

Threshold Chloride Concentration of Stainless Steels in Simulated Concrete Pore Solution

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ABSTRACT

To evaluate whether stainless steel can replace carbon steel as rebar in reinforced concrete structures exposed to aggressive environment, the threshold chloride concentration of carbon steel, austenitic and duplex stainless steels were experimentally studied in this paper. The solutions with pH ranging from 9.5 to 13.6 were used herein to simulate the pore liquids in both alkaline and carbonated concretes. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests were carried out in the solutions with chloride concentration ranging from 0 to 5.0M and at a temperature around 25°C. The activation of pitting corrosion was determined when corrosion current increased and polarization resistance decreased significantly. The test results show that the pH value has a great effect on the evolution of the film resistance, and stainless steels have much higher corrosion resistance than carbon steel subjected to chloride environments.

1. INTRODUCTION

Reinforced concrete (RC) structure is one of the most useful and economical structures in the world. However, the deficiency of durability becomes a weakness of conventional RC structure, especially in the severe corrosion conditions such as ocean, de-icing, or other chloride-contaminated environment. On the surface of steel, there is a protective, thin oxide layer formed in high alkaline media (Gancedo, Alonso, Andrade, & Gracia, 1989), which can be broken by chloride ions at a certain concentration. Fresh concrete can provide a high alkaline environment in the concrete pores, benefitting the form of this passive film. However, when the concrete is completely carbonated, the pH value of pore solution will drop to 9.5 or so, and the film of steel will not be stable any longer and starts to dissolve, leading to steel activation.

To resolve the corrosion problem, cathodic protection and the use of stainless steel reinforcements seem to be the most reliable solutions to guarantee the durability of RC structure existing in the aggressive environments (Castro-Borges et al., 2002; Knudsen, Jensen, Klinghoffer, & Skovsgaard, 1998). Using stainless steels can essentially improve the corrosion resistance of embedded bars, because the alloy elements of chromium, nickel, and molybdenum can form a more stable oxide layer protecting the metallic matrix beneath the film away from chloride corrosion. However, the increasing cost during the construction phase limits its use (Fajardo, Bastidas, Criado, Romero, & Bastidas, 2011), although it is a more economical alternative assessing from the life cycle cost.

Stainless steel is more passive but susceptible to localized corrosion in the presence of chloride ions (Freire, Carmezim, Ferreira, & Montemor, 2011). This is why most of the studies were conducted to figure out the corrosion behavior of stainless steel bars embedded in concrete or submerged in simulated pore solution. The first study on the corrosion behaviors of stainless steel reinforcements in chloride-contaminated concrete were carried out in the 1970s. And after 10 years of exposure, the stainless steel had not corroded, even in the highest chloride content (Bertolini, Bolzoni, Pastore, & Pedferri, 1996).

Recently, numerous studies were explored to discuss the stainless steel at many aspects. Freire et al. (2011) focused on the corrosion behavior of AISI304 in simulated pore solutions with different pH and chloride concentration. The results showed that the pH played an important role in the evolution of the film resistance and charge transfer process. Bertolini et al. (1996) studied the influence of carbonation on the critical chloride concentration. They found that higher temperature would decrease the critical value; however, the results are opposite in the solutions with high carbonate/bicarbonate concentration which showed an inhibitive effect to the corrosion. Furthermore, Kouřil, Novák, and Bojko (2010) figured out the relationship between the superficial state of the steel and the corrosion resistance, which confirmed that the scaled surface had lower resistance even for the most alloyed stainless steels.

As discussed above, most of the researches focused on the difference of corrosion resistance between stainless steels, but few of them considered the exact

value of threshold chloride concentrations. The main objective of this study is to figure out the critical chloride value, so that the stainless steel bars can be used in an appropriate situation. Two stainless steels (austenitic type 316 and duplex type 2205) and one carbon steel (HRB400) have been electrochemically characterized in simulated pore solutions to accomplish this aim.

2. EXPERIMENTAL PROGRAMME

Cylinder samples with a length of 1.5 mm were obtained from each kind of steel reinforcement. The side and one cross-section of the sample were covered by epoxy, and another cross-section was polished as working electrode. A three-electrode system was set up when other two electrodes were incorporated and acted as counter electrode (Platinum electrode) and reference electrode, respectively. The potential of working electrode was obtained referring to the saturated calomel electrodes (SCE). The chemical compositions of the stainless steels with the diameter of 12 mm are shown in Table 1.

Table 1. Chemical composition of steels.

