

Electrochemical Comparative Study of Q235 steel and 304 SS in Simulated Concrete Pore Solutions and the Effect of Chloride Ions on their corrosion behavior

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The corrosion behavior of Q235 carbon steel and 304 stainless steel (SS) was studied by potentiodynamic polarization in four types of simulated concrete pore solutions (pH 13.3, 11.5, 9.7). The results showed that both steels maintained good passivation in the pore solutions, demonstrating similar corrosion resistance. The addition of 0.05 mol/L of Cl⁻ had no influence on the corrosion resistance of 304 SS in the solutions, whereas pitting corrosion susceptibility of Q235 carbon steel increases in the carbonate solutions. 304 SS performed much better than Q235 carbon steel in carbonated pore solutions with the critical chloride concentration 100 times higher than that of Q235 carbon steel. The presence of NaHCO₃ and Na₂CO₃ increased the critical [Cl⁻] for pitting corrosion because of the inhibitive effect of HCO₃⁻/CO₃²⁻ on the pitting corrosion.

Keywords: Q235 carbon steel; 304 SS; simulated concrete pore solution; corrosion; potentiodynamic polarization

1. INTRODUCTION

The corrosion of reinforcing steel is one of the major causes for premature degradation of reinforced concrete structures. Normally, a passive film which naturally forms on the steel surface within the concrete environment of high alkaline (pH > 12.5) is effective at preventing corrosion of the reinforcing steel [1,2]. However, the condition of passivity may be destroyed by the loss of alkalinity from atmospheric acidification (primarily dissolved acid gases such as SO₂, NO_x, or CO₂). An alternative failure mode is caused by the uptake of chloride ions from the environment [2,3]. Simulated concrete

pore solutions (SCPs) are widely used as a substitute of concrete to study rebar corrosion in the laboratory. Yu et al. [3] studied the threshold chloride level (C_{th}) of reinforced steel bar in three kinds of SCP solutions. The results showed that C_{th} exhibited an increasing trend with increasing solution pH as the hydroxide ion has an inhibiting effect on steel corrosion. Moreno et al. [4] studied the effects of the composition of simulated pore solution on the corrosion behavior of carbon steel, and found that the increased bicarbonate concentration in pore solutions increased the stability of the passive film on carbon steel. Haleem et al. [5,6] studied the early stage of passive film formation in simulated pore solutions and the roles of some anions in the initiation and inhibition of pitting corrosion of steel. Williamson et al. [7] investigated the effect of SCP solution composition on the electronic properties of passive films on carbon steel and found that sulfates had little influence on electronic properties but chlorides caused a loss of linearity of M-S plots.

In recent years, stainless steel has been specified as reinforcement in concrete structures to extend the service life of the structure, especially in highly corrosive environments [8]. Some investigators have started to study the corrosion behavior of stainless steel rebar in simulated concrete pore solutions [9-12]. Freire et al. [9,10] investigated the electrochemical behavior and chemical composition of the passive films formed on AISI 304 and 316 stainless steels in alkaline solutions (NaOH + KOH). The results revealed that the solution pH and [chloride] had important effects on the film composition and the corrosion behavior of two stainless steels. Moser et al. [11] studied the corrosion resistance of several high-strength stainless steels in simulated concrete solutions and found that in alkaline solutions all these steels showed high corrosion resistance at $[Cl^-]$ up to 0.25 M, but when exposed to carbonated solutions only two duplex stainless steels exhibited high corrosion resistance. Alvarez et al. [12] comparatively studied the corrosion behavior of lean duplex stainless steels with the traditional 304 stainless steel in simulated concrete pore solutions, attempting to find a material which could replace 304 SS as some lean duplex steels have a similar cost to carbon steel.

Most previous studies have focused on the corrosion behavior of reinforcing stainless steel or carbon steel in simulated concrete environment separately. There are few studies to simultaneously compare the corrosion performance of carbon steel and stainless steel. Alonso et al. [13] compared the corrosion behavior of stainless steels of low Ni content, AISI 304 and 316L SS and carbon steel in mortar environment, and pointed out that without chloride the corrosion rate of carbon steel is similar to those of stainless steels but at least 10 times higher in the presence of 2% or 5% Cl^- .

In this work, four solutions were prepared to simulate the pore solutions, and the effect of pH, [carbonate] and $[Cl^-]$ studied. Potentiodynamic polarization tests, combined with XPS were used to study the electrochemical corrosion behavior of Q235 carbon steel and 304 stainless steel in these different pore solutions. The influences of chlorides on the corrosion behavior of both steels were analyzed and the critical [chloride] for pitting corrosion in the various simulated solutions were determined and compared.

2. EXPERIMENTAL

2.1 The test materials and solutions

The studied materials were Q235 carbon steel and 304 stainless steel (304 SS). The chemical composition of Q235 carbon steel was determined by XRF and the results are given in table 1.

Table 1. Compositional analysis results for the steels used.

Sample	% C	% Si	% Mn	% S	% Cu	% Ti	% Mo	%Cr	%Ni	%Fe
Q235	0.13	0.29	0.755	0.11	0.078	0.142	--	--	--	Bal.
304SS	0.062	0.35	1.59	--	0.306	0.234	0.367	16.89	8.19	Bal.

The dimension of steel sample was 8 mm × 8 mm × 10 mm. A copper wire was soldered to the end of the sample for electrical contact. The sample surface was manually abraded with 240, 600 and 1000 grit papers successively, rinsed in de-ionized water and degreased with acetone, and then covered with epoxy resin, leaving an area of 0.06 cm² exposed to the test solution.

