

Cathodic Reaction Mechanism of 3Cr Low Alloy Steel Corroded in CO₂-Saturated High Salinity Solutions

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To clarify the cathodic reaction mechanism of 3Cr steel in CO₂ environments, two types of electrochemical measurements were performed in this study: galvanostatic measurements and potentiodynamic sweeps. Different cathodic reactions were observed for pH < 3.9 and for pH > 4.7, which differed greatly from that of plain carbon steel. At pH > 4.7, the order of reaction q was zero, and the direct reduction of HCO₃⁻ was the dominating cathodic reaction. At pH < 3.9, q was 0.66, and the direct reduction of H⁺ was the dominating reaction. At intermediate pH values, a transition was apparent between reactions.

Keywords: low alloy steel; CO₂ corrosion; electrode kinetics; SEM; in-situ pH monitoring

1. INTRODUCTION

CO₂ corrosion is among main factors affecting pipeline life in the oil and gas industry [1, 2]. Because of their high CO₂ corrosion resistance and cost performance, Cr-containing (1 %, 3 %, 5 %, etc.) low alloy steels created based on traditional carbon steels have drawn considerable attention in the field of CO₂ corrosion control. Among these steels, 3Cr steel, which is used for tubing, has the highest cost-efficiency [3].

For carbon steels, such as X65 and X70, the cathodic process has been widely investigated. Recent studies have demonstrated that the early proposal without considering the effect of pH is questionable. In a breakthrough, Bockris observed the effect pH exerts on electrode reactions [4]. Further research by Schmitt [5] indicated that the dominant cathodic reaction was the direct reduction of HCO₃⁻ at pH > 6. Nescic [6] specified that the critical pH was approximately 4 and the dominant cathodic reaction was the direct reduction of carbonic acid at pH > 4. However, pertaining to 3Cr steel,

little research has been conducted on the electrode process. To interpret experimental results, current studies on 3Cr steel have constantly referred to the cathodic mechanism of carbon steel [7, 8]. Because of the addition of chromium, the cathodic reaction process of 3Cr steel should be different from that for carbon steel. Therefore, studying the cathodic process of 3Cr steel in a CO₂ environment under high temperature and high pressure (HTHP) is imperative.

As the pH of solution near 3Cr steel will change considerably during the corrosion process [9], in this study, electrochemical parameters were tested at different pH values. A simple and effective electrochemical method that can be used to characterize the kinetics of the cathodic process was used to predict cathodic reactions at various pH levels. Moreover, to verify the proposed mechanism accuracy, in situ pH monitoring of the bare solution (without steel) and the 3Cr steel were conducted.

2. EXPERIMENTAL DETAILS

2.1 Materials and solution

Commercial 3Cr low-alloy line pipe steel (X65 grade) was used as the experimental material. Table 1 lists the steel composition, and Table 2 shows the composition of the test solution. The solution, which simulated oilfield formation water, was prepared using analytical grade reagents and deionized water.

Table 1. Main chemical composition of 3Cr steel (wt, %)

Element	C	Cr	Mo	Si	Mn	Nb	S	P	Fe
3Cr (X65 grade)	0.07	2.96	0.15	0.2	0.55	0.03	0.003	0.003	Bal.

Table 2. Main composition of the test solution simulated the oilfield formation water

Composition	NaCl	CaCl ₂	KCl	MgCl•6H ₂ O	NaHCO ₃	Na ₂ SO ₄
Concentration, ×10 ⁻³ M	432.8	24.8	8.6	9.5	6.2	1.4

2.2 Immersion tests

Corrosion tests were performed in a 5-L autoclave to determine the corrosion resistance of 3Cr steel in a CO₂ environment. Before conducting weight loss tests, each specimen was weighed using an analytical balance with an accuracy of 10⁻⁴ g. After 2, 8, and 96 h of immersion, the corroded specimens were extracted from the autoclave and immediately rinsed with absolute ethyl alcohol. The corrosion products were removed according to ASTM G1-03 standards, rinsed, dried, and reweighed to determine the final weight of the specimen. The corrosion rate was calculated using the following

equation:

$$C_i = \frac{87600(W_{0i} - W_{fi})}{t\rho S}; (i=1, 2, \dots) \quad (1)$$

where C_i is the average corrosion rate, mm/y; W_{0i} and W_{fi} are the original and final weights of the specimen, g, respectively; t is the immersion time, h; ρ is the steel density, g/cm³; and S is the exposed surface area, cm².

