fig. 5, it was found that the concentration of O_2 decreases when the carbonation depth increases. It is also noteworthy to point out that the concentration of O_2 of Eq. (21) with considering the chemical reaction term decreases is the same as Eq. (18) does.

5. Conclusion

This study investigated the corrosion rate of steel in concrete due to the diffusion of dioxidation in concrete obeyed Fick's first law of diffusion. The following outcomes are reported herein: (1) The higher the steel corrosion rate is, the more the carbonation exponent increases. (2) The more the steel corrosion rate decreases, the more the steel diameter increases. (3) The higher the steel corrosion rate is, the more the concrete cover thickness decreases. (4) The more the steel corrosion rate increases, the more the exposure time decreases. Theories similar to these reported herein should be conducted using a wide variety of experiments.

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