Four types of simulated concrete pore (SCP) solutions were prepared [3,4] and the compositions are presented in table 2.

Table 2. Composition of concrete pore solution.

Solution code	pH	[NaOH] (g/L)	[KOH] (g/L)	[Ca(OH) ₂] (g/L)	[NaHCO ₃] (g/L)	[Na ₂ CO ₃] (g/L)
SCP1	13.3	3.7	10.5	2.0	--	--
SCP2	11.5	0.083	0.233	--	--	--
SCP3	9.7	--	--	--	0.53	1.26
SCP4	9.7	0.0002	0.0053	--	--	--

SCP1 solution was used to simulate the pore liquid of normal, highly alkaline concrete, and SCP2 solution (pH 11.5) simulates the typical composition of aged concrete, which is a slightly carbonated concrete environment. SCP3 (pH 9.7) represents a fully carbonated environment, corresponding to fully aged concrete, because during the carbonation process of cement, bicarbonates and carbonates are produced due to the chemical reaction taking place between carbonic acid (from rainwater ingress) and calcium hydroxide. In order to comparatively study the influence of the solution composition on the corrosion behavior of steels, SCP4 solution (pH 9.7) was prepared by dilution of the SCP2 solution such that it had the same pH value (9.7) but with different compositions. All the solutions were prepared with reagent-grade chemicals supplied by Beijing Tong Guang Fine Chemicals Company and de-ionized water. Various amounts of NaCl were then added to the solutions to introduce chloride (Cl⁻) ions.

2.2 Measurement techniques

Potentiodynamic polarization test for the samples in four SCP solutions was carried out using CS350 electrochemical workstation (Corrtest Company, China). The polarization tests were scanned from a potential of 150 mV negative to the open circuit potential at a potential scanning rate of 0.1 mV/s in the anodic direction until sustained current growth was observed. At least five tests were run under each experimental condition and the average results are reported. A three electrode system was used with a platinum as counter electrode, a saturated calomel electrode (SCE) as reference electrode and the steel sample as working electrode. All the tests were performed at ambient temperature.

XPS (X-ray photoelectron spectroscopy) experiments were performed using an ESCALAVB 250 (THERMOVG, USA) to analyze the compositions of passive films formed on samples. Peak fitting was performed using XPS PEAK4.1 data processing software.

3. RESULTS AND DISCUSSION

3.1 Polarization curves of Q235 steel and 304 SS in SCP solutions without chloride

Figure 1 shows the potentiodynamic polarization curves of Q235 steel and 304 SS in each SCP solution. Under each condition, the polarization curves of two steels show similar shapes, manifesting a broad passive region and low passivation current density with the order of 10^{-6} A/cm². When the potential increased to a high level (above +570 mV), the current increased rapidly, which is due to the oxygen evolution reaction [4,11,14].

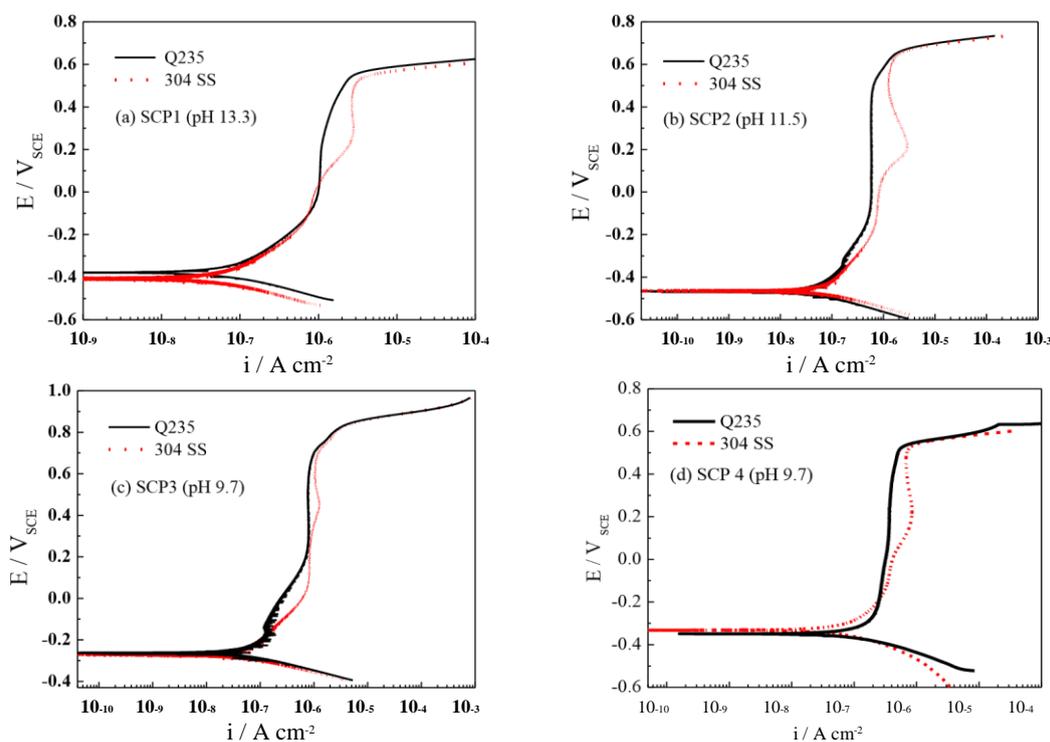


Figure 1. Polarization curves of two steel samples in four SCP solutions without chloride.

