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Electrochemical Behavior of Steel Bar in Electrolytes: Influence of pH Value and Cations

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Abstract: Steel bar corrosion on electrolytes and the influence of cation were investigated. Three electrolytes of $Ca(OH)_2$, NaOH and KOH with pH levels of 12.5, 11.5, 10.5, 9.5, 8.5 were prepared, meanwhile, the methods of free corrosion potential and electrochemical impedance spectra (EIS) were used to evaluate the influence of cations on the depassivation of the steel bar in electrolytes. The experimental results indicate that the initial corrosion pH value of the steel bar is influenced by the cation in electrolyte and the influence of K^+ in electrolyte is the most remarkable, followed by Na^+ and Ca^{2+}. The initial corrosion pH values are 10.5 in KOH electrolyte, 9.5 in NaOH electrolyte and lower than 8.5 in $Ca(OH)_2$ electrolyte.

Key words: steel bar corrosion; cation; pH value

1 Introduction

Apart from structural design failures, corrosion of steel bar is an important cause of concrete degradation[1]. It is well known that the steel bar in concrete is normally in a passive state against corrosion due to a thin iron oxide layer by the high alkaline environment of the concrete pore solution. Carbonation itself does not cause the deterioration of concrete, but it changes the pH of the pore solution in the concrete[2]. When the acidification of the concrete pore solution causes by carbonation breaks the passive layer of the steel bar, the corrosion of steel bar is initiated.

Although the corrosion behaviors of reinforcing steel were extensively studied[3-6], the exact mechanism of steel corrosion caused by decreasing pH and cations is unclear yet. Steel bar corrosion has been largely studied in simulated solution, such as saturated $Ca(OH)_2$ solution or admixture solution by $Ca(OH)_2$, NaOH and KOH are often used as simulated solution. The pH and chemical compositions of the pore solution, which mainly contains cations of Na^+, K^+, Ca^{2+}, are the important causes of steel corrosion during carbonation process. But there were only a few researches about the steel corrosion caused by decreasing pH and cations[7-10]. Thus, further study of the decreasing pH and cation influencing the steel corrosion is needed.

We focused on steel corrosion influenced by the decreasing pH and cation in electrolytes. The steel corrosion with different pH values was detected by the methods of free corrosion potential and electrochemical impedance spectra (EIS).

2 Experimental

2.1 Electrodes

A three electrodes device system was used for all experiments. A cylindrical steel bar with a diameter of 10 mm and length of 6 cm was used, with chemical composition (in% by mass) of 0.22% C, 0.30% Si, 0.65% Mn, 0.05% S, 0.045% P and the residual Fe, as working electrode. The steel bars were polished (with emery paper) then rinsed in distilled water (18 M) and then degreased in acetone. Finally, steel bars were exposed to the various electrolytes. The saturated calomel electrode and platinum electrode were connected to work as a reference and auxiliary electrode, respectively.

2.2 Electrolytes

Saturated calcium hydroxide solution, 0.1 M of sodium hydroxide solution and 0.1 M of potassium hydroxide solution were used as electrolytes. They were prepared with deionized water (18 M). The pH of the electrolytes were adjusted by pumped in CO_2. The

pH levels of the electrolytes were 12.5, 11.5, 10.5, 9.5, 8.5, respectively.

2.3 Tests in the simulated solution

The lateral surface of the steel bar had an exposed area of 2 cm^2, and the remaining areas were sealed by epoxy resin. Prior to electrochemical measurement, the steel bars were immersed in the saturated calcium hydroxide for 3 days to produce the passivating film on their surfaces[11]. Then steel samples were immersed in the electrolytes for 5days. Finally, the free corrosion potential (E_{corr}) and EIS were used to study the steel corrosion.

However, the EIS in the frequency range from 10 MHz to 100 kHz was performed. Moreover, the perturbing signal applied was 5 mV. The polarization resistance (R_p) obtained by EIS was introduced into the Stern-Geary equation to calculate the corrosion current (I_{corr}). The Stern–Geary equation is: $I_{corr} = B/R_p$. At this time, the Stern-Geary constant B was considered to be 26 mV. Furthermore, considering the pH threshold value as the pH value where the corrosion current density of steel bar is higher than 1 mA/m$^{2[12]}$.

3 Results and Discussion

The EIS spectra of the steel bars in electrolytes are complex. The EIS spectra of the steel bars in electrolytes can be divided to two parts: high frequency region, low frequency region. Nyquist plot of EIS for the steel bar in electrolyte in this work, shown in Fig.1, is representative.
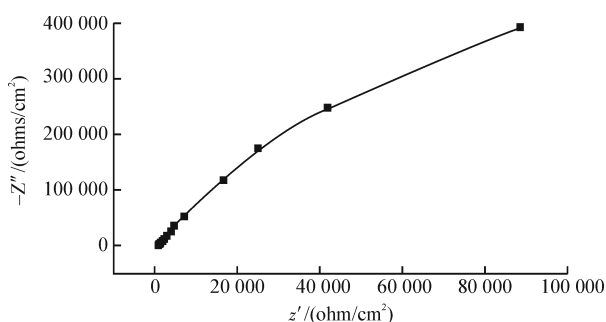

Fig.1 Representative Nyquist plot for the steel bar in electrolyte

The high frequency region (10^5-10 Hz range) are related to the dielectric properties of a layer often formed on the steel surface and reputed to be constituted by corrosion products[13]. The low frequency region (lower than 10 Hz) are related to the Faradaic corrosion process occurring on the embedded steel electrodes[14].

