



# Study of depassivation of carbon steel in simulated concrete pore solution using different equivalent circuits



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## HIGHLIGHTS

- Depassivation process of reinforcing steels subjected to chloride is investigated.
- Chloride threshold value has been obtained by electrochemical monitoring methods.
- Basic principles to determine the best fitted equivalent circuits were established.

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## ABSTRACT

Depassivation and corrosion of reinforcing steels submitted to chloride in simulated concrete pore solution was studied with electrochemical methods. Measurements included half-cell potential (HCP), linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). Three different equivalent circuits, i.e.,  $R(QR)$ ,  $R(QR)(QR)$  and  $R(Q(R(QR)))$ , were proposed to fit and elucidate the EIS data, respectively. Results showed that large-scale depassivation and corrosion of steel occurred when chloride content exceeded 0.05 mol/L. All the three equivalent circuits revealed a good fitting degree of Nyquist plots at early stage, while only circuit  $R(Q(R(QR)))$  still retained a most appropriate fitting at severe corrosion stage, of which the chi-square ranged from  $3.1E-4$  to  $8.5E-4$  throughout the whole exposure test. Verification could be obtained that circuit  $R(Q(R(QR)))$  with two time constants was effective to fit and explain the depassivation process in regard to steel corrosion induced by chloride in simulated concrete pore solution.

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## 1. Introduction

Reinforcing steels in cementitious materials normally maintains immune to corrosion due to the thin passive film attributed to the high degree of alkalinity of hydrated cement and concrete. The passive film is considered to be around 20 nm thick and mainly consists of an inner layer rich in  $Fe^{II}$  oxides/oxyhydroxides and an outer layer containing  $Fe^{III}$  oxides/oxyhydroxides [1,2]. Depassivation or breakdown of passive film occurs when carbonation and/or chloride ingress take place to a certain extent. In scenario of chloride, it is believed that once the chloride content at the steel surface reaches chloride threshold value (CTV), with moisture and oxygen in presence, rapid localized corrosion of steel is initiated [3–6]. An accurate determination and a good understanding of the depassivation process of reinforcing steel together with the

CTV is of great importance for better clarifying corrosion behavior, assessing durability issues and predicting residual service life of reinforced structures. Researchers performed numerous investigations regarding CTV [7–11], but no consensus has been reached either on the experimental configuration or on the expression of CTV itself. For example, CTV in terms of total chloride or acid-soluble chloride in concrete ranged from 0.04% to 8.34% (bw%) and from 0.07% to 1.16% (bw%) expressed by free chloride or water-soluble chloride [12].

It should be noted that the large scatter of reported values of CTV is due to many influencing factors such as steel type, experiment setup, concrete mix, moisture availability and so forth [13–15]. Therefore, many researchers have conducted tests in a saturated  $Ca(OH)_2$  solution ( $pH \approx 12.5$ ) [16–18] as a simulated concrete pore solution. Apart from the reduction in experiment time, a good reproducibility and representativeness could also be ensured and thereby provide significant results for cementitious materials.

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Equivalent circuits have been widely adopted as an effective approach to simulate and interpret electrochemical impedance results. The simple equivalent circuit of R(QR) is a modified Randles circuit [19] where a pure capacitance is replaced by a constant phase element. While Yuan [20] utilized  $R_s(R_{ct}Q_{dl})(R_fQ_f)$  to simulate corrosion process of 304 stainless steel and attribute the resistance at high frequency to charge transfer resistance, researchers [21–23] have assumed that charge transfer resistance is associated with the time constant at low frequency. The equivalent circuit of R(QR(QR)) was used to investigate the corrosion behavior of duplex stainless steel [24] and corrosion of coated steels [25]. However, a detailed comparison between different equivalent circuits needs to be discussed with regard to fitting degree and physical meaning of each circuit element.

In the present work, the depassivation process of carbon steel was investigated and the electrochemical impedance results were analyzed using three different equivalent circuits. The fitting degree between measured data and the proposed simulation circuit was evaluated by Chi-square value method. Additionally, the physical meaning of each component obtained by different equivalents was tried to be explained.

## 2. Experimental program

### 2.1. Specimen preparation and exposure conditions

Steel specimens with a diameter of 16 mm and length of 10 mm were cut from carbon steel rod. Chemical composition of steel samples (by weight) was 0.20% C, 0.55% Si, 1.42% Mn, 0.028% S, 0.026% P and the balance Fe. One cross-section surface was polished to grade 1000 as exposure surface, degreased in acetone and then washed in distilled water. The remaining surface was sealed by epoxy resin. A wire was soldered to the other cross-section surface for electrochemical testing.

The saturated  $\text{Ca}(\text{OH})_2$  solution was prepared using distilled water with some insoluble  $\text{Ca}(\text{OH})_2$ . NaCl was added to saturated  $\text{Ca}(\text{OH})_2$  solution stepwise, 0.01 mol/L each day. All chemical reagents applied were analytical reagent grade.