Figure 2 shows the variation of the open circuit potential (E_{OCP}) and corrosion current density in four simulated of solutions. The corrosion current density was obtained by Tafel extrapolation method performed on the cathodic branches. It can be seen that the E_{OCP} values of Q235 steel and 304 SS are similar in the same solution. Freire et al. [9] revealed that the shift of the E_{OCP} was related to the Fe^{3+}/Fe^{2+} redox processes. The corrosion current densities of 304 SS in all solutions and those of Q235 steel in SCP1, SCP2 and SCP3 solutions are all lower than $0.014 \mu A/cm^2$, while the current density of Q235 steel in SCP4 solution reached to $0.0415 \mu A/cm^2$, but still far below the criterion for active corrosion ($0.1 \mu A/cm^2$) [15]. The corrosion rate of Q235 steel in each solution was slightly higher than 304 SS. This was in agreement with the results reported between HSS3 stainless steel and carbon steel in mortar environment without Cl^- in literature [13].

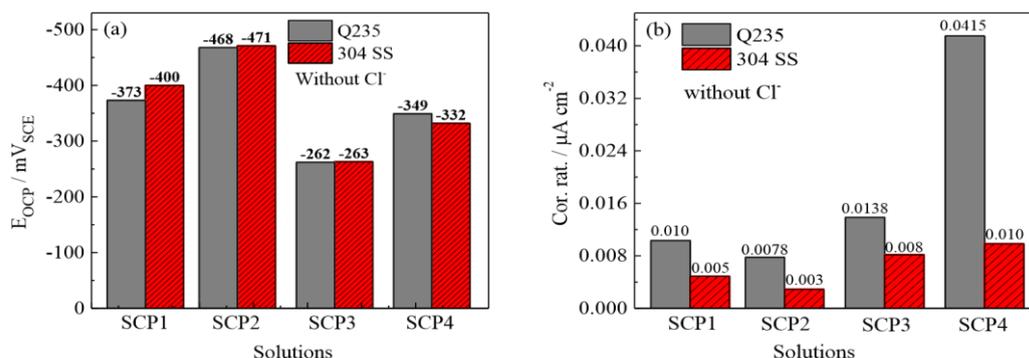


Figure 2. (a) E_{OCP} and (b) corrosion current density of two steels in four SCP solutions without Cl^- .

These results demonstrated that in the solutions tested, both Q235 steel and 304 SS maintain good passivation and demonstrate similar corrosion resistance, suggesting that there is no advantage to the use of stainless steel over carbon steel under these conditions of no chlorides.

3.2 Polarization curves of Q235 and 304 SS in SCP solutions with 0.05 mol/L chloride

0.05 mol/L NaCl were added into four SCP solutions and then potentiodynamic polarization curves were measured. Figure 3 shows the polarization curves. In the SCP1 solution (pH 13.3), both steels still present similar shape, except the passivation current density of Q235 was slightly higher than that of 304 SS. In the three low pH solutions, 304 SS maintained good passivation prior to oxygen evolution, while the broadness of the passive region for Q235 carbon steel was significantly reduced. The difference between the pitting potential (E_{pit}) and open circuit potential (E_{OCP}) for SCP2, SCP3 and SCP4 solutions was 261 mV, 231 mV and 32 mV, respectively. This indicates that the pitting corrosion susceptibility increased significantly and in the increasing order: SCP4 > SCP3 > SCP2. The curves in SCP2 and SCP3 solutions showed some evident current fluctuations in the passive region, which was due to the occurrence of metastable pitting corrosion before stable pitting corrosion [16,17]. In SCP3 solution (pH 9.7), more current fluctuations were observed for carbon steel, indicating more metastable pits occurred before stable pits. The passive current density for Q235 carbon steel in SCP 1-3 solutions were $1.3 \times 10^{-7} \mu A/cm^2$, $3.3 \times 10^{-7} \mu A/cm^2$ and $3.2 \times 10^{-8} \mu A/cm^2$, respectively, which were much larger than

those for stainless steel. In SCP4 solution the polarization curve for Q235 only exist for a very small passivation region. This result suggested that in the pH 9.7 solution, the pitting susceptibility of Q235 carbon steel was decreased when HCO_3^{3-} and CO_3^{2-} are present in the solution.