The complete equivalent-circuit molde simulating

the EIS spectra is shown in Fig.2, where, R_s is the electrolyte resistance electrolytes. Besides, the constant phase element (Qdl) is associated with the fractal nature of the electrode interface or heterogeneity of the steel surface[12] and R_p is the polarization resistance. The Qdl (CPE) can be calculated by the equation: YCPE =Y0(iw)n, where *n* generally ranges between 1 and 0.5. The frequency range from 10 MHz to 10 Hz was chosen in this study in order to obtain the polarization resistance[15].
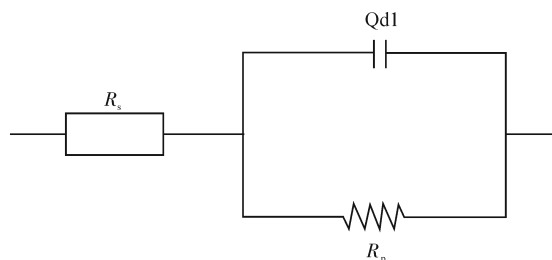

Fig.2 Equivalent circuit for the EIS simulation of steel bar in electrolyte

The Nyquist plot for the steel bars in electrolytes with different pH values are shown in Fig.3. From these curves, polarization resistances were calculated by the equivalent circuit. The free corrosion potentials (E_{corr}) and polarization resistance (R_p) for all the samples are shown in Table 1. Generally, R_p decrease with the decrease of the pH values, which shows an upgraded risk of corrosion for the steel in electrolyte. However, the samples with an identical pH value display a different polarization resistance, comparing

Table 1 The free corrosion potentials (E_{corr}) and polarization resistance (R_p) obtained by electrochemical impedance spectra (EIS) for all the samples

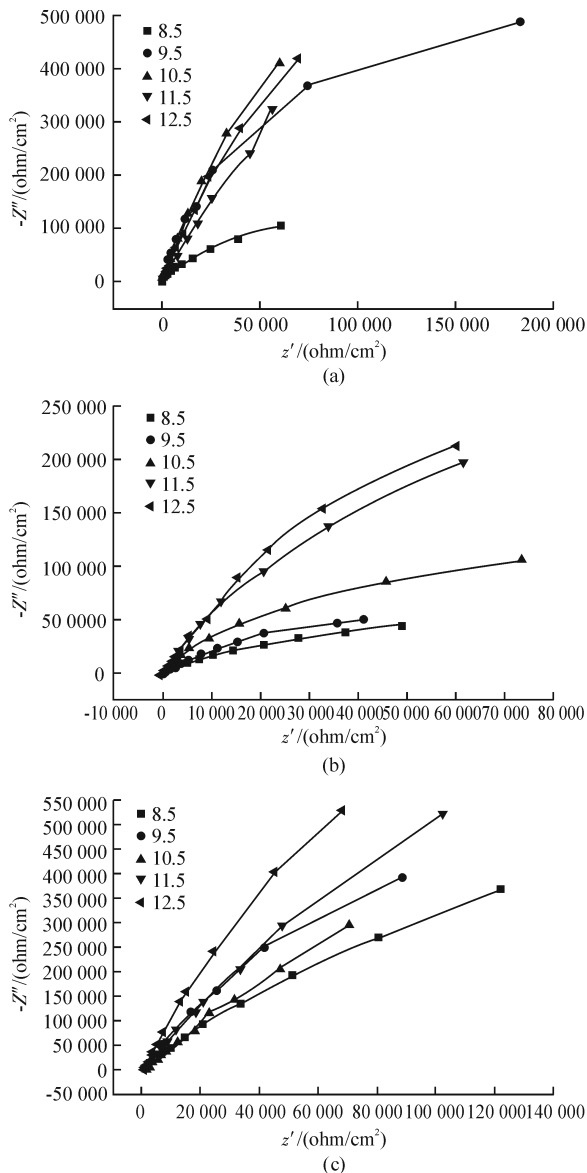|	pH value	Polarization resistance /R_p	Corrosion potential /E_{corr}
Ca(OH)$_2$	8.5	2.20E+06	−192
	9.5	3.06E+06	−159
	10.5	4.84E+06	−188
	11.5	6.86E+06	−168
	12.5	7.27E+06	−175
KOH	8.5	1.13E+05	−229
	9.5	1.90E+05	−249
	10.5	2.97E+05	−277
	11.5	1.17E+06	−218
	12.5	1.44E+06	−305
NaOH	8.5	4.00E+05	−340
	9.5	1.75E+06	−140
	10.5	5.11E+06	−120
	11.5	7.45E+06	−140
	12.5	8.17E+06	−154

Figs.3 (a) Nyquist plot for the steel bar in NaOH electrolyte for different pH levels; (b) Nyquist plot for the steel bar in KOH electrolyte for different pH levels; (c) Nyquist plot for the steel bar in Ca(OH)$_2$ electrolyte for different pH levels

with the electrolytes. The sudden shifts of R_p at pH 9.5 in NaOH electrolyte and at pH 10.5 in KOH electrolyte are clearly indicated, respectively. It shows that the passive layer of steel in electrolyte may be destroyed. However, no sudden shift of polarization resistance is clearly indicated in Ca(OH)$_2$ electrolyte.