Compo- sition	C	Mn	P	S	Si	Cr	Ni	Mo
HRB400	≤0.25	≤1.6	≤0.045	≤0.045	≤0.8	–	–	–
316	≤0.08	≤2.0	≤0.035	≤0.03	≤1.0	16– 18.5	10– 14	2–3
2205	≤0.03	≤2.0	≤0.030	≤0.02	≤1.0	22– 23	4.5– 6.5	3– 3.5

Three pH values were selected to simulate different status of concrete pore solutions:

- (i) 0.1M Na₂CO₃ and 0.2M NaHCO₃ with a pH value of 9.5, simulating completely carbonated concrete;
- (ii) 0.01M Ca(OH)₂ and 0.03M NaOH with a pH value of 12.6, simulating fresh concrete;
- (iii) 0.01M Ca(OH)₂ and 0.4M NaOH with a pH value of 13.6, simulating the concrete with a high alkali content.

All solutions were prepared with deionized water. Chloride ions would be added into the solutions with concentrations of 0–5.0M after the samples were submerged in solutions about 5 days; at this moment, the passive film of samples had formed completely.

An electrochemical test system, named Gamry Reference 600, was used to conduct the electrochemical experiments. As two important electrochemical parameters, the corrosion current and the polarization resistance, indicating the initiation of corrosion, can be figured out through potentiodynamic

test and EIS test, respectively. Both tests were carried out at a room temperature around 25°C.

The potentiodynamic test began at a potential of –70 mV (vs. Eoc) and stopped at +70mV (vs. Eoc). The scan rate was 0.15 mV/s. The EIS test was carried out in the frequencies from 10⁶ to 10^{–3} Hz. The former test was performed per 10–12 h before the addition of chloride ions. After the addition of chloride ions, both tests were carried out once per day.

The polarization curves were fitted by the software of Gamry Echem Analyst, and the EIS curves were fitted by Zsimp Win.

3. RESULTS AND DISCUSSIONS

The impedance data of EIS had been modeled using the equivalent circuits, as illustrated in Figure 1. Both capacitors in the figure had been modeled as constant phase element (CPE), which represented the double layer formed on the material surface. A CPE unit was often used instead of an ideal capacitor to account for a non-ideal capacitive response from the steel/electrolyte interface. The equivalent circuit had also been used by other authors to simulate the chemical behavior of passive layer in chloride-contaminated solutions.

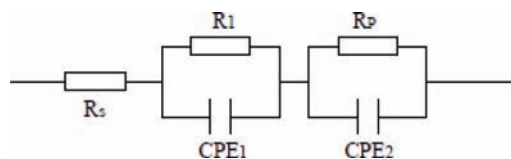


Figure 1. Equivalent circuit for EIS fitting.

The meanings of the circuit components are different. R_s represents the ohmic resistance of the electrolyte at high frequencies. The medium-frequency time constants (R_1 and CPE_1) seem to be related with a redox reaction on the steel surface. At low frequency, the time constants (R_p and CPE_2) represent the charge transfer process, and R_p is considered as the polarization resistance. Furthermore, the R_p correspond with corrosion intensities (i_{corr}) is similar to the i_{corr} obtained from potentiodynamic test (Blanco, Bautista, & Takenouti, 2006).

Figures 2 and 3 show the polarization resistance (R_p) and the corrosion current (i_{corr}) of austenitic stainless steel 316 subjected to various chloride concentration solutions. It can be seen that after immersion the value of i_{corr} dropped slightly, while the corrosion initiated, the i_{corr} increased significantly, just as the case of chloride content increasing from 1.0 to 3.0M at the pH value of 12.6, as shown in Figure 3. At the same time, the value of R_p decreased suddenly. It can

be concluded that the critical chloride concentration at pH 12.6 was in the range of 1.0–3.0M. However, there were no obvious changes at the pH values of 9.5 and 13.6; therefore, the critical value in these two conditions can be deemed as more than 5.0M. Moreover, the value of R_p maintained in the magnitude from 10^5 to 10^6 ohm, and the value of i_{corr} maintained in the magnitude from 10^{-8} to 10^{-7} A.

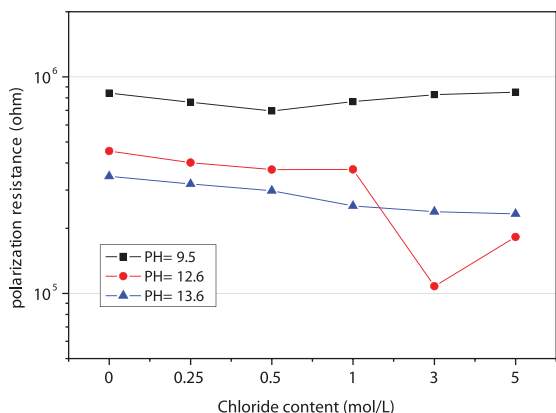


Figure 2. Influence of pH value and chloride contents on the value of R_p for austenitic stainless steel 316.