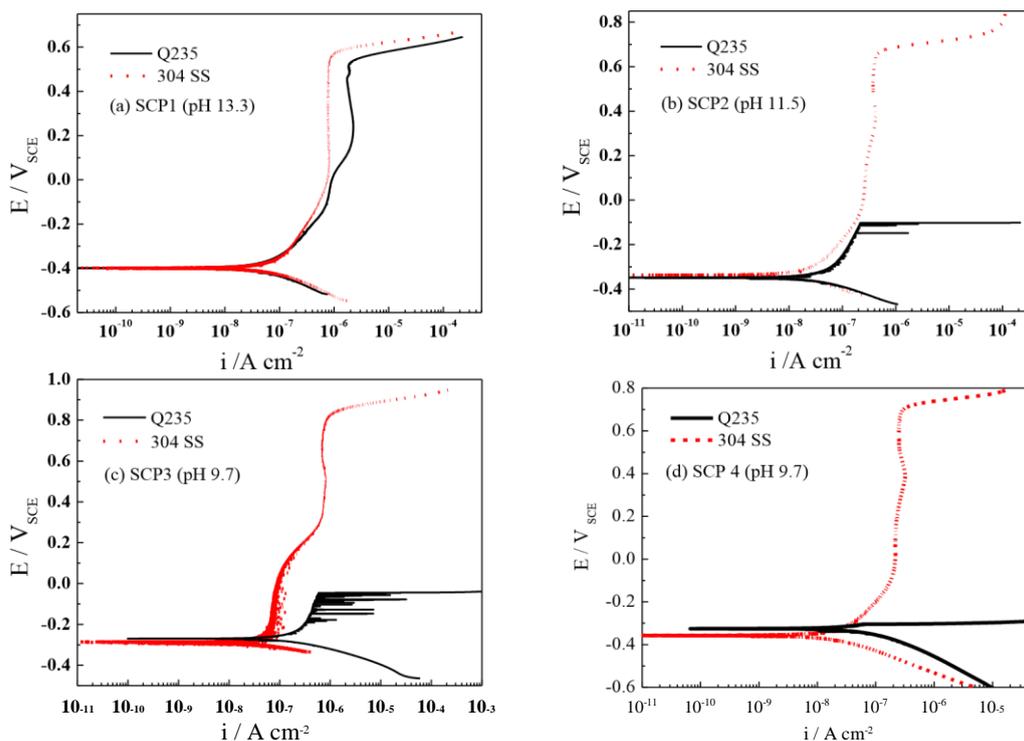


Figure 3. Polarization curves for both steels in four SCP solutions with 0.05 mol/LCl⁻.

Figure 4 shows the corrosion current density of both steels in four SCP solutions containing 0.05 mol/L Cl⁻, which was obtained by Tafel extrapolation method on the cathodic branches. 304 SS still presented a very low corrosion rate (< 0.017 $\mu\text{A}/\text{cm}^2$) and are almost unchanged by the solutions, which is in accordance with the result in literature [10]. For Q235 carbon steel, in SCP1 and SCP2 solutions (pH 13.3 and 11.5), the corrosion rate value was close to that of 304 SS, while in SCP3 and SCP4 solutions (pH 9.7) the corrosion rate increased to 0.03 $\mu\text{A}/\text{cm}^2$ and 0.062 $\mu\text{A}/\text{cm}^2$, respectively, but still lower than 0.1 $\mu\text{A}/\text{cm}^2$ (the criterion for active corrosion). Comparing Figure 4, 2(b) and 3, it can be seen that 0.05 mol/L Cl⁻ had little influence on the corrosion resistance of 304 SS in the four solutions and also had no obvious influence on Q235 carbon steel in a highly alkaline solution (pH 13.3). In the slightly carbonated SCP2 solution (pH 11.5), the corrosion rate of Q235 steel was still quite low, but the pitting corrosion susceptibility increased significantly. In the SCP3 solution (fully carbonated, pH 9.7) and SCP4 solution (acidified SCP2 to pH 9.7), both the uniform corrosion rate and the pitting corrosion susceptibility of Q235 steel were increased, especially in SCP4 solution. We can see that NaHCO_3 and Na_2CO_3 in SCP4 solution has an inhibition effect on both uniform corrosion and pitting corrosion for Q235 steel.

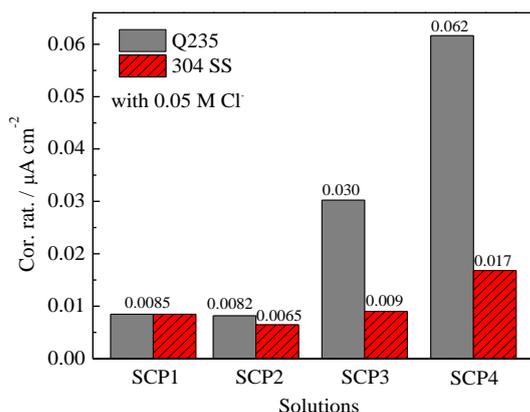


Figure 4. Corrosion current density of two steels in SCP solutions with 0.05 mol/L Cl^- .

3.3 XPS results for Q235 steel and 304 SS in three SCP solutions

The Q235 steel samples were immersed in three SCP solutions with and without 0.05 mol/L Cl^- ions for 4 h respectively, then cleaned with alcohol and analyzed by XPS. The fitted Fe $2p_{3/2}$ XPS spectra are shown in Figure 5. Three iron oxidation states were identified: Fe^0 , Fe^{2+} and Fe^{3+} . The peak at 711 eV corresponds to ferric compounds (Fe^{3+}) such as $\text{Fe}_2\text{O}_3/\text{FeOOH}$, the peak at 709.5 eV is assigned to iron compounds (Fe^{2+}) such as $\text{Fe}_3\text{O}_4/\text{FeO}$, and the peak at 706.5 eV is attributable to metallic iron [18]. The ratio of the Fe(II) to Fe(III) oxides ($\text{Fe}^{3+}/\text{Fe}^{2+}$) was obtained by the curve fitting results. In the absence of chlorides, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is 1.78, 2.22, 1.56 and 1.60 in SCP1 to SCP4 solutions, respectively. The higher ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$, the higher the content of Fe_2O_3 and FeOOH in the film, meaning a better film stability and protective performance. It can be seen that the ratio in SCP2 solution was higher than those in SCP1, SCP3 and SCP4 solutions, manifesting a better film stability. This is in agreement with the corrosion rate results in Figure 2, in which the corrosion rate in SCP2 solution is lower than those in other solutions. After chlorides were added, the ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ decreased to 1.71, 1.29, 0.71 and 1.52, respectively. It can be seen that the decreased magnitude for $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in SCP2 and SCP3 carbonated solutions is much larger than that in the SCP1 alkaline solution. This could explain the above corrosion results. The addition of 0.05 mol/L Cl^- apparently decreased the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the film formed in SCP2 and SCP3 solutions, so as to decrease the ability of the film and increase the susceptibility for pitting corrosion. For the steel immersed in the same pH value solution (SCP3 and SCP4), the chemical component of solution could also affect the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. In SCP3 the HCO_3^- and CO_3^{2-} can reversibly form a precipitate with Fe^{2+} , so the ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ was much lower than that in SCP4.