The corrosion current densities for the steel bars were obtained by introducing the polarization resistances (shown in Table 1) into Stern–Geary equation, plotted with pH values, as shown in Fig. 4. Furthermore, considering the pH threshold value of steel corrosion as the pH value where the corrosion current density of steel bar is higher than 1 mA/m^2, the pH threshold value in KOH electrolyte is 10.5. The corrosion current densitie for the steel bar suddenly

changed at the pH 9.5 in the NaOH electrolyte, which indicates that corrosion for the sample may happen at pH 9.5. The corrosion current densities for the steel bar in Ca(OH)$_2$ electrolyte are lower than 1 mA/m^2, which indicates that no corrosion for all the samples happens. The pH threshold value of steel corrosion in Ca(OH)$_2$ electrolyte may lower than 8.5.
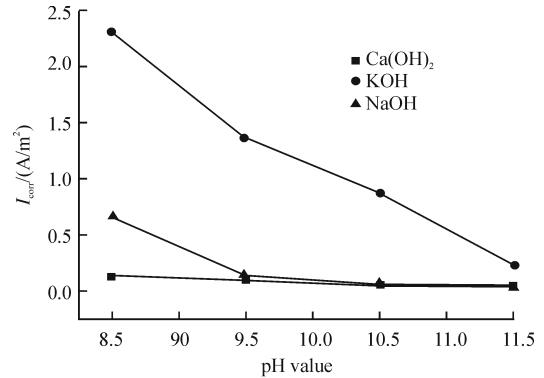

Fig.4 Corrosion current densities changed with the pH values for the samples in electrolytes, obtained by EIS
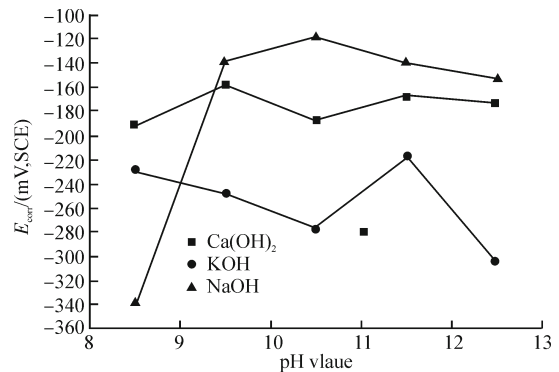

Fig.5 Free corrosion potentials for all the samples changed with the increase of pH values in the electrolytes

The free corrosion potentials for all the samples have been plotted with the pH values in electrolytes are shown in Fig.5. The free corrosion potentials in Ca(OH)$_2$ electrolyte are more positive than -200 mV SCE, according to ASTM C-876, which indicates that no corrosion for all the samples happens at this time. It is agree with the conclusion from EIS. The free corrosion potential suddenly changed at the pH 9.5 in the NaOH electrolyte, which indicates that corrosion for the sample may happen. The Free corrosion potentials in KOH electrolyte are in the range of -200 to -350 mV SCE, according to ASTM C-876, which suggests the possible occurrence of active corrosion for them.

From the above results, the initial corrosion pH value of the steel bar is influenced by the cation in electrolyte. It can conclude that the initial corrosion

pH values of the steel bar decided by two different detection methods keep identical in electrolytes. The cation of K^+ influenced the initial corrosion is largest, then followed by Na^+ and Ca^{2+}. The initial corrosion pH values of the steel bar in NaOH electrolyte and in KOH electrolyte are lower than 9.5. This is not in accordance with the Pourbaix diagram of iron (Fe/H_2O). Previous results of the literature indicate that the transition conditions depend probably not only on the pH but also on the carbonate content of the interstitial solution. The initial corrosion pH value of the steel bar in $Ca(OH)_2$ electrolyte is lower than 8.5 which may due to the factor that the steel bars were immersed in the saturated calcium hydroxide for 3 days to produce the passivating film on their surfaces. It means that the carbonation products may influence the initial corrosion pH value.

4 Conclusion

Three electrolytes with different cations and pH levels were presented in this paper. The initial corrosion pH values are 10.5 in KOH electrolyte, 9.5 in NaOH electrolyte and lower than 8.5 in $Ca(OH)_2$ electrolyte. The results have indicated that the initial corrosion pH value of the steel bar is influenced by the cation in electrolyte and the influence of K^+ in electrolyte is largest, followed by Na^+ and Ca^{2+}.

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