2.3 Morphology observation

The cross-sectional morphology of the corrosion film formed on 3Cr steel was observed using scanning electron microscope (SEM) and quadrant back scattering detector (QBSD) techniques.

2.4 Electrochemical measurements

The electrochemical measurements were conducted in situ in the homemade 5-L HTHP electrochemical autoclave (Fig. 1). A platinum ring served as the counter electrode (CE) and a saturated silver/silver-chloride (Ag/AgCl) electrode (SSE) was used as the reference electrode (RE). The surface area of the CE was 18.84 cm², which was much larger than the surface area of working electrode (WE).

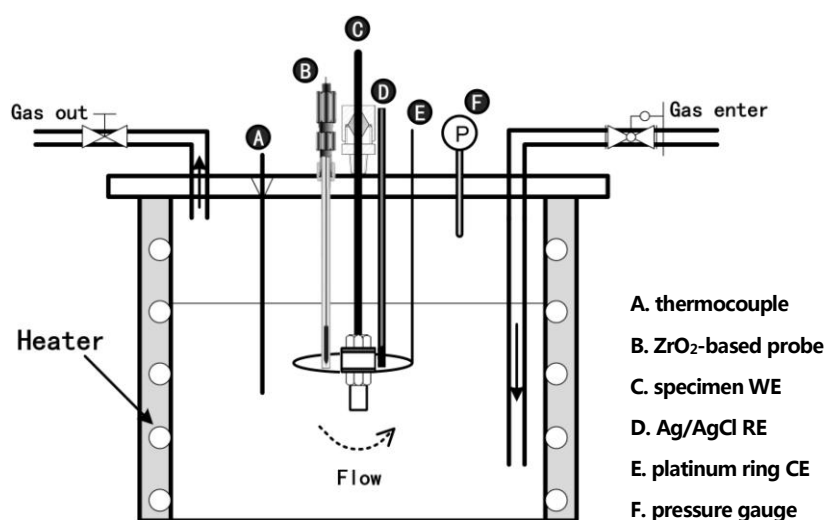


Figure 1. Schematic diagram of the electrochemical autoclave showing the electrode locations

Galvanostatic measurements were performed to obtain the potential at various pH values; a cylindrical 3Cr steel WE with an exposed area of 6.59 cm² was used and a constant cathodic current was applied. According to the potentiodynamic sweep data, the eventual cathodic current, which was determined through trial and error, was 0.5 mA/cm² (3.295 mA), a current that was high to render the anodic partial current negligible. In potentiodynamic sweeps, the scan rate was 1 mV/s. Moreover, a

wire-shaped WE was used, ensuring that the cathodic Tafel slope test was accurate. The wire WE had a minute exposed area (only $4 \times 10^{-4} \text{ cm}^2$), which could weaken the influence the anodic dissolution exerted on the cathodic polarization process. Fig. 2 shows the microscopic cross-section photo of the 3Cr steel wire WE. Before each galvanostatic and potentiodynamic test, the pH was adjusted using HCl and NaHCO_3 .

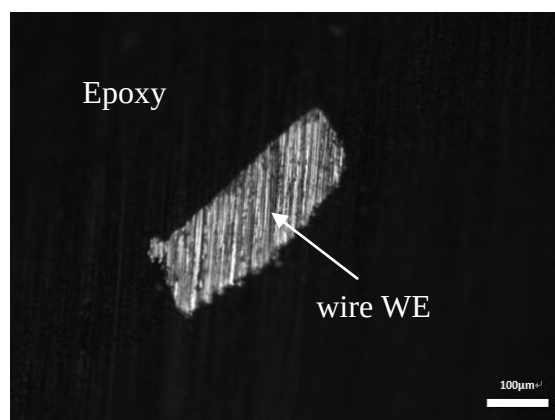


Figure 2. Microscopic cross-section photo of the 3Cr steel wire WE

2.5 *In situ* pH monitoring

In Fig. 1, the SSE and ZrO_2 -based probe together served as the pH probe used to measure the pH values of the solution near the steel surface. To ensure the pH shift was more prominent, the specimen used for pH monitoring had a large exposed area of 19.77 cm^2 , and the solution volume was merely 500 ml. The pH values were displayed on pH meters, and the pH-Time curves were automatically recorded by a computer.

All tests were performed at 353 K and a CO_2 partial pressure of 8 bar. The rotation speed was 228 rpm.

3. RESULTS AND DISCUSSION

3.1 *Potentiodynamic sweeps and galvanostatic measurements*

For 3Cr steel, the substrate corrosion naturally introduces chromium into the solution as a result of the Cr addition.