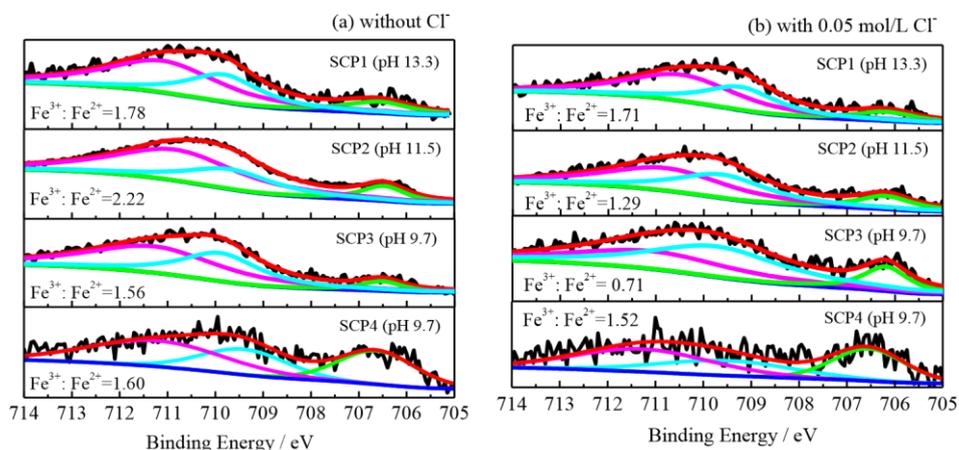


Figure 5. Fitted Fe $2p_{3/2}$ XPS spectra of Q235 sample surface in three SCP solutions: (a) without Cl^- and (b) with 0.05 mol/L Cl^- .

XPS analysis was also performed for 304 SS samples after immersed in three SCP solutions with and without 0.05 mol/L Cl^- ions for 4 h. It was found that chromium could not be detected for the film formed in SCP1 solution (pH 13.3). For the film formed in SCP2 solution (pH 11.5) the amounts of detected chromium oxides are very low, and for the film formed in SCP3 and SCP4 solution (pH 9.7) chromium could be detected clearly. This is accordance with the result in literature [10], in which the amount of oxidized chromium increased as pH decreased. It was reported that the passive film on stainless steel has a bilayer structure, composed of an external Fe rich layer and inner Cr-rich layers. That no Chromium in the film formed in SCP1 solution was detected was probably because that the outer Fe oxides rich layer hindered the photoelectron signal of chromium [10]. Figure 6 shows the fitted $\text{Fe}2p_{3/2}$ XPS spectra for 304 SS. It shows that without Cl^- ions, the obtained $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio for 304 SS is 0.76, 2.16, 0.57 and 0.83 in SCP1 to SCP4 solutions, respectively. Similar to Q235 carbon steel, the ratio in SCP2 solution shows the highest value, which could explain the corrosion rate result in Figure 2. Freire et al. [19] analyzed the composition of the surface film on the 316L SS formed in $\text{NaOH} + \text{KOH}$ solution with pH value from 13 to 9 and reported that the film become enriched in Fe(III) species and depleted in Fe(II) species as the pH decreases. These could explain why the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in SCP2 solution is higher than that in SCP1 solution. It was reported that the presence of bicarbonate favors the formation of a stable Fe(II) film [20]. This is probably the reason for the lower $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in SCP3 solution than in SCP2 solution. With 0.05 mol/L Cl^- added, the ratio decreased slightly to 0.65, 2.10, 0.51 and 0.61, respectively, showing a small influence by Cl^- on the film stability. This is in agreement with the result from the polarization test, that is, the addition of 0.05 mol/L Cl^- had no effect on the electrochemical behavior of 304SS in four SCP solutions.

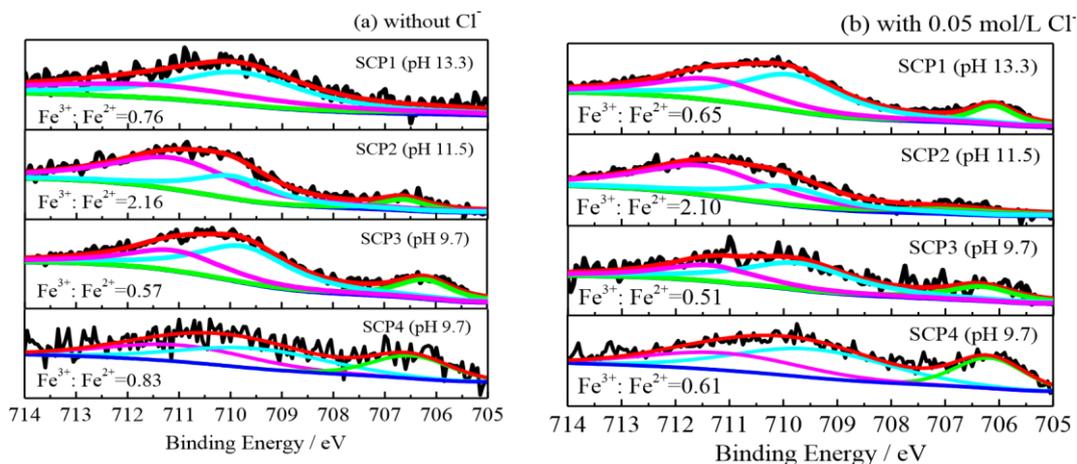


Figure 6. Fitted Fe $2p_{3/2}$ XPS spectra of 304 SS sample surface in three SCP solutions: (a) without Cl^- and (b) with 0.05 mol/L Cl^- .

