

## Research Article

# Effect of Nitrite Ions on Steel Corrosion Induced by Chloride or Sulfate Ions

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The influence of nitrite concentration on the corrosion of steel immersed in three simulated pH environments containing chloride ions or sulfate ions has been investigated by comparing and analyzing the change of half-cell potential, the change of threshold level of  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ , the change of threshold level of  $\text{NO}_2^-/\text{Cl}^-$  or  $\text{NO}_2^-/\text{SO}_4^{2-}$  mole ratio, and the changes of anodic/cathodic polarization curves and Stern-Geary constant  $B$ . The corrosivity of chloride ions against sulfate ions also has been discussed in pH 12.6, pH 10.3, and pH 8.1 environments containing 0, 0.053, and 0.2 mol/L  $\text{NO}_2^-$ , respectively.

## 1. Introduction

The corrosion of reinforcing steel in concrete has become one of the most severe deterioration mechanisms in concrete structures. It is generally accepted that due to the high alkalinity of cement hydration products, a protective layer of iron oxides is formed on the surface of steel, which provides adequate corrosion resistance. However, with the penetration of chloride, sulfate, and carbon dioxide and the appearance of concrete cracking, this protective layer becomes unstable and corrosion initials.

As one of the methods is to prevent steel corrosion, nitrite-based corrosion inhibitors, irrespective of being directly added into concrete during the mixing process or penetrating into concrete by the surface-applied remedial treatment, have been widely investigated in chloride-contaminated concrete [1–3], carbonated concrete [4–6], and cracked concrete [7, 8], and their inhibiting efficiencies also have been checked in simulated concrete pore solution, such as in highly alkaline solution [9–12], carbonated solution [12–14], and neutral and acid solution [12, 15]. Most of these results confirm the effectiveness of nitrite in increasing the chloride threshold level, delaying the onset of corrosion, and reducing the corrosion rate once the corrosion was initiated, but there is no general consensus on the  $\text{NO}_2^-/\text{Cl}^-$  mole ratio above that the preservation of the passive state can be ensured;

suggested values for this threshold range from 0.11 to 1.0 in concrete and from 0.07 to greater than 2 in simulated pore solution. This difference in the threshold level of  $\text{NO}_2^-/\text{Cl}^-$  mole ratio obtained from various literatures might be due to the way of determining the concentrations of chloride and nitrite in concrete (free ions and total ions, etc.), the different qualities of mortar and concrete used in the experiments, the different components of simulated pore solution, and the different surface topographies and compositions of the steel. Comparing and analyzing these literatures, the authors find the contents of available nitrite are different in these studies. So whether it is possible that the nitrite concentration has an influence on this threshold value attracts the interest of us, and up to now, no published literature gives the answer. Another problem here is that the inhibiting efficiency of nitrite in carbonated concrete with or without chloride is not ideal, so whether the high pH environment plays a role in assisting nitrite to inhibit chloride-induced corrosion, as far as known by the authors, no literature clarifies this.

As described above, many researches have been done for chloride-induced steel corrosion. However, fewer works are focused on sulfate-induced steel corrosion, even the corrosion mechanism of sulfate ions is still not clear, and there are also some controversies on the corrosivity of sulfate against chloride ions in alkaline and neutral environments [16–23]. Additionally, all of these works for sulfate-induced

corrosion are just performed in concrete or solution without the addition of any corrosion inhibitor. Little attention has been given to the effect of nitrite ions on sulfate-induced corrosion, and furthermore, reports on the corrosivity of sulfate against chloride, under the action of nitrite, are extremely scarce.

Besides these, the effect of nitrite ions on the polarization behaviors of steel also has attracted the interest of the authors. As it is known that the corrosion current density of steel is usually calculated by the use of the Stern-Geary equation defined as  $i_{\text{corr}} = B/Rp$ , where  $Rp$  is the polarization resistance and  $B$  is a constant which varies with the expression that  $B = \beta_a\beta_c/(2.3(\beta_a + \beta_c))$ , where  $\beta_a$  and  $\beta_c$  are the anodic and cathodic Tafel slopes obtained from the anodic and cathodic polarization curves of steel, respectively. Generally, the calculation of  $i_{\text{corr}}$  mainly focuses on the determination of  $Rp$  and rarely gives an attention to the value of  $B$ . The value of  $B$  is commonly considered to be 26 mV for steel in corroded state and 52 mV for steel in passive state [24]. As we know, the polarization behavior of steel is affected by many factors, such as oxygen and corrosion inhibitors, so the direct use of these  $B$  values is suitable or not, is worthy of discussing. What is more, with the increasing application of corrosion inhibitors, some concern should be given to the effect of corrosion inhibitors on  $B$  value. Nitrite that performs as an anodic inhibitor can repair the passive film and improve the polarization resistance  $Rp$ ; however, whether it has an effect on Stern-Geary constant  $B$  should be checked and clarified, because in most cases, especially for onsite measurement of corrosion rate, the value of  $B$  is taken for granted without any experimental verification, so the calculation of corrosion current density might be misled if any influence of nitrite on the Tafel slope exists.

For all these reasons, the main objective of this paper was to investigate and clarify the influence of nitrite concentration and pH environments on the inhibiting efficiency of nitrite and the influence of nitrite on the anodic/cathodic polarization curves of steel and Stern-Geary constant  $B$ . Additionally, the corrosivity of chloride and sulfate on steel was also compared. Because the corrosion of steel in concrete is difficult to be investigated, and so all experiments in this study were carried out in simulated chemical environments.

## 2. Experimental

Cold-rolled carbon steel sheets (JIS G3141 SPCC-SB) with a dimension of  $60 \times 60 \times 1$  mm were selected to use in this study. The composition of the steel sheet was (wt%): 0.1025% C, 0.5204% Mn, 0.0193% P, 0.0097% S, and balance Fe. At one corner, lead wire was fixed to the steel by screw and the connection area was sealed by epoxy resin. The exposed area of the steel was  $67.7 \text{ cm}^2$ . Before the experiments, steel sheets were polished by sandpaper and cleaned with acetone.

The corrosion of steel sheets was investigated in three different pH environments (pH 12.6, pH 10.3, and distilled water) simulating the highly alkaline environment, weakly alkaline environment, and neutral environment that really existed on the surface of steel in concrete. The pH 12.6 and pH

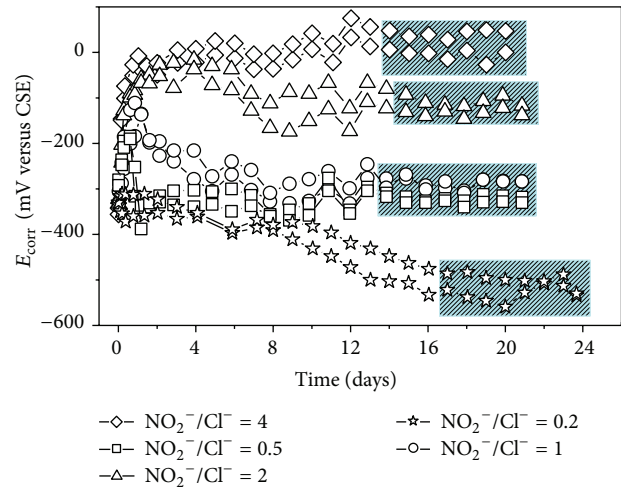


FIGURE 1: Time evolution curves of  $E_{\text{corr}}$  in distilled water containing 0.2 mol/L  $\text{NO}_2^-$  and with different mole ratio of  $\text{NO}_2^-/\text{Cl}^-$ .

10.3 environments were made by mixing different contents of LiOH and  $\text{H}_3\text{BO}_3$ . LiOH and  $\text{H}_3\text{BO}_3$  were chosen for the following reasons. Firstly, they worked as buffer solution which could make the pH in a constant level during the whole experiment process, and secondly LiOH was often used as electrolyte for electrochemical removal of chloride from concrete structures, and thirdly  $\text{Li}^+$  that is mainly in the form of  $\text{LiNO}_2$  was usually added into concrete to prevent the concrete expansion caused by alkali-silica reaction. The use of LiOH and  $\text{H}_3\text{BO}_3$  could not reflect the real concrete pore solution that is composed of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , and so forth, but it still can simulate the possible pH environments that exist in concrete. Although the pore solution compositions (cation type and anion type) had an effect on the protective properties of the passive oxide films and the corrosion behavior of steel [6, 13, 25–27], the focus of this work was to investigate the influence of pH environments and nitrite ions on steel corrosion induced by chloride or sulfate, not to study the effect of other cation/anion ions. Therefore, the use of LiOH and  $\text{H}_3\text{BO}_3$  might be not the best, but it was suitable in this work.

For each pH environment, sodium nitrite was added with the concentration of 0, 0.02, 0.053, 0.2, 0.53 mol/L, respectively, while sodium chloride or sodium sulfate was added according to the mole ratio of  $\text{NO}_2^-/\text{Cl}^-$  or  $\text{NO}_2^-/\text{SO}_4^{2-}$  given in Table 1 or Table 2, respectively. With the presence of nitrite, the pH of distilled water increased to about 8.1.

For each combination of  $\text{NO}_2^-$  and  $\text{Cl}^-$  or each combination of  $\text{NO}_2^-$  and  $\text{SO}_4^{2-}$  in three different pH environments as given in Table 1 or Table 2, two specimens were performed at the same time, and half-cell potential referred to as Cu/CuSO<sub>4</sub> Electrode (CSE) was measured at set intervals until the potential reached a constant value. The time taken for the stable of potential was more than 10 days as shown in Figure 1. The final half-cell potential of steel, in each given combination, was calculated by averaging the potential value of two specimens, where the value of each specimen was

TABLE 1: Experimental design for chloride-induced corrosion.

pH	NO <sub>2</sub> <sup>-</sup> mol/L			Cl <sup>-</sup> mol/L					
pH 12.6 ± 0.3	0	—	—	0.4	0.2	0.1*	0.05	—	0*
	0.02	—	0.1*	—	—	—	—	—	—
	0.053	0.53	0.265	0.106	0.053	0.027	—	—	0
	0.2	—	1	0.4	0.2	0.1*	0.05	—	0*
	0.53	—	—	1.06	0.53	0.265	0.133	0.066	0
pH 10.3 ± 0.3	0	—	—	0.4	0.2	0.1*	0.05	—	0*
	0.02	—	0.1*	—	—	—	—	—	0*
	0.053	0.53	0.265	0.106	0.053	0.027	—	—	0
	0.2	—	1	0.4	0.2	0.1*	0.05	—	0*
	0.53	—	—	1.06	0.53	0.265	0.133	0.066	0
Distilled water	0	—	—	0.4	0.2	0.1*	0.05	—	0*
	0.02	—	0.1*	—	—	—	—	—	0*
	0.053	0.53	0.265	0.106	0.053	0.027	—	—	0
	0.2	—	1	0.4	0.2	0.1*	0.05	—	0*
	0.53	—	—	1.06	0.53	0.265	0.133	0.066	0
Mole ratio of NO <sub>2</sub> <sup>-</sup> /Cl <sup>-</sup>		0.1	0.2	0.5	1	2	4	8	—