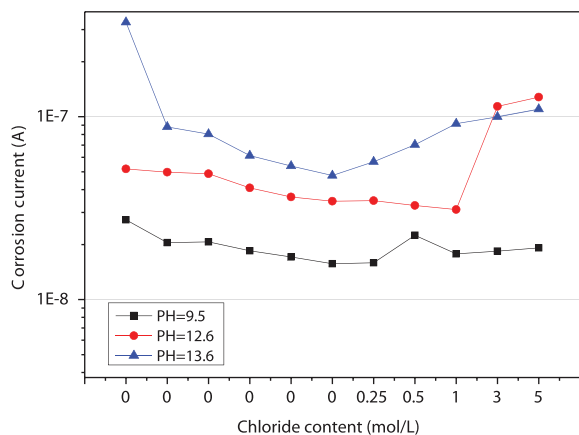


Figure 3. Influence of pH value and chloride contents on the value of i_{corr} for austenitic stainless steel 316.

Figures 4 and 5 showed the value of R_p and i_{corr} of duplex stainless steel 2205 subjected to various chloride concentration solutions. At pH 12.6, the value of R_p decreased at the first level of chloride content, while i_{corr} increased a lot as well. Thereby, the critical chloride concentration for 2205 at this pH value ranges from 0 to 0.25M. Similarly, at pH 9.5, the critical chloride concentration lies in the range of 0.25–0.5M. The results of polarization resistance at pH 13.6 were not presented in Figure 4, for the reason that the curves were almost linear, which will result in great errors of fitting results. The original curves were displayed in Figure 6. No sharp reduction in the

diameters of circular arcs means no pitting corrosion in the steel. It can also be found that the R_p of 2205 varied in the magnitude from 10^4 to 10^6 ohm, and the value of i_{corr} stabilized around the magnitude of 10^{-7} A.

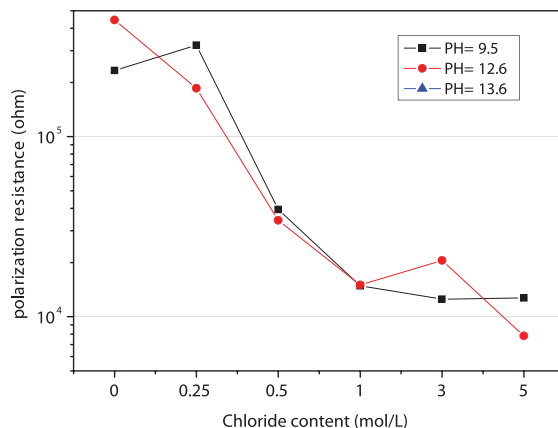


Figure 4. Influence of pH value and chloride contents on the value of R_p for duplex stainless steel 2205.

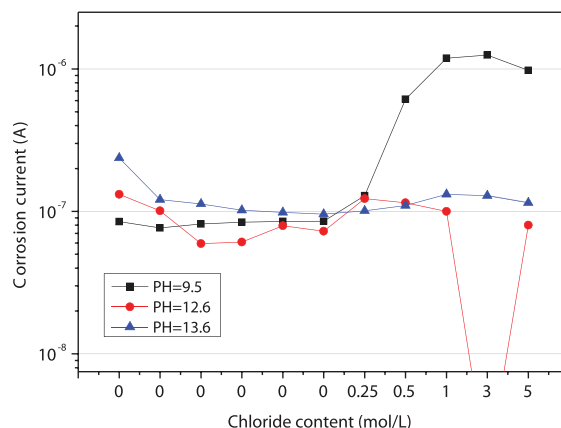


Figure 5. Influence of pH value and chloride contents on the value of i_{corr} for duplex stainless steel 2205.

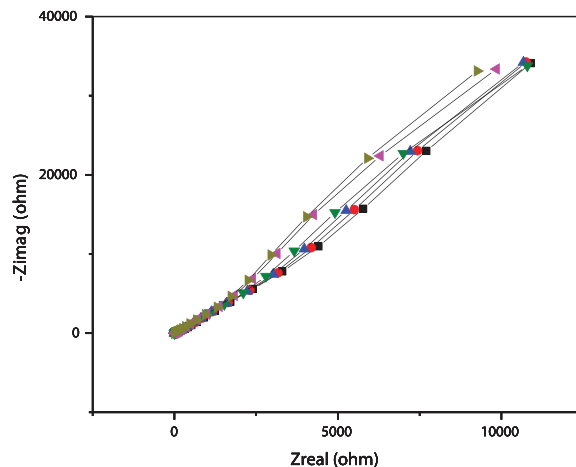


Figure 6. Nyquist chart in EIS test for duplex stainless steel 2205 at the pH value of 9.5.