3.4 The critical chloride thresholds for pitting corrosion of Q235 steel and 304 SS in the pore solutions

The above results showed that in SCP2, SCP3 and SCP4 solutions, after 0.05 mol/L Cl^- ions were added, the pitting corrosion susceptibility of Q235 carbon steel increased significantly. Therefore, further experiments with differing concentrations of Cl^- ions were added to the four solutions, and potentiodynamic polarization curves were performed to determine the critical [chloride] thresholds for pitting corrosion for the two steels. Figure 7 shows the polarization curves of 304 SS and the pitting potentials are listed in Table 3. In SCP1 solution, the stainless steel maintained good passivation when the Cl^- concentration was less than 5 mol/L, but suffered from pitting corrosion after the $[\text{Cl}^-]$ increased to 5.2 mol/L Cl^- . The critical $[\text{Cl}^-]$ for 304 SS in SCP1 solution was therefore between 5 - 5.2 mol/L. In SCP2 solution, with the $[\text{Cl}^-]$ less than 0.1 mol/L, 304 SS could maintain good passivation where the current density was of the order of 10^{-6} A/cm² before the oxygen evolution. When the $[\text{Cl}^-]$ was higher than 0.16 mol/L, small pits could be observed on the sample surface after the test. With the Cl^- ions increased further, the pitting potential of 304 SS shifted negatively with a small amount of current fluctuation on the curves, indicating the critical $[\text{Cl}^-]$ of 304 SS in SCP2 solution is between 0.10 and 0.16 mol/L. In SCP3 solution, 304 SS maintained good passivation during the test with $[\text{Cl}^-]$ less than 0.25 mol/L and began to suffer pitting corrosion when the $[\text{Cl}^-]$ was higher than 0.30 mol/L. So the critical $[\text{Cl}^-]$ of 304 SS in SCP3 solution is between 0.25 and 0.30 mol/L. This is consistent with the result reported by Bertolini et al., in which the critical chloride content of 304 SS in pH 9 solution (containing the same concentration of NaHCO_3 and Na_2CO_3 with SCP3) was in the range 2-3% (0.34 - 0.52 mol/L) [21]. The critical $[\text{Cl}^-]$ of 304 SS in SCP4 solution is between 0.08 and 0.1 mol/L. Thus, the critical $[\text{Cl}^-]$ threshold for pitting corrosion decreases as the pH decreases, but the NaHCO_3 and Na_2CO_3 inhibits the pitting corrosion to some degree for 304 SS.