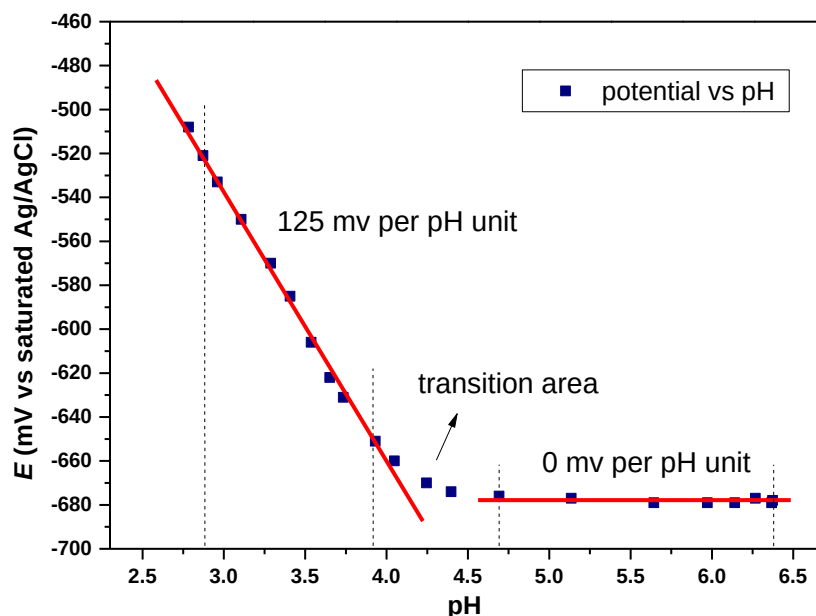
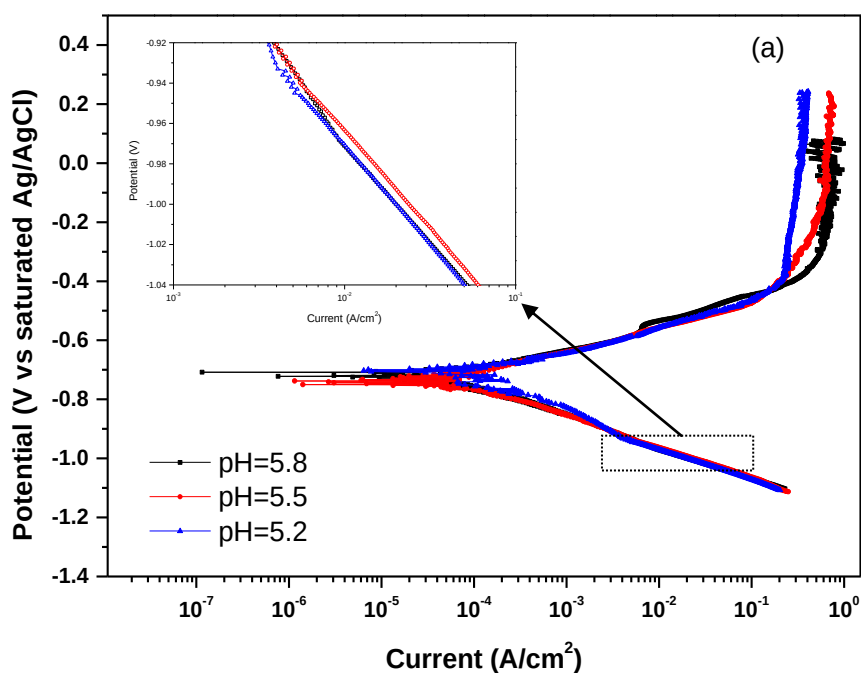
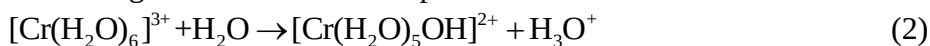


Figure 3. Potential plots of 3Cr steel at different pH values and a constant cathodic current (i_c) of 0.5 mA/cm². The pH was adjusted using HCl and NaHCO₃

The hydrolysis of Cr³⁺ (Eq. (2)) considerably decreases the pH of solution [9]. In the corrosion process, the pH is a critical factor affecting the electrode reaction. Therefore, the cathodic process of 3Cr steel must differ from that of carbon steel. Thus, which cathodic reaction occurs first and whether the reaction changes with the corrosion process must be determined.