TABLE 2: Experimental design for sulfate-induced corrosion.

pH	NO <sub>2</sub> <sup>-</sup> mol/L			SO <sub>4</sub> <sup>2-</sup> mol/L					
pH 12.6 ± 0.3	0	—	—	—	0.2	0.1*	0.05	0.025	—
	0.02	0.2	0.1*	0.04	0.02	0.01	—	—	—
	0.053	—	0.265	0.106	0.053	0.027	0.013	—	—
	0.2	—	—	0.4	0.2	0.1*	0.05	0.025	—
	0	—	—	—	0.2	0.1*	0.05	0.025	—
pH 10.3 ± 0.3	0.02	0.2	0.1*	0.04	0.02	0.01	—	—	—
	0.053	—	0.265	0.106	0.053	0.027	0.013	—	—
	0.2	—	—	0.4	0.2	0.1*	0.05	0.025	—
	0	—	—	—	0.2	0.1*	0.05	0.025	—
	0.02	0.2	0.1*	0.04	0.02	0.01	—	—	—
Distilled water	0.053	—	0.265	0.106	0.053	0.027	0.013	—	—
	0.2	—	—	0.4	0.2	0.1*	0.05	0.025	—
	Mole ratio of NO <sub>2</sub> <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>		0.1	0.2	0.5	1	2	4	8

determined by averaging the data obtained in the stable part of potential versus time curve (as shaded part shown in Figure 1). During the whole experimental process, the pH value and temperature of solution were monitored all the time to make sure that they still maintained a constant level, and the time taken for the visible formation of rust was also recorded. At the end of the experiments, specimens were taken out from the solutions and examined the formation of any visual rust on their surface. Whether the corrosion occurred or not for each combination was judged according to Table 3.

Anodic and cathodic polarization curves of steel were only carried out in the combinations marked as “\*” in Tables 1 and 2. The reference electrode used here was Ag/AgCl electrode and the counter electrode was platinum. Prior to the polarization measurement, the steel had been immersed in the solution more than 15 days and the  $E_{\text{corr}}$  had reached

a stable value. The cathodic polarization was done firstly, which started from  $E_{\text{corr}}$  toward the negative direction with the interval of -25 mV (at the changing rate of 1 mV/s). After the potential was set, 30 seconds were necessary to wait before writing down the current value. After finishing cathodic polarization, the steel was continued to be immersed in the solution about one day for the recovery of  $E_{\text{corr}}$ . And after that, the anodic polarization was started from  $E_{\text{corr}}$  toward the positive direction with the interval of 25 mV (at the speed of 1 mV/s). After setting the potential, 30 seconds are necessary to wait before writing down the current value. Generally, a potential scan greater than ±(50 to 100) mV about  $E_{\text{corr}}$  is required to reach the potential at which the anode Tafel or cathode Tafel behavior dominates and linear polarization is expected [28]. Tafel slopes  $\beta_a$  and  $\beta_c$  in this study were calculated by using the data that obtained between  $E_{\text{corr}} \pm 75$  and  $E_{\text{corr}} \pm 300$ .

TABLE 3: Corrosion judgment defined in this study.

Case	Specimen 1	Specimen 2	Judgments	Marked as
1	Corrosion	Corrosion	Corrosion	◆▲●■
2	Corrosion	No corrosion	Uncertain	◆▲●■
	No corrosion	Corrosion	Uncertain	◆▲●■
3	No corrosion	No corrosion	No corrosion	◇△○□

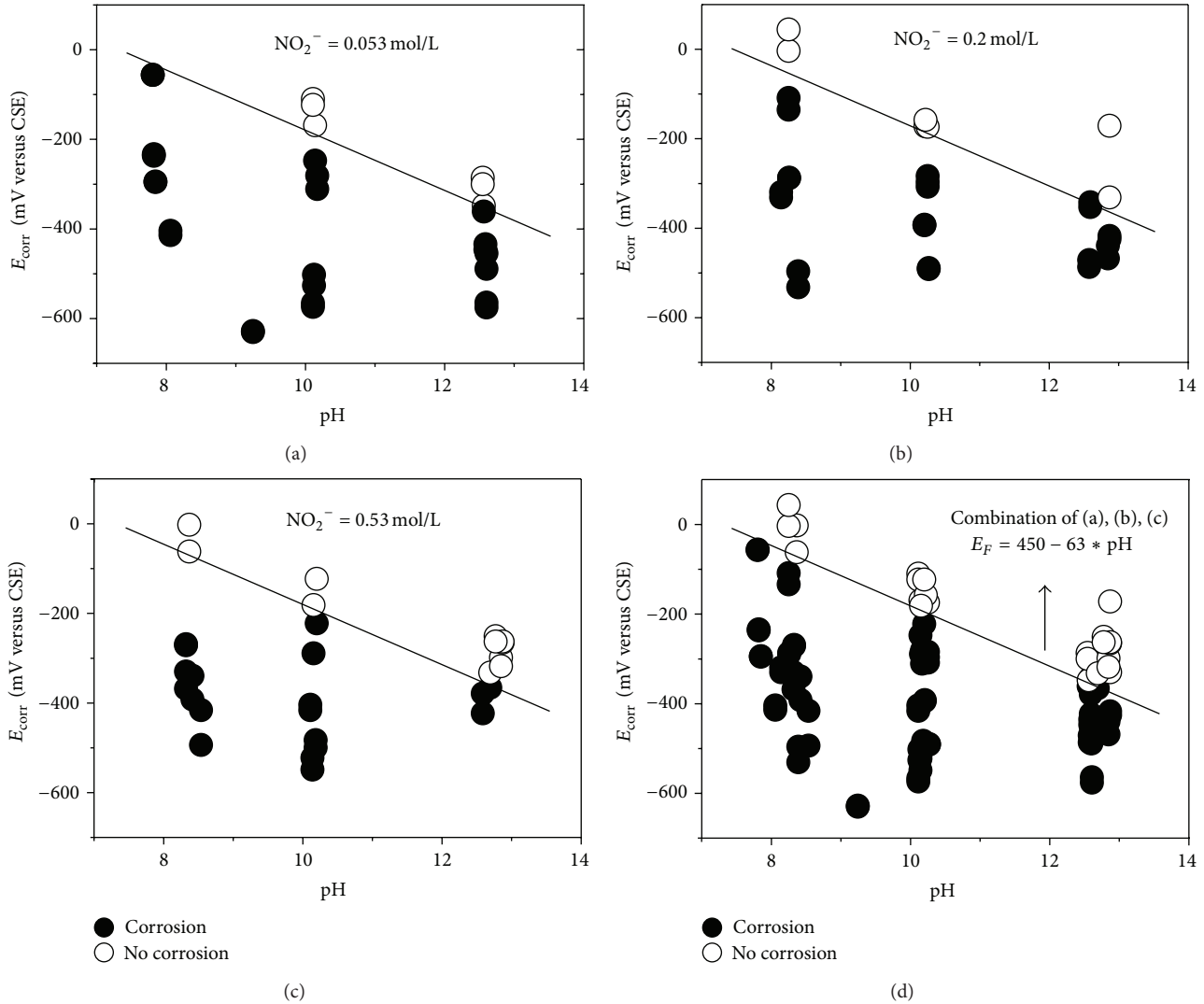


FIGURE 2: Relationship between  $E_F$  and pH for chloride-induced corrosion. (a)  $\text{NO}_2^- = 0.053 \text{ mol/L}$ , (b)  $\text{NO}_2^- = 0.2 \text{ mol/L}$ , (c)  $\text{NO}_2^- = 0.53 \text{ mol/L}$ , and (d) combination of (a), (b), and (c).

### 3. Results and Discussion

According to the experimental results, the  $E_{\text{corr}}$  of steel immersed in different pH environments with the absence and presence of  $\text{NO}_2^-/\text{Cl}^-$  or  $\text{NO}_2^-/\text{SO}_4^{2-}$ , as given in Tables 1 and 2, was shown in Figures 2 and 3. The  $E_{\text{corr}}$  presented here was calculated by averaging the data obtained in the stable part of potential versus time curve. The surface state of steel was marked as filled circle for corrosion and empty circle for no corrosion. From the figure, it can be found that

there was a pretty clear dividing line between passive state and corrosion state. The potential that changes abruptly from passive state to corrosion state is called Flade potential ( $E_F$ ), which is the lowest potential of film formation and has a good linear relationship with pH values as reported by other literatures [29, 30]. Usually, the lower the  $E_F$  is, the stronger the passivation ability of steel is, and the passive film becomes more stable.

The possible influence of  $\text{NO}_2^-$  concentration on the relationships between  $E_F$  and pH for chloride-induced corrosion