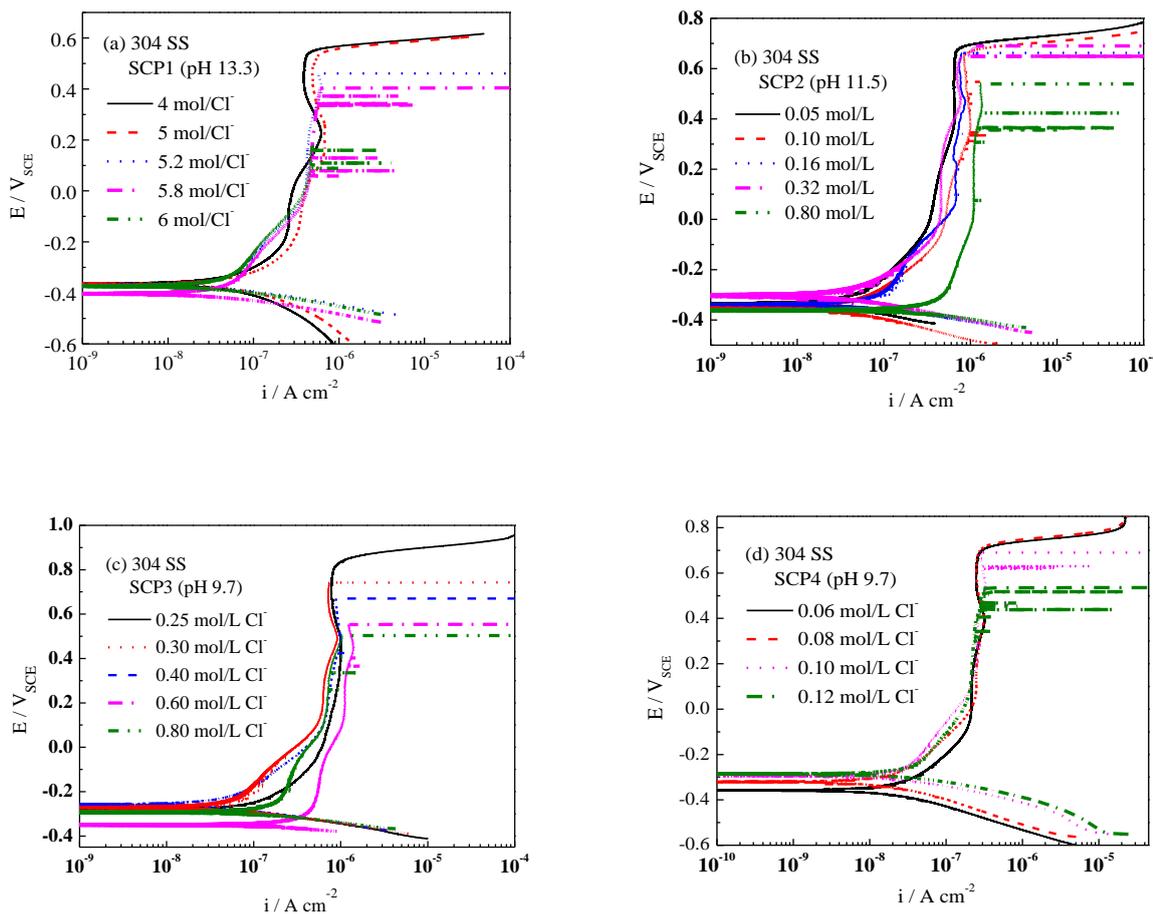


Figure 7. Polarization curves of 304 SS in four SCP solutions with different contents of Cl⁻

Figure 8 shows the polarization curves of Q235 steel in three SCP solutions with different [Cl⁻] and Table 3 shows the pitting potential for Q235 steel. In SCP2 solution, when the [Cl⁻] was lower than 0.0005 mol/L no pits could be observed. At the [Cl⁻] higher than 0.0001 mol/L, pitting corrosion began to occur. Therefore, the critical [Cl⁻] of Q235 steel in SCP2 solution is between 0.0001 and 0.0005 mol/L. In the SCP3 solution, Q235 steel maintained a good passivation during the test when the [Cl⁻] was less than 0.001 mol/L and began to suffer pitting corrosion with [Cl⁻] higher than 0.003 mol/L. Thus, the critical [Cl⁻] is between 0.001 and 0.003 mol/L. In the presence of the [Cl⁻] higher than 0.15 mol/L, Q235 carbon steel presented active corrosion. The critical [Cl⁻] of Q235 steel in SCP4 solution is between 0.0001 and 0.0003 mol/L. The critical [Cl⁻] of Q235 steel in SCP1 solution is between 0.44 and 0.46 mol/L. These results are summarized in table 4. Similar to the result of 304 SS, the critical [Cl⁻] for pitting corrosion decreases as the pH decrease. NaHCO₃ and Na₂CO₃ can inhibit the pitting corrosion of Q235 efficiently.

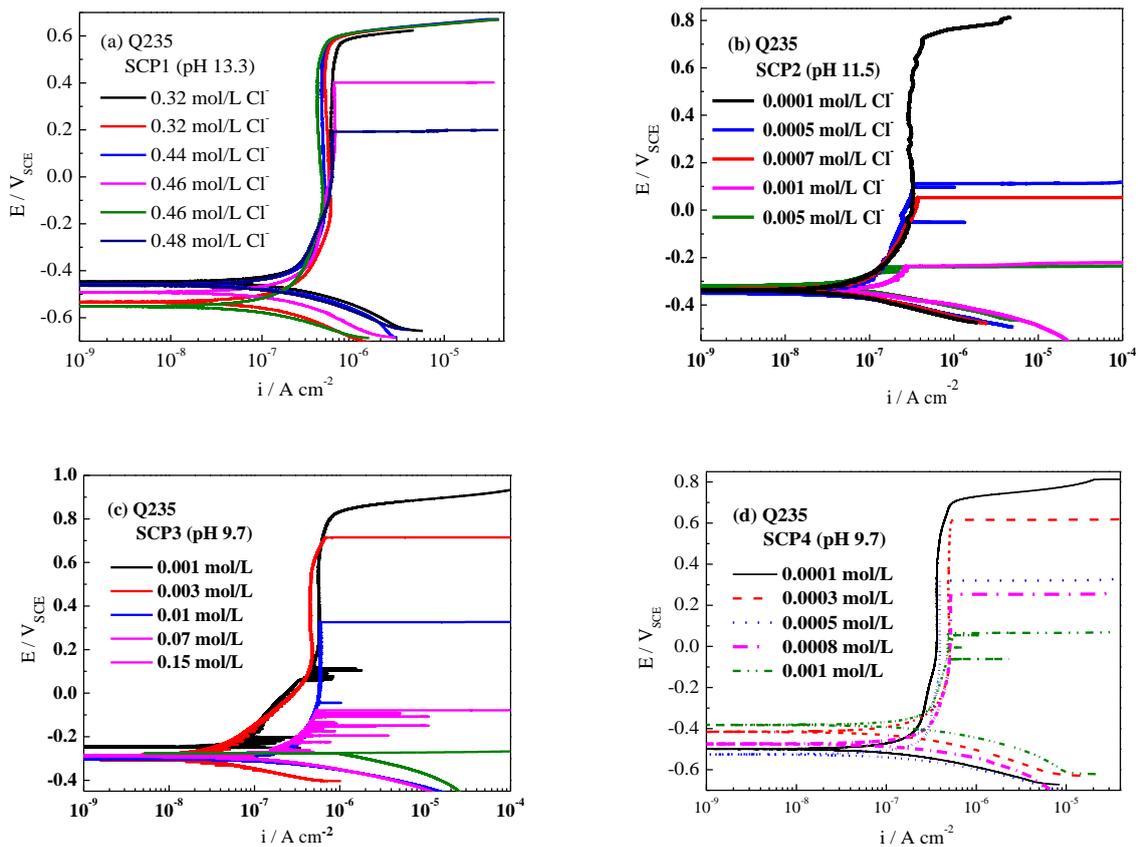


Figure 8. Polarization curves of Q235 steel in four SCP solutions with different contents of Cl⁻