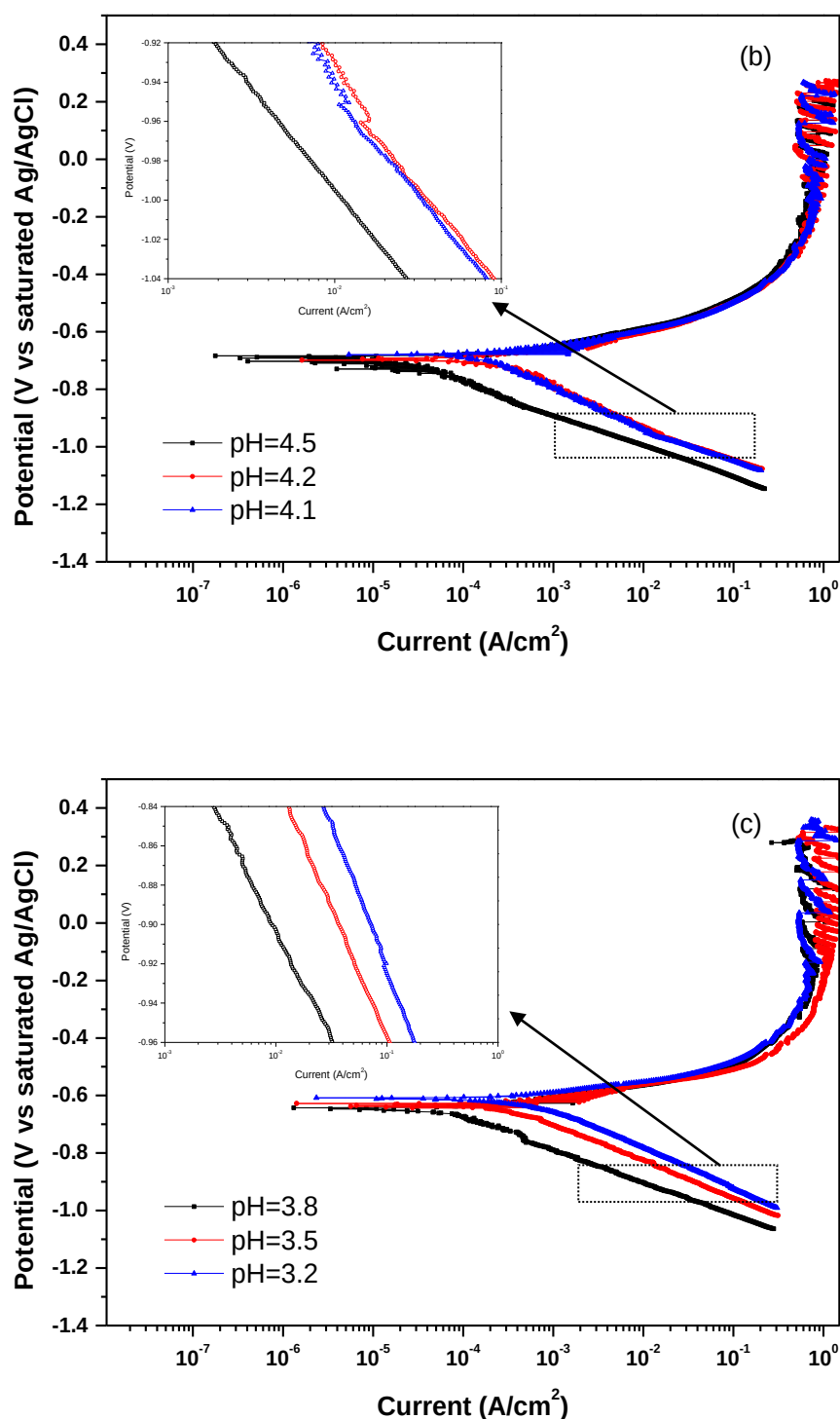


Figure 4. Polarization curves measured over a wire-shaped 3Cr steel working electrode at different pH levels: (a) pH > 4.7, (b) 3.9 < pH < 4.7, and (c) pH < 3.9. Temperature = 353 K, P_{CO_2} = 8 bar, and scan rate = 1mV/s. The pH was adjusted using HCl and NaHCO₃

To ascertain the cathodic process of 3Cr steel, galvanostatic measurements and potentiodynamic sweeps were performed at various pH levels. The galvanostatic measurements were

conducted by applying a constant cathodic current (0.5 mA/cm^2), which was sufficiently high to render the anodic partial current negligible, and the potential was then measured at different pH values.