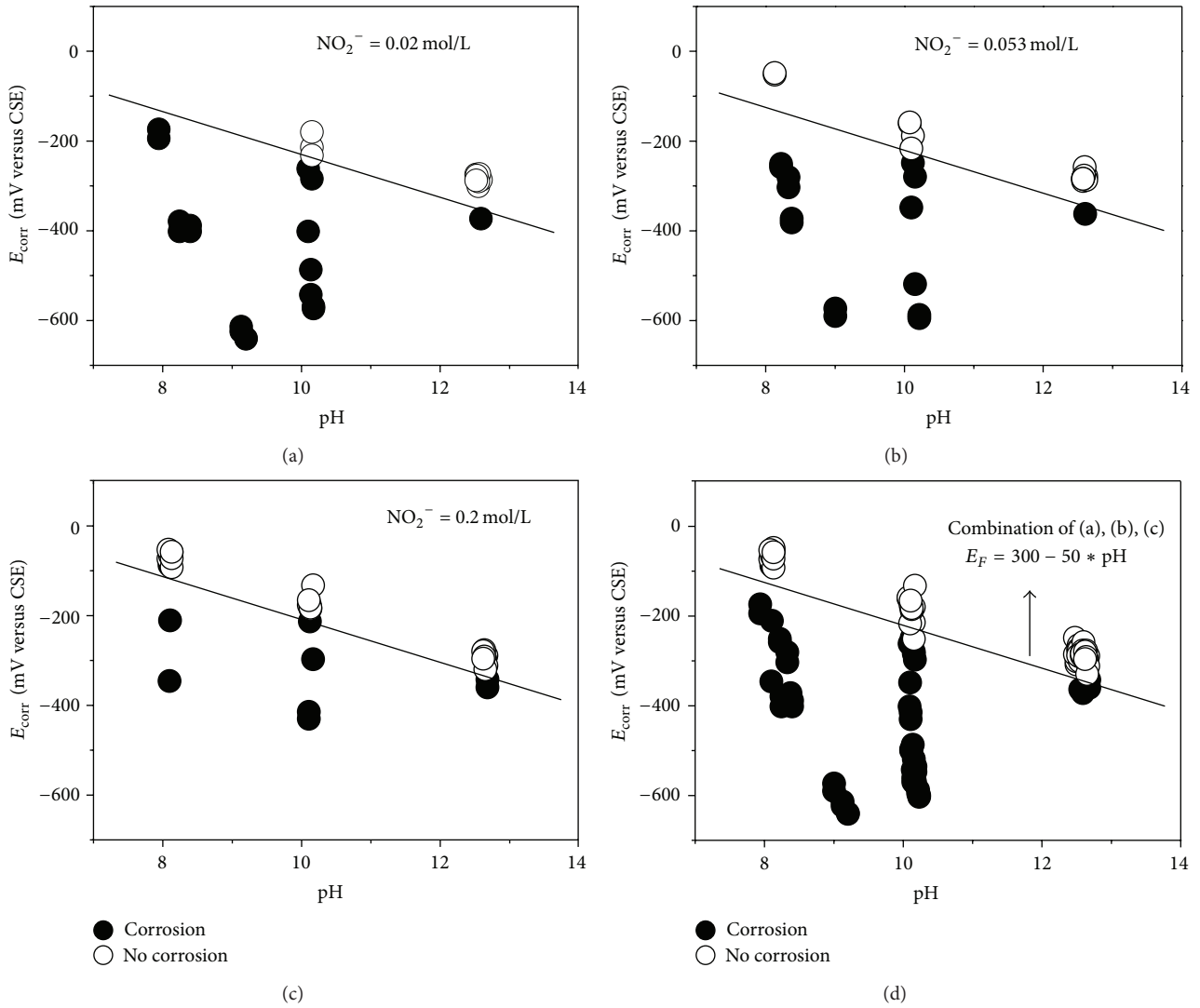


FIGURE 3: Relationship between  $E_F$  and pH for sulfate-induced corrosion. (a)  $NO_2^- = 0.02 \text{ mol/L}$ , (b)  $NO_2^- = 0.053 \text{ mol/L}$ , (c)  $NO_2^- = 0.2 \text{ mol/L}$ , and (d) combination of (a), (b), and (c).

and sulfate-induced corrosion also had been investigated. From Figures 2 and 3, it can be found that the  $NO_2^-$  concentration that changed from 0.053 mol/L to 0.53 mol/L for chloride-induced corrosion or from 0.02 mol/L to 0.2 mol/L for sulfate-induced corrosion had little influence on the linear relationship between  $E_F$  and pH, which also means that the use of the relationship between  $E_F$  and pH as the criterion for corrosion judgment is reasonable in this work. So, in this study, based on the experimental results, the relationships between  $E_F$  and pH were given out in the form of  $E_F = 450 - 63 * pH$  for chloride-induced corrosion as shown in Figure 2(d) and  $E_F = 300 - 50 * pH$  for sulfate-induced corrosion as given in Figure 3(d), which were used as the corrosion criterion for the following result analysis.

3.1.  $E_{corr}$  Induced by  $Cl^-$ . Figure 4 describes the effect of nitrite concentration on  $E_{corr}$  induced by chloride in three pH environments. The  $E_{corr}$  of steel obviously increased with

the presence of nitrite for all pH environments, especially for low pH environment. The increment of potential in pH 8.1 was greater than that in pH 12.6. So with the decreasing of pH, nitrite became more effective to increase the  $E_{corr}$ , but it was not helpful to inhibit the corrosion. This was because the  $E_F$  was  $-344 \text{ mV}$  for pH 12.6,  $-199 \text{ mV}$  for pH 10.3, and  $-60 \text{ mV}$  for pH 8.1, increased with the decreasing of pH. If the  $E_{corr}$  was greater than  $E_F$ , the steel would be passivated; otherwise, the steel was corroded.

Nitrite concentration and pH had an influence on the increment of  $E_{corr}$ . In pH 12.6 environment, for the given chloride content, the  $E_{corr}$  of steel increased with the increasing of nitrite concentration, and this increment was more evident when chloride content was higher. However, in pH 10.3 and pH 8.1 environments, when nitrite was increased from 0.2 to 0.53 mol/L, the increment of steel potential was not obvious. The  $E_{corr}$  with 0.53 mol/L nitrite was equal to or even lower than that with 0.2 mol/L nitrite. No benefit

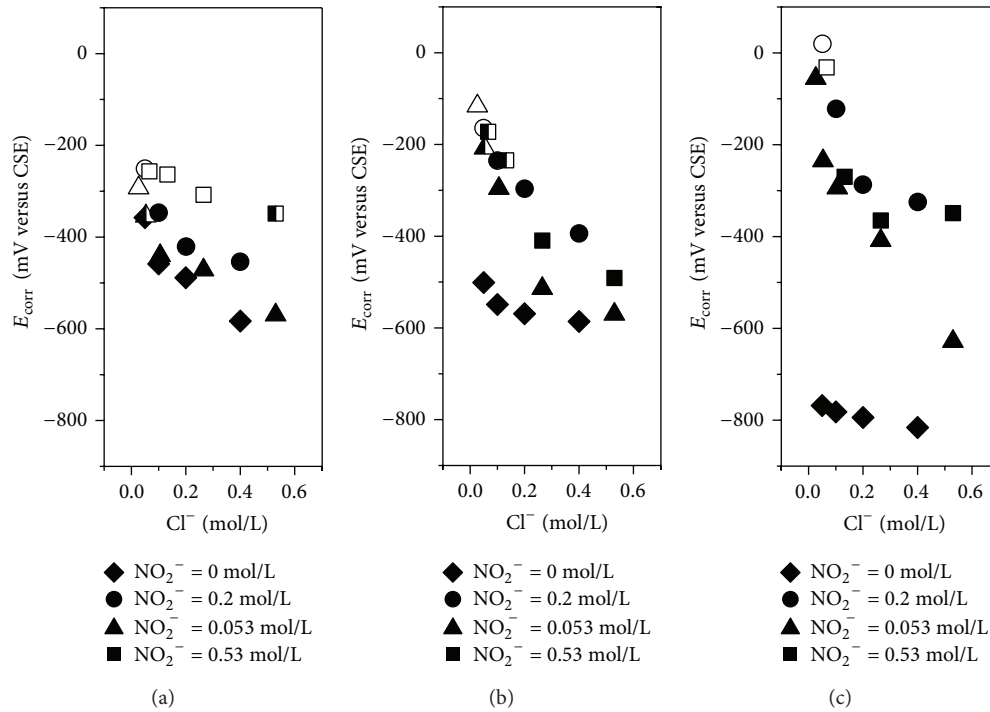


FIGURE 4: Effect of  $\text{NO}_2^-$  and pH on  $E_{\text{corr}}$  induced by  $\text{Cl}^-$ . (a) pH = 12.6, (b) pH = 10.3, and (c) pH = 8.1.

on the further increase of  $E_{\text{corr}}$  can be obtained from higher nitrite concentration in pH 10.3 and pH 8.1 environments, and this indicates that the ability of nitrite to improve steel potential was limited and weakened.

**3.2.  $E_{\text{corr}}$  Induced by  $\text{SO}_4^{2-}$ .** Figure 5 presents the effect of nitrite on  $E_{\text{corr}}$  induced by sulfate in three pH environments. In pH 12.6, irrespective of the presence or absence of nitrite,  $E_{\text{corr}}$  did not change significantly with the increasing of sulfate, even no rust can be found on the surface of steel after 23 days. The increment of  $E_{\text{corr}}$  was negligible after the presence of nitrite. In pH 10.3,  $E_{\text{corr}}$  decreased with the increasing of sulfate concentration. Rust can be found on the surface of steel, but most of the area was still in good state. In pH 8.1, with the absence of nitrite, the entire steel surface was corroded severely.  $E_{\text{corr}}$  increased with the presence of nitrite, but low concentration of nitrite (0.02 mol/L) resulted in the formation of corrosion pitting on the surface of steel. The concentrations of nitrite had an influence on steel potential. For highly alkaline environment with pH 12.6, with the increasing of nitrite concentration, the increment of potential was not obvious, even the decrease of potential can be found according to the experimental results. However, for the conditions of pH 10.3 and pH 8.1, with the raising of nitrite concentration, the potential increased significantly, and this increment was more evident when sulfate content was high.

**3.3. Relationship between  $E_{\text{corr}}$  and  $\text{NO}_2^-/\text{Cl}^-$ .**  $E_{\text{corr}}$  had a good linear relationship with  $\log(\text{NO}_2^-/\text{Cl}^-)$  and increased with the increasing of  $\text{NO}_2^-/\text{Cl}^-$  mole ratio, as shown in

Figure 6. In pH 12.6 environment, the concentration of nitrite almost had no influence on the curve of  $E_{\text{corr}}$  versus  $\log(\text{NO}_2^-/\text{Cl}^-)$ , but in pH 10.3 and pH 8.1 environments, with the increasing of nitrite concentration, the curve shifted toward the direction of higher  $\text{NO}_2^-/\text{Cl}^-$  mole ratio, which resulted in the decrease of  $E_{\text{corr}}$  for the same  $\text{NO}_2^-/\text{Cl}^-$ . This means that the inhibiting ability of nitrite to per unit of chloride was weakened in pH 10.3 and pH 8.1 environments compared to that in pH 12.6 environment.

For the specified nitrite concentration at constant pH, the changing of  $\text{NO}_2^-/\text{Cl}^-$  mole ratio not only affected the  $E_{\text{corr}}$ , but also influenced the initial time of corrosion. For example, in distilled water with 0.2 mol/L nitrite (as shown in Figure 1), when the mole ratio of  $\text{NO}_2^-/\text{Cl}^-$  was changed with 4, 2, 1, 0.5, and 0.2, the stable self-potential was changed correspondingly with 20, -121, -288, -325, and -514 mV, and the initial time of corrosion was also changed correspondingly with >20, 5.8, 1.6, 0.8, and 0.1 days. Both  $E_{\text{corr}}$  and the corrosion initial time increased with the increasing of  $\text{NO}_2^-/\text{Cl}^-$ , which can also be confirmed in other conditions shown in Table 1. All this indicates that the value of  $\text{NO}_2^-/\text{Cl}^-$  had great influence on steel corrosion. The higher value of  $\text{NO}_2^-/\text{Cl}^-$  makes the steel passivate, while the lower value of  $\text{NO}_2^-/\text{Cl}^-$  makes the steel corrode. So the use of  $\text{NO}_2^-/\text{Cl}^-$  mole ratio as parameter to evaluate the inhibiting efficiency of nitrite on chloride-induced corrosion is feasible, and there must be a threshold level of  $\text{NO}_2^-/\text{Cl}^-$  which can determine whether the steel is corroded or not. In this study, the threshold levels of  $\text{NO}_2^-/\text{Cl}^-$  can be calculated based on the  $E_F$  and the good linear relationship between  $E_{\text{corr}}$  and  $\log(\text{NO}_2^-/\text{Cl}^-)$ , as given in Table 4.

