Probability distribution and influence factors on corrosion initiation of reinforcing steel induced by chloride

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Abstract. Chloride-induced corrosion of steel in reinforced concrete structures is one of the major causes of their deterioration over time. Chlorides from de-icing salts or marine breeze penetrate through the concrete cover and break down the natural protective oxide layer formed around the reinforcements by the strong alkalinity of pore solution. As a matter of fact, the free chloride in concrete could not transport through reinforcing steel and accumulated at front point of reinforcing steel rapidly which made reinforcement corrosion initiation earlier. Therefore, the current studies on corrosion initiation might be hazardous without considering the obstruction action of reinforcing steel. In this paper, the Fick's second law was used to describe the free chloride concentration evolution in concrete and obstruction action of reinforcing steel was considered. The influences of the variability on boundary chloride concentration, thickness of concrete cover, and chloride diffusion coefficient on cumulative distribution of corrosion initiation of reinforcing steel were studied thoroughly. The obstruction of reinforcing steel gave much influence on corrosion initiation, especially for thinner concrete cover, higher concrete strength, and higher environmental temperature.

1. Introduction
Reinforced concrete (RC) structure was very commonly used due to its easy material resource, simplified preparation and low cost. Corrosion of reinforcing steel due to chloride ingress had been a critical issue for the durability design and construction of RC structures in marine environments. The high alkalinity of the concrete pore solution provided a protection of reinforcing steel in concrete against corrosion by forming a thin oxide layer so called passivation film. When the concentration of chloride ion on the reinforcing steel surface reached a threshold value called critical concentration, depassivation of reinforcing steel initiated and corrosion started to occur [1]. Chloride ingressed into concrete involved several transport processes such as diffusion (i.e., the motion of chloride ion within the pore solution caused by the concentration gradient), convection (i.e., the motion of chloride ion together with the pore solution within the concrete caused by the moisture gradient), capillary absorption and migration[2]. It was generally agreed that the governing mechanism was diffusion. So the Fick's second law and its general solution was widely applied in the estimation of initial corrosion time. However, it was presented based on the following assumptions: 1) concrete was a homogeneous material; 2) chloride ion didn’t react with the material; 3) the diffusion coefficient was constant; 4) there was no cracks in concrete. In
fact, these assumptions didn’t apply because of obstruction of reinforcing steel, the adsorption of cementing material in concrete and diffusion coefficient changing with the time and space. In this paper, finite element model was established to calculate corrosion initiation time.

2. Prediction model of the corrosion initiation time

2.1. Modelling chloride ingress

The 2-D ingress of chloride ion into saturated concrete due to diffusion can be described by the following partial differential equation [3-7]:

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left( D_x^* \cdot \frac{\partial C_i}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_y^* \cdot \frac{\partial C_i}{\partial y} \right)$$

(1)

$$D_x^* = \frac{D_x}{1 + \frac{\omega_e}{\omega_x} \frac{\partial C_i}{\partial C_i}}$$

(2)

$$C_i = C_b + \omega_e C_i$$

(3)

where $C_i$ was the free chloride ion concentration (kg/m$^3$ of pore solution), $C_i$ was the total chloride ion concentration (kg/m$^3$ of concrete), $C_b$ was the bound chloride ion concentration (kg/m$^3$ of concrete), $\omega_e$ was the evaporable water content (m$^3$ pore solution/m$^3$ concrete), $D_x^*$ was the apparent chloride diffusion coefficient, $D_x$ was the effective diffusion coefficient.

The effective chloride diffusion coefficient was considered depending on temperature, time, pore relative humidity and free chloride ion content

$$D_x = D_0 f(h) f_2(T) f_3(t) f_4(C_i^\alpha)$$

(4)

Where $D_0$ was the initial diffusion coefficient of concrete after 28 days of standard curing, it can be described by the following equation:

$$D_0 = 10^{2.40\sqrt{h} - 12.06}$$

(5)

2.2. Chloride binding capacity

To complete Equation. (2) the chloride binding capacity $\partial C_b/\partial C_i$ need to be determined. The binding capacity was the slope of a relationship between free and bound chloride ion in concrete. To describe chloride binding two isotherms were usually employed:

- Langmuir isotherm

$$C_b = \frac{\alpha L C_i}{1 + \beta L C_i}$$

(6)

and Freundlich isotherm

$$C_b = \alpha F C_i^{\beta F}$$

(7)

Where $\alpha_{L(F)}$ and $\beta_{L(F)}$ were binding constants, which were found by fitting the isotherms to experimental data using regression analysis. According to Tang and Nilsson [8], the Langmuir isotherm provided a better description when the concentration of free chloride ion in the pore solution was low (less than 1.773 kg/m$^3$ pore solution), while the Freundlich isotherm was better for higher concentration (starting from 0.355 kg/m$^3$). In this paper, the Freundlich isotherm was adopted, and the $\alpha_F=1.05$, $\beta_F=0.36$. 


2.3. Finite element modelling

The free chloride ion concentration on the surface of reinforcing steel placed in corner or middle of square cross-section was calculated through finite element model. Square cross-section of reinforced concrete components and chloride diffusivity schematic diagram was shown in Figure 1. The diameter of reinforcing steel was 25 mm, where c was the thickness of cover. The finite element model based on program the Comsol Multiphysics was established, the boundary concentration at exposed surface of concrete was fixed, and the boundary conditions of the other surface of concrete and reinforcing steel surface were insulated. Through the evolution of free chlorine ion concentration at point A, B, C and D with time and critical concentration, corrosion initiation time at each point can be estimated.