The results of HRB400 were presented in Figures 7 and 8. The chloride content increased from 0.05 to 0.35M with an increment of 0.05M. In the solutions of pH 12.6 and 13.6, the critical chloride concentrations were lower than 0.05M, those was different with that at pH 9.5. At this pH value, the corrosion did not happened even the chloride content was up to 0.35M. At the pH values of 12.6 and 13.6, the values of R_p were in the range of 10^4 – 10^5 ohm, and i_{corr} was around the value of 10^{-6} A. Compared with the results of R_p and i_{corr} of stainless steels, it is obvious that the carbon steel has the lowest corrosion resistance.

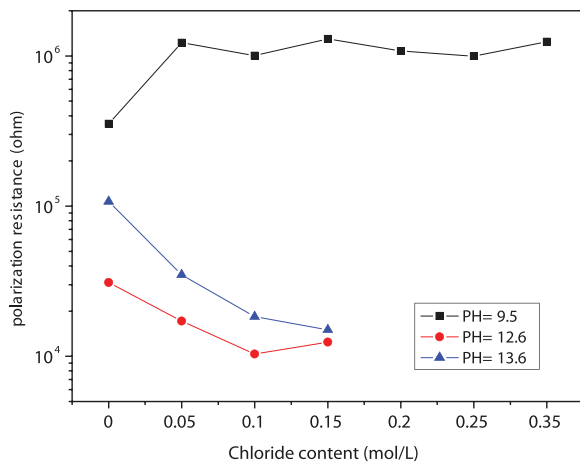


Figure 7. Influence of pH value and chloride content on the value of R_p for steel HRB400.

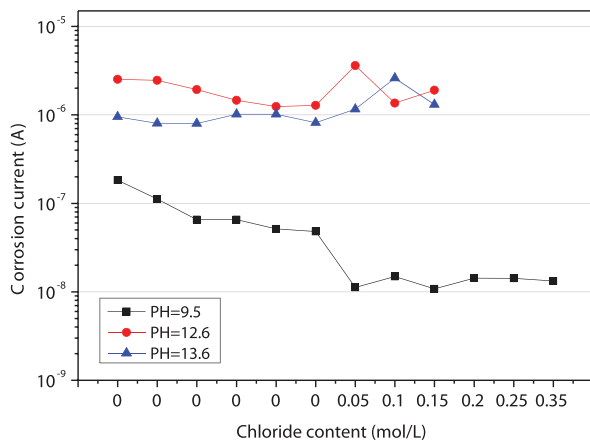


Figure 8. Influence of pH value and chloride content on the value of i_{corr} for steel HRB400.

Concluded from the test results, the stainless steels behaved much better than the carbon steel, those can be employed in the RC structures under chloride environment. The chromium content in the 2205 is higher than 316, which means the corrosion resistance of 2205 should be better

theoretically. However, the austenitic stainless steel 316 performed better than the duplex stainless steel 2205 in this study. It can be seen that the nickel content is only half of the content of 316, maybe it is the reason for the lower resistance of 2205 (Addari, Elsener, & Rossi, 2008). More experiments about the contribution of alloy to the corrosion resistance of these two stainless steels are needed in the future.

The corrosion behaviors of three steels evidenced the influence of pH on the critical chloride concentration except for pH 9.5. With the increase of pH value, the film formed on the surface of steel became more stable, which enhanced the threshold chloride concentration as well. However, the critical values at pH 9.5 were higher than those at pH 12.6. Blanco et al. (2006) reported a similar result, but with no explanation. Bertolini et al. (1996) prepared two different solutions of pH 9 as shown in Table 2, their experiment concluded that the high carbonate/bicarbonate concentration had an inhibiting effect on the chloride corrosion. The results of pH 9.5 in this paper also gave an evidence of the inhibiting effect.

Table 2. Solutions in Bertolini's study (Bertolini et al., 1996).

pH = 9	0.015M NaHCO ₃ + 0.005M Na ₂ CO ₃
pH = 9	0.3M NaHCO ₃ + 0.1M Na ₂ CO ₃

4. CONCLUSION

The critical chloride concentrations of three different steel bars were experimentally studied in this paper. On the basis of the test results, the following conclusions can be reached:

- The value of critical chloride concentration is greatly affected by the pH value of simulated pore solution, and there is a positive correlation between these two parameters.
- High concentration of carbonate/bicarbonate did have an effect of inhibition. Further experiments should be conducted to figure out the regulation and the mechanisms.
- Nickel was an important composition of alloy for the corrosion resistance of stainless steels.

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