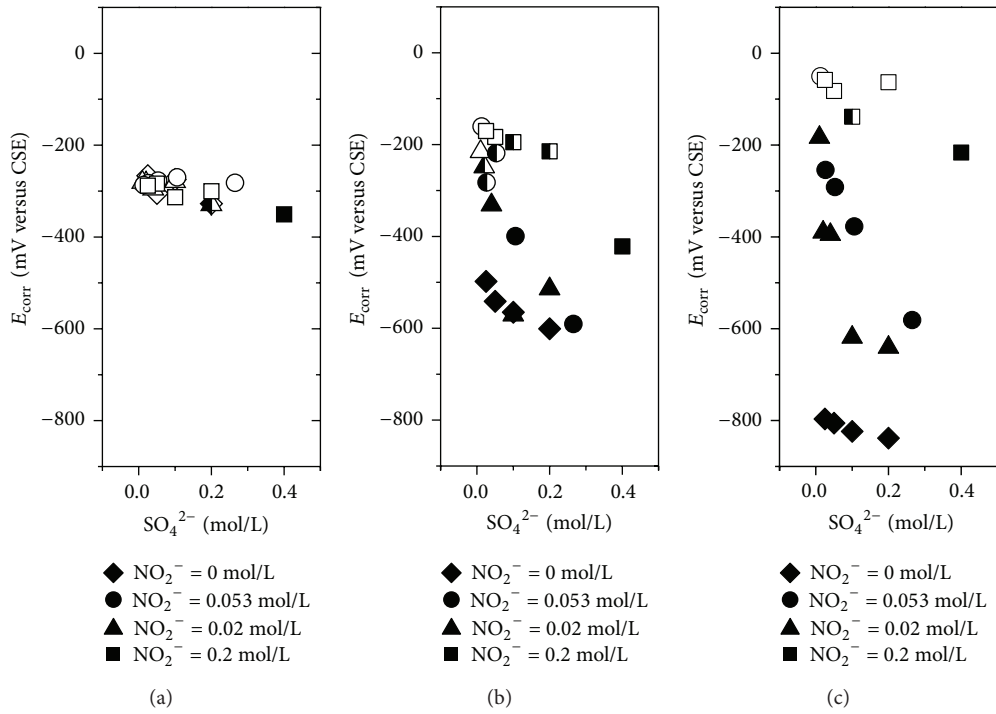


FIGURE 5: Effect of  $NO_2^-$  and pH on  $E_{corr}$  induced by  $SO_4^{2-}$ . (a) pH = 12.6, (b) pH = 10.3, and (c) pH = 8.1.

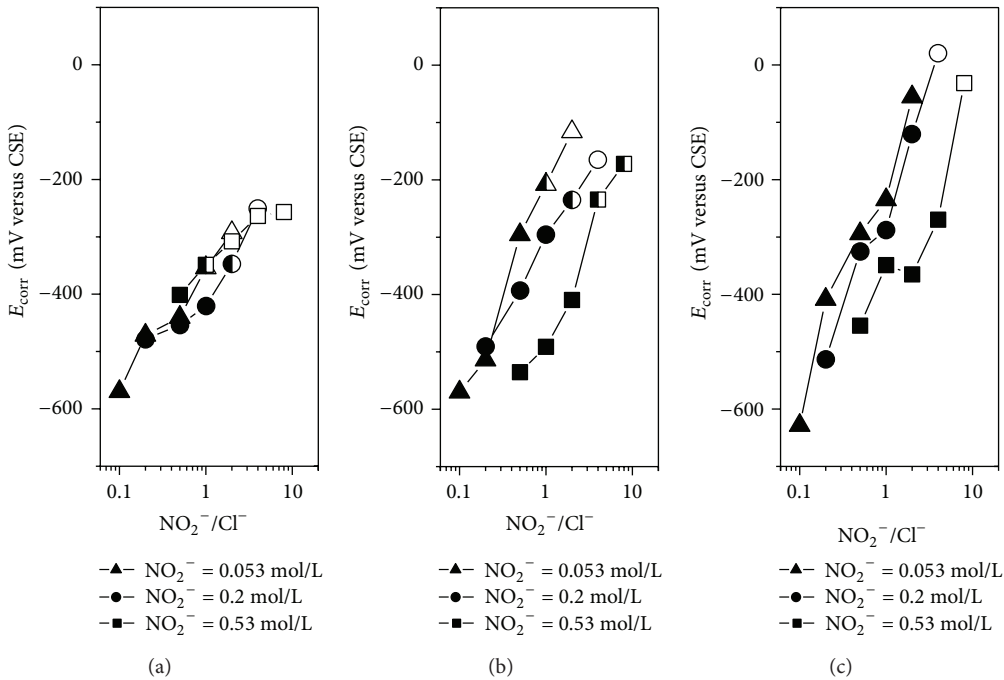


FIGURE 6: Effect of  $NO_2^-$  on  $E_{corr}$  versus  $\log(NO_2^-/Cl^-)$  curves. (a) pH = 12.6, (b) pH = 10.3, and (c) pH = 8.1.

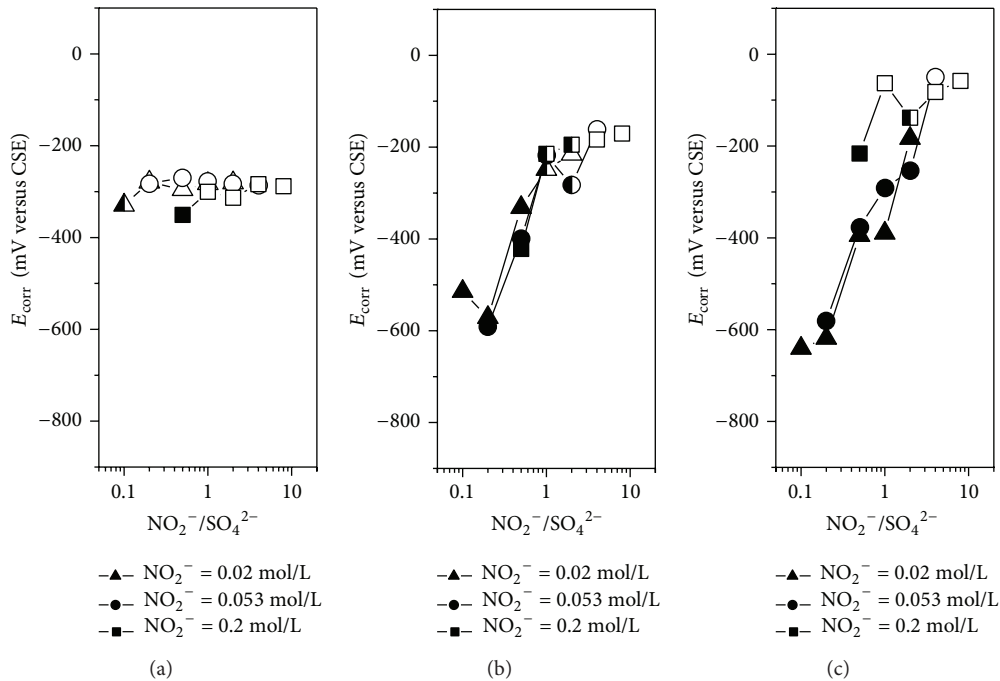
3.4. Relationship between  $E_{corr}$  and  $NO_2^-/SO_4^{2-}$ . The relationship between  $E_{corr}$  and  $\log(NO_2^-/SO_4^{2-})$  shown in Figure 7 indicates that, in pH 12.6 environment, the mole ratio of  $NO_2^-/SO_4^{2-}$  had little influence on  $E_{corr}$ , while in pH 10.3 and pH 8.1 environments,  $E_{corr}$  increased with the increasing of  $NO_2^-/SO_4^{2-}$  mole ratio. For sulfate-induced corrosion, the nitrite concentration almost had no influence

on the curve of  $E_{corr}$  versus  $\log(NO_2^-/SO_4^{2-})$ , which was completely different from the condition for chloride-induced corrosion. The linear relationship between  $E_{corr}$  and  $\log(NO_2^-/SO_4^{2-})$  was shown in Table 5.

3.5. Threshold Level of  $NO_2^-/Cl^-$ . Figure 8 presents the effect of nitrite concentration and pH on the threshold level of

TABLE 4: Relationship between  $E_{\text{corr}}$  and  $\log(\text{NO}_2^-/\text{Cl}^-)$ .

$\text{NO}_2^-$ mol/L	pH	$E_F$ , mV versus CSE	$E_{\text{corr}} = a * \log(\text{NO}_2^-/\text{Cl}^-) + b$		
			$a$	$b$	$R^2$
0.053	12.58	-342.5	201.9	-357.2	0.97
0.2	12.72	-351.4	172.6	-386.9	0.90
0.53	12.71	-350.7	124.3	-353.1	0.95
0.053	10.13	-188.2	370.2	-215.1	0.98
0.2	10.24	-195.1	253.0	-310.9	0.995
0.53	10.14	-188.8	326.5	-466.8	0.96
0.053	7.88	-46.4	398.0	-189.3	0.96
0.2	8.26	-70.4	396.7	-237.7	0.98
0.53	8.42	-80.5	307.4	-386.6	0.83

FIGURE 7: Effect of  $\text{NO}_2^-$  on  $E_{\text{corr}}$  versus  $\log(\text{NO}_2^-/\text{SO}_4^{2-})$  curves. (a) pH = 12.6, (b) pH = 10.3, (c) pH = 8.1.