![Image](image_url)

Figure 1 Cross-section of reinforced concrete components and chloride diffusivity

3. The influence of the obstruction of reinforcing steel

In order to illustrate the influence on the chloride ion diffusion, a RC structure exposed to tidal/ splash zone after 100 years of service was simulated. Computational conditions used in the simulation were: surface chlorine ion concentration remained constant with time and equaled 88.75 kg/m³ of pore solution[9]; the capillary system of concrete had a very strong ability of absorbing water, for concrete exposed to tidal/ splash zone which frequently contacted with sea water, pore relative humidity was taken as 100%; concrete temperature was taken as 296.8ºK; evaporable water content was 8%; thickness of cover was 50mm; concrete strength was C50, the mixture proportion of concrete was shown in Table 1.

![Table](image_url)

|     | w/b | cement | fly ash | slag | fine aggregate | coarse aggregate | water | water reducing agent | expanding agent |
|-----|-----|--------|---------|------|----------------|-----------------|-------|---------------------|-----------------|
| C50 | 0.317 | 240 | 72 | 168 | 678 | 1107 | 152 | 4.5 |                  |
| C60 | 0.2915 | 293 | 114 | 142 | 585 | 1090 | 165 | 20 | 17.07              |

Contour line of free chlorine ion concentration was shown in Figure 2. On the chloride ion diffusion front direction, because of the obstruction of reinforcing steel, the chloride ion cannot continue to move forward and accumulated at front point of reinforcing steel. Compared to the same depth where reinforcing steel didn’t exist, the chloride ion concentration was higher.
Figure. 2 Contour of free chloride concentration for square cross-section

As shown in Figure 3, from Haikou bay to Dalian bay, the corrosion initiation time was 20.24% to 19.31% smaller for C50 concrete and 21.37% to 20.56% for C60 concrete. The equations of section 2.1 showed that the concrete temperature only affected diffusion coefficient. It was found that as the diffusion coefficient increases, the blocking effect becomes more significant.

4. Influence analysis of different parameters

The influence of COV of Cs, c, concrete strength and external environment on failure probability and durability service lives of RC structure by Monte Carlo method. The train sample of Kriging model was established by CCD method for each case, and 1000 sets of random numbers generated based on distributions of each influencing parameters were substituted into the model to estimate corrosion initiation time.

4.1. Coefficient of variation of surface chloride ion concentration

A C50 RC structure located at Haikou bay was simulated to analyze the influence of COV of surface chloride ion concentration on durability service life. The mean of thickness of concrete cover was 50mm. 1000 sets of random numbers were generated based on distributions of each influencing parameter for Monte Carlo simulation. The random numbers for Cr, D0, and c under two cases were identical. Empirical cumulative distribution functions of the random numbers about surface chloride ion concentration were shown in Figure 4. As can be seen, when COV=0.3, the range of surface chloride ion concentration was bigger.
4.2. Influence of concrete strength

The C50 and C60 RC structure exposed to splash and tidal zone located at Haikou bay was simulated to analyze the influence of concrete strength on durability service life. The mean of thickness of concrete cover was 70mm. The empirical cumulative distribution function of corrosion initiation time under the cases that the concrete strength was C50 and C60 were shown in Figure 5. As can be seen, during the whole service time, the failure probability of under the case that the concrete strength was C60 was smaller.

Figure 4 Empirical cumulative distribution for different COV

Figure 5 Empirical cumulative distribution for different concrete strength
4.3. The thickness of concrete cover

Increasing concrete cover was an intuitive way to significantly improve the durability service life of RC structure, as shown in Figure 6. However, the improvement was lesser at higher levels of concrete cover. Therefore, it might not be economic that improving the durability of RC structure by increasing concrete cover only. During design phase, synthetically considering the factors and finding out the best solution to reduce cost was necessary.

![Figure 6 Durability service life of concrete structure for different concrete cover](image)

(a) COV=0.3

(b) COV=0.1

4.4. The external environment

A C50 RC structure exposed to splash and tidal zone was simulated to analyze the influence of external environment on durability service life. The mean of thickness of concrete cover was 65mm. As can be seen, as the ambient temperature decreases, the probability of failure decreases. As shown in Figure 7, the durability life of concrete decreases with the increase of ambient temperature.

![Figure 7 Durability service life of concrete structure at point B and A for different bay](image)

(a) COV=0.3

(b) COV=0.1

5. Conclusion

In this paper, the influences of the variability on boundary chloride concentration, thickness of concrete cover, and chloride diffusion coefficient on cumulative distribution of corrosion initiation of reinforcing steel were studied thoroughly.

1. It was dangerous to ignore the obstruction of reinforcing steel for corrosion initiation time assessment, especially for thinner concrete cover, higher concrete strength, and higher diffusion coefficient.

2. The influence of COV of surface chloride ion concentration on durability service life was not obvious. Increasing thickness of concrete cover and concrete strength would significantly improve the
durability service life.

(3) For different external environment and exposed zone, the durability service lives were largely
different. As the ambient temperature increases, the durability life will be significantly shortened.

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