### 2.2. Electrochemical techniques

All steel samples were immersed in saturated  $\text{Ca}(\text{OH})_2$  solution for ten days to obtain stable pre-passivation before adding NaCl. After a sufficiently steady condition was achieved, electrochemical tests were performed using PARSTAT4000 immediately before addition of NaCl each day. A classic three-electrode system was adopted with steel sample being working electrode, a saturated calomel electrode (SCE) and a platinum electrode as reference and counter electrode, respectively. The  $I_{\text{corr}}$  as an index of corrosion current density was usually calculated by linear polarization based on the Stern–Geary method [26] as in Eq. (1)

$$I_{\text{corr}} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \frac{1}{R_p} = \frac{B}{R_p} \quad (1)$$

where  $I_{\text{corr}}$  is the corrosion current density,  $R_p$  the polarization resistance,  $B_a$  constant related to  $\beta_a$  and  $\beta_c$ , the anodic and cathodic slopes of Tafel curve, respectively. Though  $B$  is usually assumed to vary from 26 mV to 52 mV [27], a value of 26 mV was used in present study. The  $R_p$  was obtained directly by built-in software and the exposed area of nearly  $2.0 \text{ cm}^2$  was used as an input parameter. EIS test was performed with a perturbation amplitude 10 mV and a frequency range of  $10^5$ – $10^{-2}$  Hz. HCP was determined after stable open circuit potential was achieved. In LPR tests, reinforcing steels were polarized to  $\pm 10$  mV at  $E_{\text{corr}}$  with a scan rate of 10 mV/min.

## 3. Results and discussion

### 3.1. HCP and corrosion current density

A series of identical steel samples with adequate pre-passivation are submitted to chloride added stepwise by 0.01 mol/L each day. The evolutions of half-cell potential ( $E_{\text{corr}}$ ) are presented in Fig. 1. It can be seen that the average  $E_{\text{corr}}$  of specimens after ten days of pre-passivation reads around  $-230$  mV vs. SCE. With increasing concentrations of chloride, the  $E_{\text{corr}}$  decreases gradually and shifts to more negative values, which implies a higher corrosion risk. Then a noteworthy drop of  $E_{\text{corr}}$  occurs when the chloride content reaches 0.05 mol/L. This dramatic drop of open circuit potential is supposed to be indicative of relatively large scale breakdown of passive film and initiation of active corrosion. Samples subjected to chloride above 0.05 mol/L should be the most prone to corrosion, with respect to those with lower chloride concentrations. It should be noted that the scatter of  $E_{\text{corr}}$  values among the samples is a consequence of the stochastic nature of passive film.

While corrosion thermodynamics is reflected by  $E_{\text{corr}}$ , reaction kinetics of passive film could be further understood with  $I_{\text{corr}}$  changes depicted in Fig. 2.  $I_{\text{corr}}$  keeps between  $0.25 \mu\text{A}/\text{cm}^2$  and  $0.40 \mu\text{A}/\text{cm}^2$  at low chloride concentrations. However, once chloride exceeds 0.05 mol/L,  $I_{\text{corr}}$  increases to values greater than  $0.97 \mu\text{A}/\text{cm}^2$ . The calculated  $I_{\text{corr}}$  is an average corrosion rate, while the specific corrosion current density in corrosion pit could be several times higher [8]. From abovementioned evolution of  $E_{\text{corr}}$  and  $I_{\text{corr}}$ , the CTV could be assumed to be in the vicinity of 0.05 mol/L in simulated concrete pore solution.

Another commonly used expression of chloride threshold value is  $\text{Cl}^-/\text{OH}^-$  molar ratio, which means free chloride versus hydroxyl ion in the concrete pore solution.  $\text{Cl}^-/\text{OH}^-$  could reflect corrosion risk induced by either chloride or carbonation effect in reinforced concrete structures. Based on the simulated concrete pore solution of saturated  $\text{Ca}(\text{OH})_2$  in this study, a sudden drop of  $E_{\text{corr}}$  and a noteworthy increase in  $I_{\text{corr}}$  occurred when  $\text{Cl}^-/\text{OH}^-$  ratio reached in between 1.12 and 1.34, of which the chloride contents were 0.05 and 0.06 mol/L, respectively.

### 3.2. EIS analysis

#### 3.2.1. Nyquist plot and data fitting

The typical EIS plot in Nyquist format is shown in Fig. 3. Topology evolution of Nyquist plots also reveals substantial information about the depassivation process of steels [6,11]. Theoretically, the

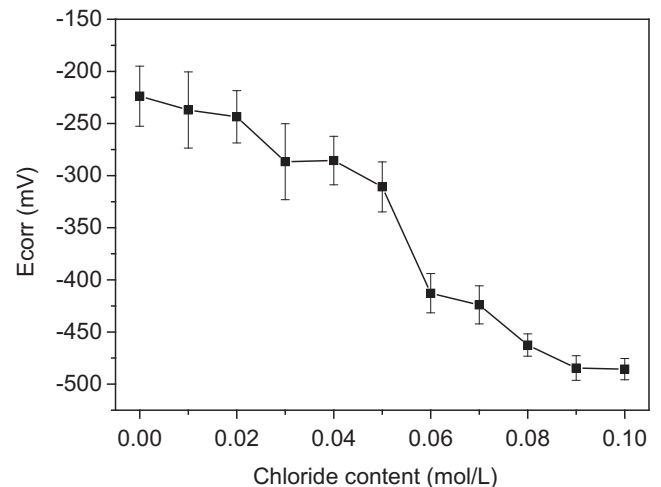


Fig. 1. Evolution of  $E_{\text{corr}}$  with increasing chloride concentrations.

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