$\text{NO}_2^-/\text{Cl}^-$  that was determined by using the  $E_F$  and the relationship between  $E_{\text{corr}}$  and  $\log(\text{NO}_2^-/\text{Cl}^-)$  as shown in Table 4. In pH 12.6 environment, nitrite concentration almost had no influence on the threshold level of  $\text{NO}_2^-/\text{Cl}^-$ , while in pH 10.3 and pH 8.1 environments, the threshold level increased with the increasing of nitrite concentration. The constant of the threshold level of  $\text{NO}_2^-/\text{Cl}^-$  in pH 12.6 environment means that  $\text{NO}_2^-/\text{Cl}^-$  mole ratio can be performed as the parameter to evaluate the corrosion of steel in highly alkaline environment, but it is not suitable for the situation in weakly alkaline and neutral environments because the threshold level of  $\text{NO}_2^-/\text{Cl}^-$  changed greatly with different nitrite concentrations.

**3.6. Threshold Level of  $\text{NO}_2^-/\text{SO}_4^{2-}$ .** In the  $\text{NO}_2^-/\text{Cl}^-$  system, there was a good linear relationship between  $E_{\text{corr}}$  and  $\log(\text{NO}_2^-/\text{Cl}^-)$  for each nitrite concentration in pH 12.6, pH 10.3, and pH 8.1 environments, but in  $\text{NO}_2^-/\text{SO}_4^{2-}$  system, the good linear relationship between  $E_{\text{corr}}$  and  $\log(\text{NO}_2^-/\text{SO}_4^{2-})$  only can be found in pH 8.1 and pH 10.3 environments with 0.02 and 0.053 mol/L  $\text{NO}_2^-$ . So the threshold level of  $\text{NO}_2^-/\text{SO}_4^{2-}$  in pH 8.1 and pH 10.3 environments with 0.02 and 0.053 mol/L  $\text{NO}_2^-$  was obtained by using the  $E_F$  and the relationship between  $E_{\text{corr}}$  and  $\log(\text{NO}_2^-/\text{SO}_4^{2-})$  as shown in Table 5, while the threshold levels of  $\text{NO}_2^-/\text{SO}_4^{2-}$  in pH 12.6 environment with 0.02, 0.053, and 0.2 mol/L  $\text{NO}_2^-$  and in pH 8.1 and pH 10.3 environments



TABLE 5: Relationship between  $E_{corr}$  and  $\log(\text{NO}_2^-/\text{SO}_4^{2-})$ .

$\text{NO}_2^-$ mol/L	pH	$E_F$ , mV versus CSE	$E_{corr} = a * \log(\text{NO}_2^-/\text{SO}_4^{2-}) + b$		
			$a$	$b$	$R^2$
0.02	12.6	-330	27.9	-284.1	0.47
0.053	12.6	-330	-6.3	-279.8	0.25
0.2	12.6	-330	47.0	-321.4	0.69
0.02	10.1	-205	283.1	-280.2	0.87
0.053	10.1	-205	310.3	-324.3	0.85
0.2	10.1	-205	177.3	-290.4	0.65
0.02	8.26	-113	347.6	-327.5	0.93
0.053	8.26	-113	371.4	-303.7	0.96
0.2	8.1	-105	98.7	-141.4	0.50

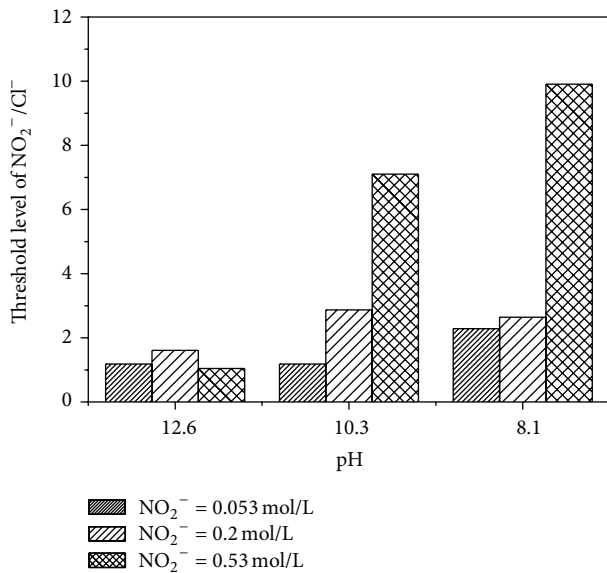


FIGURE 8: Effect of  $\text{NO}_2^-$  on the threshold values of  $\text{NO}_2^-/\text{Cl}^-$ .

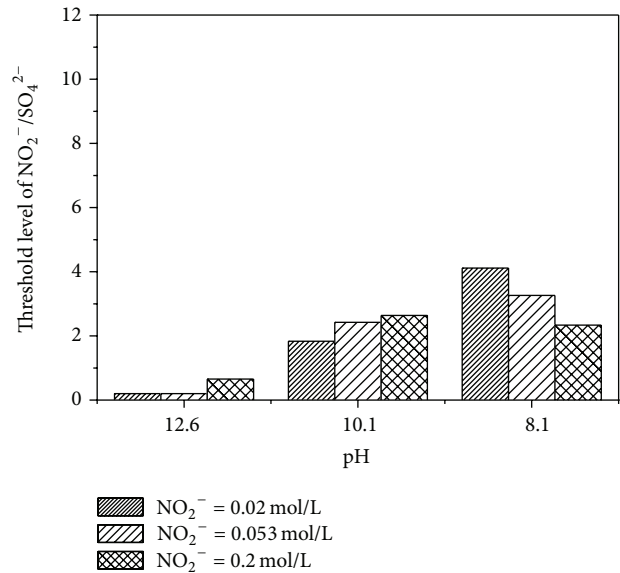


FIGURE 9: Effect of  $\text{NO}_2^-$  on the threshold values of  $\text{NO}_2^-/\text{SO}_4^{2-}$ .

with 0.2 mol/L  $\text{NO}_2^-$  were judged according to the results of corrosion judgment as described in Table 3 and shown in Figure 7. The threshold levels of  $\text{NO}_2^-/\text{SO}_4^{2-}$  obtained here might be not accurate, but they were well consistent with the experimental results and could provide some information on the influence of nitrite concentrations.

Figure 9 presents the effect of nitrite concentrations and pH values on the threshold levels of  $\text{NO}_2^-/\text{SO}_4^{2-}$ . It can be seen that the threshold value of  $\text{NO}_2^-/\text{SO}_4^{2-}$  was greatly influenced by pH values and nitrite concentrations and decreased with the increasing of pH values. In pH 8.1 environments, this threshold value decreased with the increasing of nitrite content, while in pH 10.3 environments, it showed the opposite trend, increased with the increasing of nitrite content. In pH 12.6 environments, the threshold value of  $\text{NO}_2^-/\text{SO}_4^{2-}$  was 0.2, 0.2, and 0.656 for 0.02, 0.053, and 0.2 mol/L nitrite, respectively. The change of the threshold value in these pH environments means that it cannot be used

as the parameter to evaluate the inhibiting efficiency of nitrite on sulfate-induced corrosion.

3.7. Threshold Level of  $\text{Cl}^-$ . The effect of nitrite concentration and pH on the threshold level of chloride is shown in Figure 10. In pH 12.6 environment, the chloride threshold level increased markedly when the concentration of nitrite was raised from 0 mol/L to 0.53 mol/L, while in pH 10.3 and pH 8.1 environments, if the concentration of nitrite was less than 0.2 mol/L, the chloride threshold level had an increasing trend, and if the nitrite content was higher than 0.2 mol/L, there was almost no increase in the chloride threshold level, even the decrease could also be found with the experimental results. The chloride threshold level in pH 12.6 environment was greater than that in pH 10.3 and pH 8.1 environments, especially for the presence of higher nitrite concentration, indicating that the highly alkaline environment played an important role in assisting nitrite to increase the chloride threshold level. The combined effect of  $\text{OH}^-$  and  $\text{NO}_2^-$  on

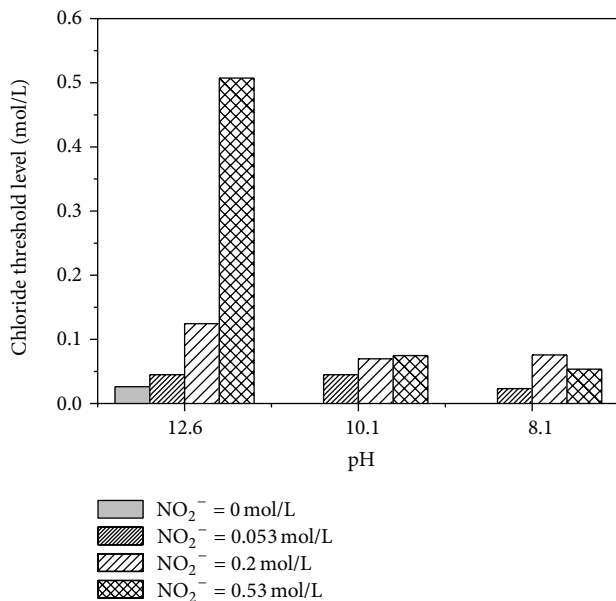


FIGURE 10: Effect of  $\text{NO}_2^-$  on the threshold values of  $\text{Cl}^-$ .

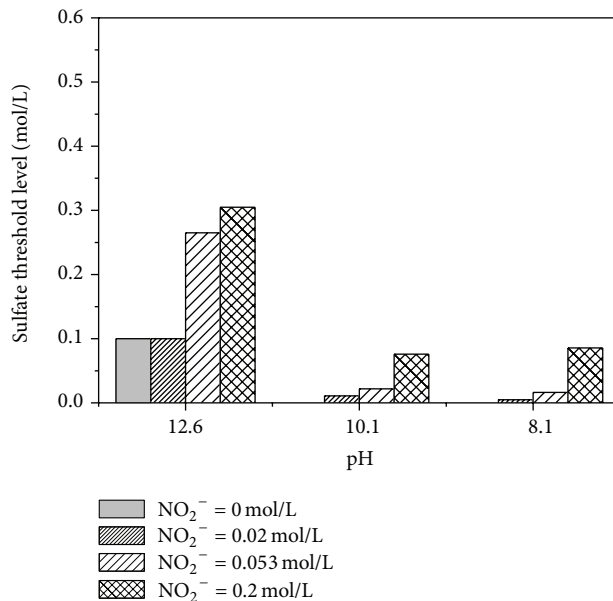


FIGURE 11: Effect of  $\text{NO}_2^-$  on the threshold values of  $\text{SO}_4^{2-}$ .

inhibiting corrosion was superior to the individual effect. However, the use of  $\text{NO}_2^-/\text{Cl}^-$  mole ratio as the parameter to guarantee the inhibition efficiency did not take into account the effect of  $\text{OH}^-$ . So whether  $\text{NO}_2^-/\text{Cl}^-$  is the most suitable parameter to evaluate chloride-induced corrosion in highly alkaline environments is worthy of further study. Besides this, why the inhibiting efficiency of nitrite on steel corrosion in neutral environment is weakened should be further investigated. The results obtained in this study are mainly based on the methods of half-cell potential and visual examination; they should be further confirmed by corrosion current measurement.