Table 3. Pitting Potential (E_{pit}) for different SCP solutions

SCP solution	Q235 carbon steel		304 stainless steel	
	[Cl ⁻] (mol/L)	E_{pit} (mV)	[Cl ⁻] (mol/L)	E_{pit} (mV)
SCP 1 (pH 13.3)	0.44	oxygen evolution	5	oxygen evolution
	0.46	401.3	5.2	461.0
	0.48	192.3	5.8	403.9
	--	--	6	159.0
SCP 2 (pH 11.5)	0.0001	oxygen evolution	0.10	oxygen evolution
	0.0005	112.3	0.16	662.1
	0.0007	53.3	0.32	648.5
	0.001	-236.2	0.80	539.1
SCP 3 (pH 9.7)	0.001	oxygen evolution	0.25	oxygen evolution
	0.003	714.9	0.30	742.4
	0.01	326.0	0.40	670.1
	0.07	-78.6	0.60	553.5
SCP 4 (pH 9.7)	0.0001	oxygen evolution	0.08	oxygen evolution
	0.0003	616.3	0.10	690.0
	0.0005	320.5	0.12	535.2
	0.0008	253.6	--	--

Table 4. Critical $[\text{Cl}^-]$ thresholds for different pore solutions.

Pore solution	Critical $[\text{Cl}^-]$ for Q235 (mol/L)	Critical $[\text{Cl}^-]$ for 304SS (mol/L)
SCP 1	0.44 - 0.46	5 - 5.2
SCP 2	0.0001 - 0.0005	0.10 - 0.16
SCP 3	0.001 - 0.003	0.25 - 0.30
SCP4	0.0001 - 0.0003	0.08 - 0.10

The chloride threshold has been reported to be dependent on a wide range of parameters, including the pore solution composition, materials, the sample preparation and test methods [3,20,22]. In the work of Yu et al. [3], the chloride threshold for A-615 carbon steel in pH 11.6 SCP solution was 0.001 mol/L, which was about 2-20 times larger than the result in this work (0.0001 - 0.0005 mol/L). The difference may be associated with different test methods in the two studies. Yu's result was obtained by means of open circuit potential (OCP) and linear polarization resistance (LPR) methods. The potentiodynamic polarization method applied in this work might be more sensitive so as to obtain a smaller critical value.

The chloride threshold values for the two steels were compared. The result shows that the chloride threshold values of 304 SS are about 16 times, 430 times, 138 times and 450 times larger than that of Q235 carbon steel in SCP1 to SCP4 solution, respectively (taking the intermediate value of the threshold range), indicating that the Cl^- pitting corrosion resistance of 304 SS is much higher than that of Q235 carbon steel, especially in the carbonated solutions. This is in correspondence with the result in literature that in mortars the critical chloride levels causing pitting corrosion in austenitic and duplex stainless steels are estimated at least 10 times higher than those of the carbon steel for cement [13].

It is worth noting that the chloride threshold for both steels in the SCP3 solution is higher than that in the SCP2 solution, even though the pH value of SCP3 is lower than that of SCP2. Tan et al. [20] found similar results for carbon steel, in that the critical chloride threshold for pitting was higher in pH 9 pore solution (containing more NaHCO_3) compared to that in pH 10 and pH 11 solutions (containing less or non NaHCO_3). Moreno et al. [4] also found that in pH 9 alkaline pore solution, the presence of high levels of bicarbonate and carbonate had a beneficial effect on the chloride threshold for carbon steel. This is because that the bicarbonate help stabilize an Fe(II) film, which would prevent dissolution of the passive film and improved the resistance to localized corrosion. Some researchers [3,24] reported that when the pH of pore solution increased, the critical chloride threshold showed an increasing trend. This should refer to those alkaline pore solutions in which hydroxyl ions are the main anions [3,10,11,24]. In the process of concrete carbonation, with the drop in pH, bicarbonate and carbonate anions are also generated, which could adsorb competitively with chloride on the active sites of the surface film and promote the formation of a protective FeCO_3 film on the steel surface, so as to have inhibitive effect on the pitting corrosion [4,23]. So, in the carbonated SCP3 solution containing NaHCO_3 and Na_2CO_3 , higher critical chloride threshold is obtained.

4. CONCLUSIONS

(1) In four simulated SCP solutions without chlorides, both 304 SS and Q235 carbon steel maintained a good passivation state, demonstrating good corrosion resistance that was not affected by the solution pH value or the chemical components of solution.

(2) The addition of 0.05 mol/L Cl⁻ increased the pitting corrosion susceptibility of Q235 carbon steel in the three carbonated solutions, which is related to the decrease of the Fe³⁺/Fe²⁺ ratio in the surface film. In comparison, 0.05 mol/L Cl⁻ addition had no influence on the corrosion resistance of 304 SS.

(3) As the pH value decreased (SCP1, SCP2 and SCP4), the 304 SS performed much better than Q235 carbon steel in carbonated pore solutions with the chloride threshold value 100 times higher than that of Q235 carbon steel.

(4) For both steels, the critical chloride contents for pitting corrosion in SCP3 solution containing NaHCO₃ + Na₂CO₃ were higher than that in SCP4 solution containing NaOH + KOH because of the inhibitive effect of HCO₃⁻/CO₃²⁻ on the pitting corrosion.

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