**3.8. Threshold Level of  $\text{SO}_4^{2-}$ .** The effect of nitrite concentration and pH on the threshold level of sulfate was given in Figure 11. As seen from the figure, irrespective of the pH values, with the increasing of nitrite concentration, the sulfate threshold level increased significantly. For the same nitrite content, sulfate threshold level in pH 12.6 environments was much greater than that in pH 10.3 and pH 8.1 environments. So the highly alkaline environment played an important role in assisting nitrite to increase the sulfate threshold level.

**3.9. Comparing the  $E_{\text{corr}}$  Induced by  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ .** Figure 12 compares the  $E_{\text{corr}}$  induced by  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in three pH environments containing 0, 0.053, and 0.2 mol/L  $\text{NO}_2^-$ . It can be seen that, in pH 10.3 and pH 8.1 environments with 0 and 0.053 mol/L  $\text{NO}_2^-$ , when  $\text{SO}_4^{2-}$  content was equal to  $\text{Cl}^-$  content, the  $E_{\text{corr}}$  resulted from sulfate-induced corrosion was lower than that resulted from chloride-induced corrosion. The corrosivity of sulfate was stronger than that of chloride in this condition. However, there was a dramatic change after the content of nitrite was raised to 0.2 mol/L  $\text{NO}_2^-$ ; the  $E_{\text{corr}}$  in sulfate environment was higher than that

in chloride environment and the corrosion extent of steel immersed in sulfate environment was greatly reduced. In pH 12.6 environment, regardless of the absence or the presence of nitrite, the  $E_{\text{corr}}$  resulted from sulfate-induced corrosion was higher than that resulted from chloride-induced corrosion, and almost all specimens were in passivation state when sulfate ions were equal to or less than 0.2 mol/L. So the corrosivity of sulfate ions on steel in pH 12.6 environment was weaker than that of chloride. From the above analysis, a conclusion could be obtained that the corrosivity of sulfate against chloride was variable and greatly affected by the value of pH and the concentrations of nitrite.

**3.10. Comparing the Threshold Level of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ .** The threshold level of  $\text{Cl}^-$  and the threshold level of  $\text{SO}_4^{2-}$  were compared and analyzed in pH 12.6, pH 10.3 and pH 8.1 environments containing 0, 0.053, and 0.2 mol/L  $\text{NO}_2^-$  respectively. The results were presented in Figure 13. In pH 12.6 environment, whatever the concentration of nitrite was, sulfate threshold level was always higher than chloride threshold level under the same condition. This means that chloride-induced corrosion was more prone to initiate than sulfate-induced corrosion in highly alkaline environment. However, in pH 10.3 and pH 8.1 environments, with the presence of 0.053 mol/L nitrite, the sulfate threshold level was lower than chloride threshold level, and after nitrite concentration increased to 0.2 mol/L, the sulfate threshold level became higher than chloride threshold level. This means that sulfate-induced corrosion was more likely to occur than chloride-induced corrosion in carbonated and neutral environments in which nitrite concentration was equal to or less than 0.053 mol/L. Whether sulfate threshold level was higher or lower than chloride threshold level in carbonated and neutral environments was determined by nitrite content.

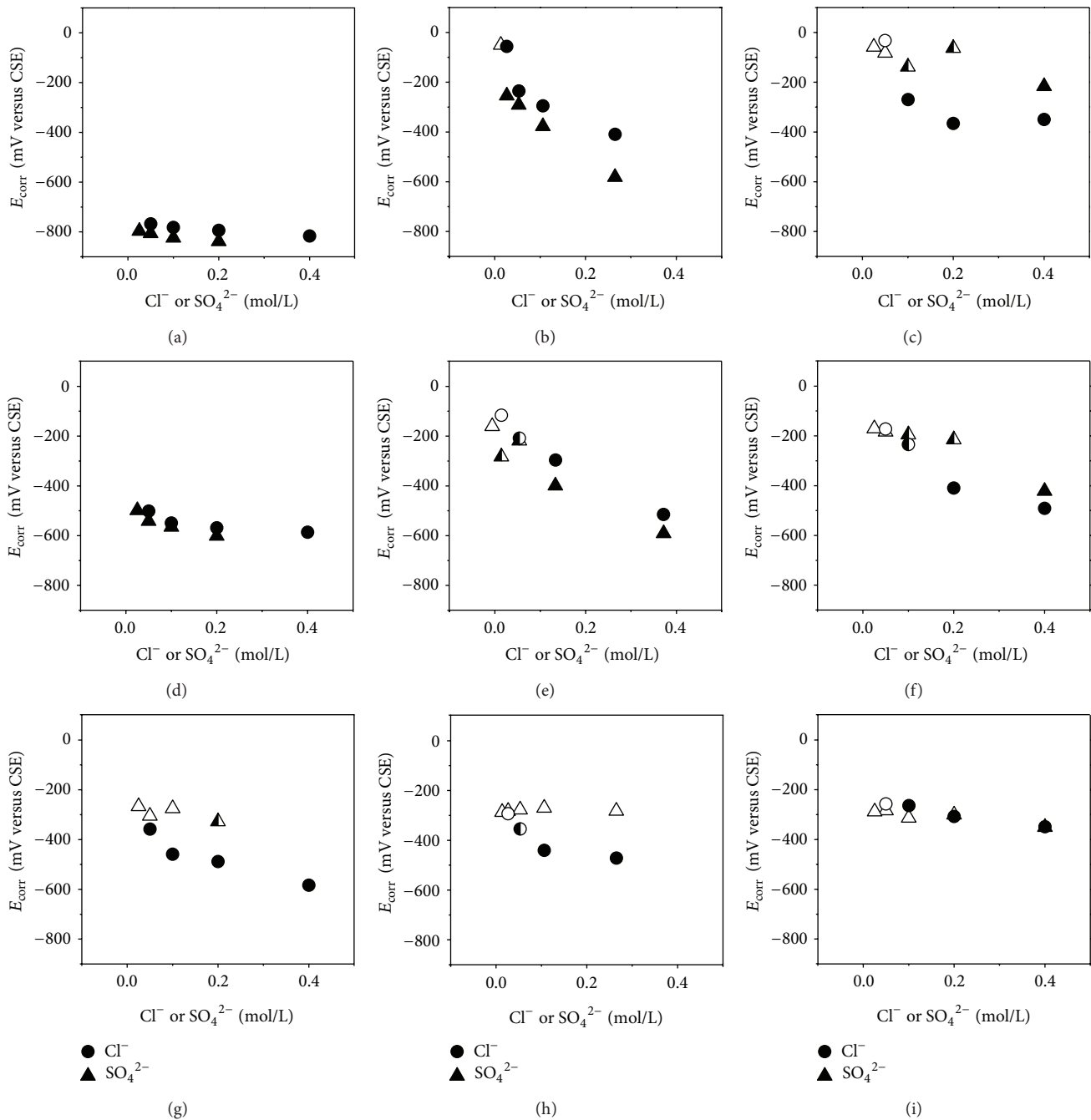


FIGURE 12: Comparing the  $E_{corr}$  induced by  $Cl^-$  and  $SO_4^{2-}$ . (a) pH 8.1,  $NO_2^- = 0$  mol/L, (b) pH 8.1,  $NO_2^- = 0.053$  mol/L, (c) pH 8.1,  $NO_2^- = 0.2$  mol/L, (d) pH 10.3,  $NO_2^- = 0.0$  mol/L, (e) pH 10.3,  $NO_2^- = 0.053$  mol/L, (f) pH 10.3,  $NO_2^- = 0.2$  mol/L, (g) pH 12.6,  $NO_2^- = 0.0$  mol/L, (h) pH 12.6,  $NO_2^- = 0.053$  mol/L, (i) pH 12.6,  $NO_2^- = 0.2$  mol/L.

So both pH and nitrite concentration had greater influence on chloride threshold level and sulfate threshold level.

3.11. *Effect on Anodic/Cathodic Polarization Curves, Tafel Slope, and Stern-Geary Constant.* Anodic/cathodic polarization curves of steel were obtained based on the method described above. After the cathodic (anodic) polarization, some changes might occur on the surface of steel and thus

would have an influence on the further polarization of anodic (cathodic). In order to clarify this influence and give an answer to this problem, a preliminary experiment was carried out on the steel that had been immersed in distilled water for 3 days. Firstly, the cathodic polarization was done, and after finishing it, the steel was continued to be immersed in the solution about one day for the recovery of  $E_{corr}$ . And then, the anodic polarization was performed. The result was shown in Figure 14 and marked as black square “■”. After

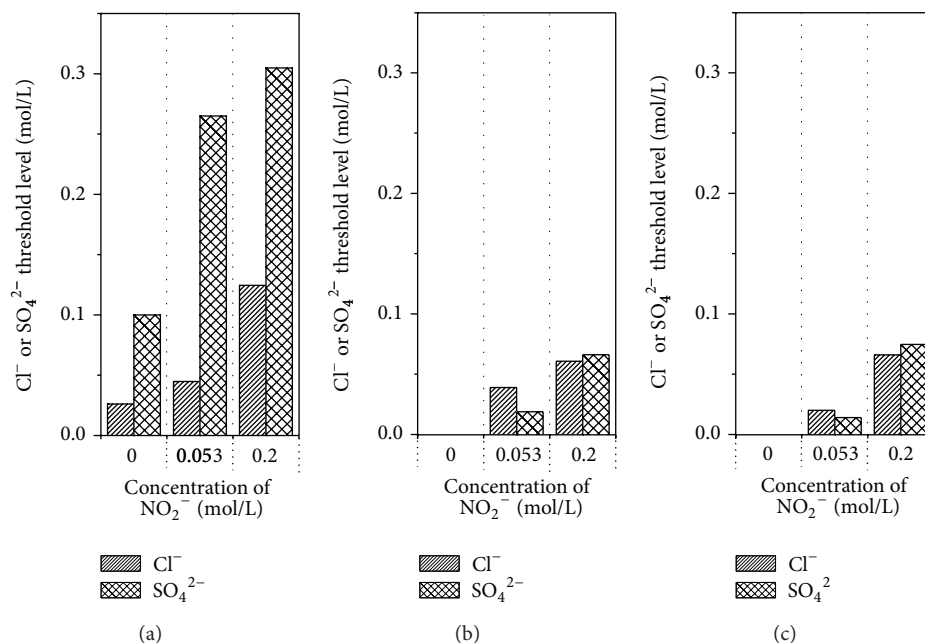


FIGURE 13: Comparing the threshold level of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . (a) pH = 12.6, (b) pH = 10.3, and (c) pH = 8.1.

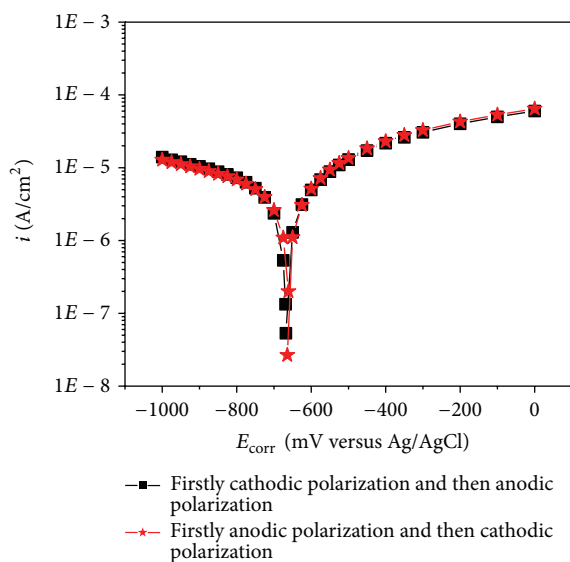


FIGURE 14: Polarization curves of steel immersed in distilled water for 3 days.

the cathodic and anodic polarization curves were obtained, the steel was continued to be immersed in the solution for the recovery of  $E_{\text{corr}}$ . About three days later, the cathodic and anodic polarization were performed again, and this time, the anodic polarization was done firstly, and one day later, the cathodic polarization curve was obtained. The result was also presented in Figure 14 and marked as red star “★”. Comparing the results, little difference can be observed from the two polarization curves. Some changes of the surface state of steel might occur after the cathodic (anodic) polarization, but after

the recovery of  $E_{\text{corr}}$ , they were not enough to affect the further polarization of anodic (cathodic).

The effect of nitrite concentrations on the anodic and cathodic polarization curves, Tafel slope, and Stern-Geary constant  $B$  in pH 12.6, pH 10.3, and pH 8.1 environments with and without 0.1 mol/L  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  was shown in Figures 15 and 16, respectively.

Steels immersed in pH 12.6 environment without any chloride or sulfate (Figure 15(a)), and in the same solutions with 0.1 mol/L  $\text{SO}_4^{2-}$  (Figure 15(g)) they were all in the passive state. With the presence of 0.02 and 0.2 mol/L nitrite, both the  $E_{\text{corr}}$  and polarization curves of steel did not show any obvious change. So the presence of nitrite had little influence on the anodic and cathodic polarization behaviors of steel. There was almost no change in  $\beta_a$ ,  $\beta_c$ , and  $B$  in these conditions (Figures 16(a), 16(d), and 16(g)). However, in pH 12.6 environment with 0.1 mol/L  $\text{Cl}^-$  (Figure 15(d)), the steel was corroded with the presence of 0 and 0.02 mol/L nitrite and was in passive state when nitrite concentration was 0.2 mol/L. With the increase of nitrite concentration, there was almost no change in the cathodic polarization curve, but the anodic polarization curves moved toward the direction of lower current density. Corresponding to this,  $\beta_a$  decreased, while  $\beta_c$  remained constant, which resulted in the decrease of  $B$  value as described in Figures 16(a), 16(d), and 16(g).

In pH 10.3 environment without any  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  (Figure 15(b)), the steel was corroded with the absence of nitrite and was in passive state when nitrite concentration was 0.02 and 0.2 mol/L. With the increase of nitrite concentration, little difference in the cathodic polarization curves was observed. The presence of 0.02 mol/L nitrite made the anodic polarization curves shift towards the direction of lower current density, but higher nitrite concentration (0.2 mol/L) seemed to have no significant effect on the further decrease of

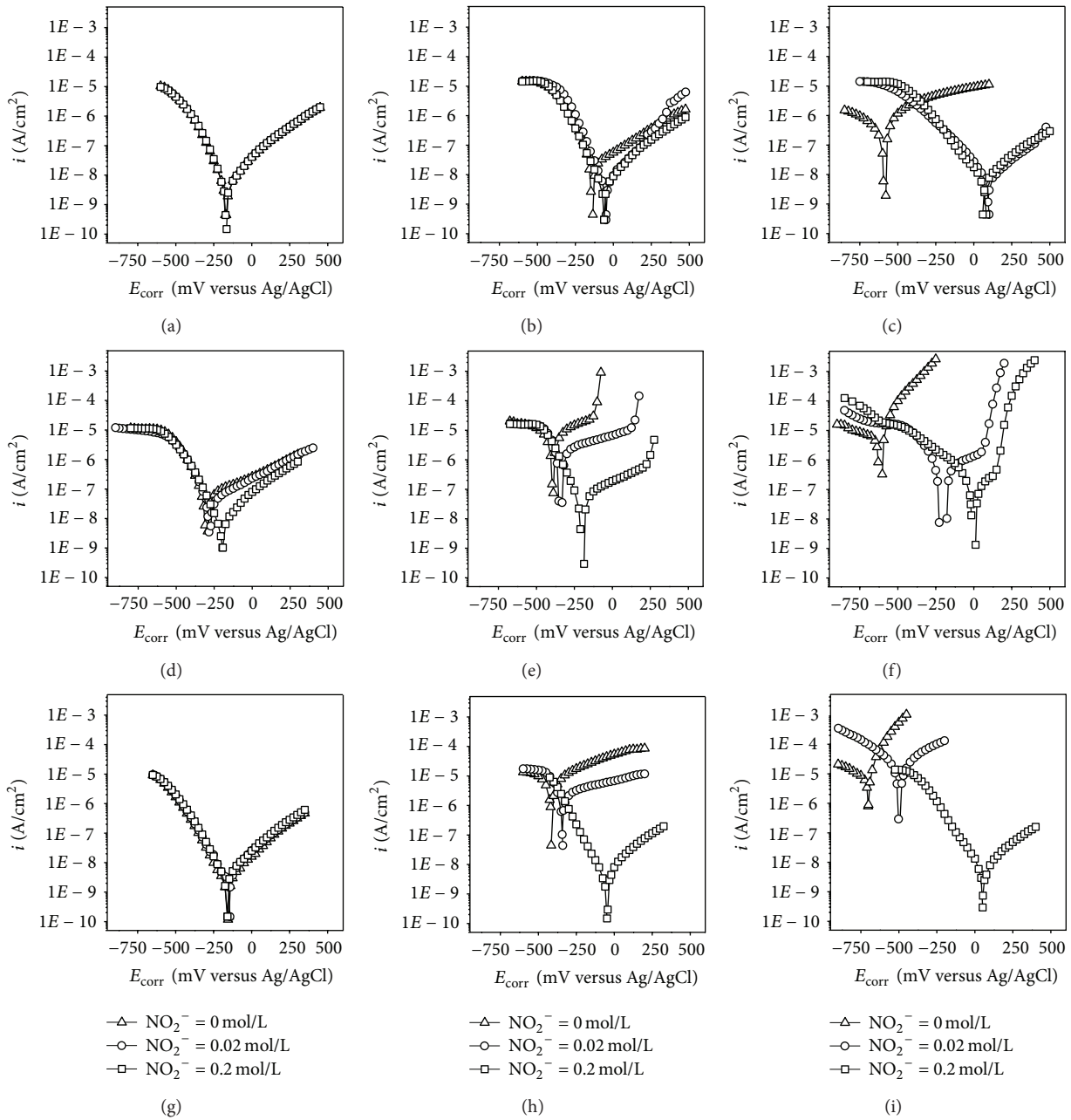


FIGURE 15: Effect of  $\text{NO}_2^-$  concentration on anodic and cathodic polarization curves of steel immersed in different pH solutions with and without 0.1 mol/L  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ . (a) pH 12.6 without  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ , (b) pH 10.3 without  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ , (c) pH 8.1 without  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ , (d) pH 12.6 with 0.1 mol/L  $\text{Cl}^-$ , (e) pH 10.3 with 0.1 mol/L  $\text{Cl}^-$ , (f) pH 8.1 with 0.1 mol/L  $\text{Cl}^-$ , (g) pH 12.6 with 0.1 mol/L  $\text{SO}_4^{2-}$ , (h) pH 10.3 with 0.1 mol/L  $\text{SO}_4^{2-}$ , and (i) pH 8.1 with 0.1 mol/L  $\text{SO}_4^{2-}$ .

current density of anodic polarization. Tafel slopes  $\beta_a$  and  $\beta_c$  and Stern-Geary constant  $B$  all decreased with the presence of nitrite as presented in Figures 16(b), 16(e), and 16(h).

In pH 10.3 environment with 0.1 mol/L  $\text{Cl}^-$  (Figure 15(e)), the steel was corroded seriously with the absence of nitrite. Upon increasing the potential above the self-potential, a passive region was found where the current density was of the order of  $10^{-5} \text{ A/cm}^2$ . At potential value higher than  $-125 \text{ mV}$  versus Ag/AgCl, an abrupt increase in the current

density was observed resulting from the onset of the oxygen evolution reaction. The anodic polarization curves obtained in the presence of 0.02 mol/L nitrite were different from the one obtained in the absence of nitrite ions. The presence of higher nitrite contents had a substantial effect on the anodic behavior of the steel. The anodic polarization curves showed a passive zone, where the passive current density decreased with the increasing of nitrite concentrations. It was in the order of  $10^{-6} \text{ A/cm}^2$  for 0.02 mol/L nitrite and

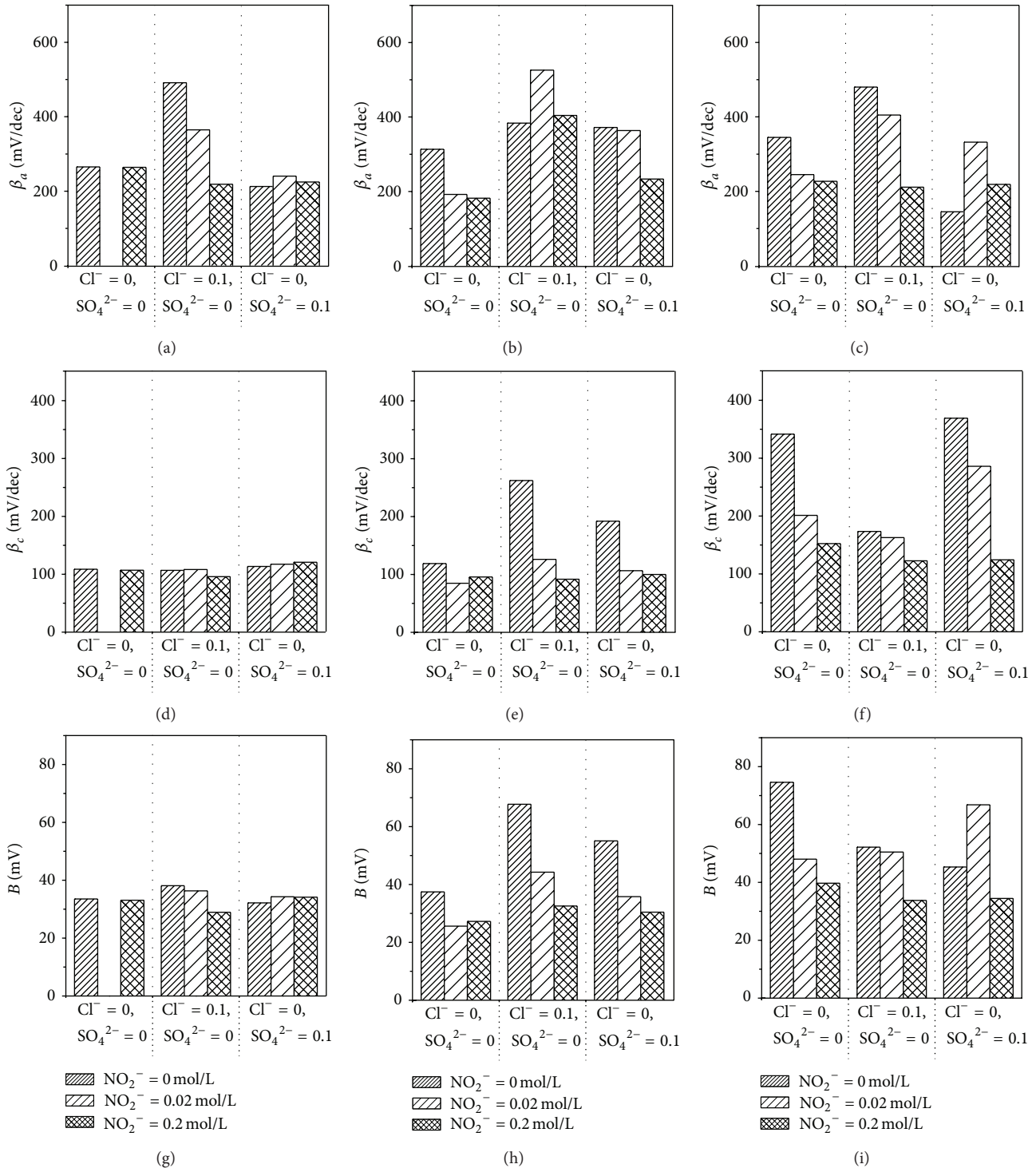


FIGURE 16: Effect of  $\text{NO}_2^-$  concentration on Tafel slope and Stern-Geary constant  $B$ . (a)  $\beta_a$  in pH 12.6, (b)  $\beta_a$  in pH 10.3, (c)  $\beta_a$  in pH 8.1, (d)  $\beta_c$  in pH 12.6, (e)  $\beta_c$  in pH 10.3, (f)  $\beta_c$  in pH 8.1, (g)  $B$  in pH 12.6, (h)  $B$  in pH 10.3, and (i)  $B$  in pH 8.1.

$10^{-7} \text{ A/cm}^2$  for 0.2 mol/L nitrite. On the other hand, the passivity breakdown potential was observed and increased with the increasing of nitrite concentration. It was 125 mV for 0.02 mol/L nitrite and 225 mV for 0.2 mol/L nitrite. Besides this, Tafel slopes  $\beta_a$  and  $\beta_c$  and Stern-Geary constant  $B$  were greatly influenced by the nitrite concentration. The value of  $\beta_c$

and  $B$  decreased with the increasing of nitrite concentration. The  $B$  value with 0 mol/L nitrite was almost twice that with 0.2 mol/L nitrite as shown in Figures 16(b), 16(e), and 16(h).

In pH 10.3 environment with 0.1 mol/L  $\text{SO}_4^{2-}$  (Figure 15(h)), with the absence of nitrite, the steel was corroded. As the potential was raised from the self-potential,

the current density increased with the potential and attained a value of the order of  $10^{-4}$  A/cm<sup>2</sup>. No breakdown potential was observed even when the potential reached 200 mV versus Ag/AgCl. The presence of 0.02 and 0.2 mol/L nitrite ions not only shifted the self-potential toward higher values but also decreased the current density of anodic and cathodic polarization in the condition of the same over potential. The higher the nitrite concentration, the lower the current density of anodic and cathodic polarization. In this case, both Tafel slopes  $\beta_a$  and  $\beta_c$  and Stern-Geary constant  $B$  decreased with the presence of nitrite as given in Figures 16(b), 16(e), and 16(h).

In pH 8.1 environment without any Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup> (Figure 15(c)), the steel was corroded seriously with the absence of nitrite, and it was in passive state when nitrite concentration was 0.02 and 0.2 mol/L. The presence of low content of nitrite (0.02 mol/L) not only greatly raised the steel potential and reduced the current density of anodic polarization but also markedly decreased the current density of cathodic polarization. Under the same over potential, the cathodic polarization current density obtained in the solution containing 0.02 mol/L nitrite was about one order of magnitude lower than that obtained in the absence of nitrite, and further increase of nitrite concentration (0.2 mol/L) did not result in the further decrease of current density of cathodic polarization. In this case, Tafel slopes  $\beta_a$  and  $\beta_c$  and Stern-Geary constant  $B$  decreased with the presence of nitrite as presented in Figures 16(c), 16(f), and 16(i).

In pH 8.1 environment with 0.1 mol/L Cl<sup>-</sup> (Figure 15(f)), the steel was corroded seriously with the absence of nitrite. Upon increasing the potential above the self-potential, no passive region can be found. With the presence of nitrite, the self-potential shifted toward the positive direction and was function of nitrite concentration. The anodic polarization behavior of steel in pH 8.1 environment containing 0.1 mol/L Cl<sup>-</sup> and 0.02 or 0.2 mol/L NO<sub>2</sub><sup>-</sup> was found to be similar to that observed in pH 10.3 environment (Figure 15(e)). A passive region followed by an abrupt increase of current density at the potential higher than 50 mV for 0.02 mol/L nitrite or 150 mV for 0.2 mol/L nitrite was observed. The presence of nitrite also had an effect on the cathodic behavior of steel, which caused the cathodic polarization curve to shift to the direction of lower current density. In this case,  $\beta_a$  firstly increased when nitrite content was very low (0.02 mol/L) and then decreased when nitrite content was high (0.2 mol/L), while  $\beta_c$  and Stern-Geary constant  $B$  decreased with the presence of nitrite as shown in Figures 16(c), 16(f), and 16(i).

In pH 8.1 environment only containing 0.1 mol/L SO<sub>4</sub><sup>2-</sup> (Figure 15(i)), the steel was corroded seriously with the absence of nitrite. The presence of 0.02 mol/L nitrite led to the increase of cathodic polarization current density and the decrease of anodic polarization current density. Higher nitrite concentration (0.2 mol/L) resulted in further decrease of anodic polarization current density and also had an influence on cathodic polarization current density. It can be seen that under the same over potential, the cathodic polarization current in the case of 0.2 mol/L nitrite was lower than that in the case of 0 mol/L nitrite. After the anodic and cathodic

polarization were finished, visual examination of steel surface was performed. Many small pitting holes with the sizes of 0.2 mm to 1 mm were observed on the surface of steels immersed in pH 8.1 solutions containing 0.02 mol/L nitrite and 0.1 mol/L SO<sub>4</sub><sup>2-</sup>, while no rust and no pitting hole were found on the surface of steels immersed in pH 8.1 solutions containing 0.2 mol/L nitrite and 0.1 mol/L SO<sub>4</sub><sup>2-</sup>. Cathodic Tafel slope  $\beta_c$  decreased with the presence of nitrite, while anodic Tafel slope  $\beta_a$  and Stern-Geary constant  $B$  firstly increased when nitrite content was very low (0.02 mol/L) and then decreased when nitrite content was high (0.2 mol/L) as shown in Figures 16(c), 16(f), and 16(i).

When steel is polarized anodically, the steel potential set by potentiostat is greater than self-potential. The electrons produced per unit time by the Fe → Fe<sup>2+</sup> + 2e<sup>-</sup> reaction exceed those consumed per unit time by the O<sub>2</sub> + 2H<sub>2</sub>O + 4e<sup>-</sup> → 4OH<sup>-</sup> reaction, and net oxidation occurs at the steel surface. A positive value is consistent with the sign convention that assigns a positive value to the external circuit current. When steel is corroded, the presence of nitrite accelerates the oxidation of Fe<sup>2+</sup> into Fe<sub>2</sub>O<sub>3</sub> or γ-FeOOH and causes the formation of a less porous and more compact passive film which inhibits the Fe → Fe<sup>2+</sup> + 2e<sup>-</sup> reaction. The reduction of electrons produced per unit time by the Fe → Fe<sup>2+</sup> + 2e<sup>-</sup> reaction results in the decrease of anodic polarization current. When steel is in passive state, the properties and composition of the passive film are similar to those found in the presence of nitrite [13], so the Fe → Fe<sup>2+</sup> + 2e<sup>-</sup> reaction is little affected and the electrons assigned to the external circuit is not changed. Therefore, there is almost no change in anodic polarization current.

#### 4. Conclusions

In this study, the effect of nitrite concentration and pH on the corrosion of steel has been investigated by means of visual examination, half-cell potential, and anodic and cathodic polarization curves. Based on the above analysis, the following conclusions can be obtained.

With the presence of nitrite, the corrosion of steel can be inhibited effectively. Chloride threshold level and sulfate threshold level are not only increased with the increasing of nitrite concentration but are also affected by pH. Highly alkaline environment plays an important role in assisting nitrite to inhibit corrosion.

Chloride-induced corrosion is more prone to initiate than sulfate-induced corrosion in highly alkaline environment, but in neutral environment, when nitrite concentration is equal to or less than 0.053 mol/L, sulfate-induced corrosion is more likely to occur than chloride-induced corrosion.

For chloride-induced corrosion, using NO<sub>2</sub><sup>-</sup>/Cl<sup>-</sup> mole ratio as the parameter to guarantee the inhibition effect is suitable in highly alkaline environment, but not appropriate in weakly alkaline and neutral environments. For sulfate-induced corrosion, NO<sub>2</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> cannot be used as the parameter to guarantee the inhibition effect due to the change of its threshold level with nitrite concentration.

When the steel is in passive state, the presence of nitrite has little influence on anodic/cathodic polarization curves and Stern-Geary constant  $B$ . When the steel is corroded, the addition of nitrite has a significant effect on the anodic polarization curve of steel and the Stern-Geary constant  $B$ .

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