As shown in Fig. 3, the E versus pH curve can apparently be divided into three regions: 0 mV/pH at $\text{pH} > 4.7$, 125 mV/pH at $\text{pH} < 3.9$, and a transition area at $3.9 < \text{pH} < 4.7$. Correspondingly, the cathodic Tafel slope (b_c) obtained by linearly fitting the Tafel plots in Fig. 4 can also be divided into three regions: $190 \pm 8 \text{ mV/dec}$ at lower pH level, $75 \pm 2 \text{ mV/dec}$ at the higher pH level, and $120 \pm 7 \text{ mV/dec}$ in the transition area. Accordingly, the various pH levels can preliminarily be predicted to cause different cathodic reactions. The following subsection discusses calculating the cathodic process kinetics and how the cathodic reaction changes with the pH.

3.2 Kinetics of the cathodic process

In the CO_2 -saturated solution, the known cathodic reactions mainly consisted of the reduction of H_2CO_3 , HCO_3^- , and H^+ [10–12].



In the aforementioned galvanostatic measurements and potentiodynamic sweeps, the only independent variable was pH. Therefore, the following general expression for the cathodic current can be considered [13]:

$$I_c = k [\text{H}^+]^q \exp\left(\frac{\alpha_c n F}{RT} \varphi\right) \quad (6)$$

where $[\text{H}^+]$ is the hydrogen ion concentration, M; q is the order of the reaction (with respect to $[\text{H}^+]$), which represents the degree of influence the H^+ concentration has on the corrosion current density; α_c is the apparent transfer coefficient; n is the molar weight of the substance, mol; F is the Faraday constant (96485 C/mol); φ is the overpotential, mV vs. saturated Ag/AgCl; R is the universal gas constant (8.314 J/mol K); and T is the absolute temperature, K.

At a constant cathodic current density, the potential can be expressed as a function of the pH by the following equation, which was obtained by transforming Eq. (6):

$$\varphi = q \cdot b_c \cdot \text{pH} + c \quad (7)$$

where $b_c = -2.303RT/\alpha_c F$ is the cathodic Tafel slope in mV/dec and c is a constant.

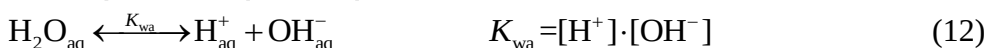
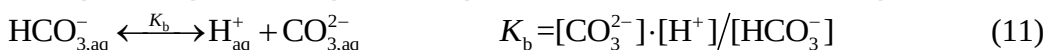
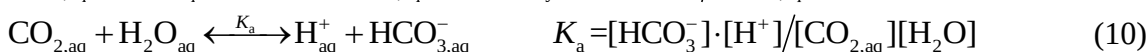
The order of the reaction reflects the reaction kinetics of a macro reaction in certain conditions, which represents the degree of influence a variable has on the reaction rate. In this study, the only variable was the pH of the solution. Therefore, in Eqs. (6) and (7), the q represents the degree of influence the H^+ concentration has on the corrosion current density. Apparently, the higher the q value, the greater was the influence the H^+ concentration had on the corrosion current density. If q is zero, the corrosion current is independent of the H^+ concentration.

From the plot in Fig. 3, the values of $q \cdot b_c$ can be obtained by piecewise linear fitting of the curve. The q values were obtained by inserting the value of b_c into $q \cdot b_c$ (Table 3). At the higher pH level, the order of the reaction regarding the pH was zero, indicating that the cathodic reaction was independent of H^+ . Therefore, the cathodic reaction at $pH > 4.7$ should be Eq. (3) or Eq. (4). However, the dominant one had to be determined.

Table 3. Kinetics parameters of cathodic process of 3Cr steel at different pH levels

pH	$q \cdot b_c$, mV per pH	$-b_c$, V/dec	Order of reaction, q
High, $pH > 4.7$	0	0.075 ± 0.002	0
Intermediate, $4.7 > pH > 3.9$	transition area	0.12 ± 0.007	transition area
Low, $pH < 3.9$	-125	0.19 ± 0.008	0.66 ± 0.03

For clarification, the water chemistry model of a HTHP CO_2 -saturated solution (open system) was considered in this study. The main homogenous chemical reactions involved in CO_2 -saturated solutions were assumed to be basically the same. These reactions are listed below:



In high CO_2 partial pressure systems, the relationship between the concentration and pressure is no longer linear and Henry's law cannot be used. However, the literature indicates that the concentration and pressure can fit the linear relation well in environments in which the CO_2 partial pressure is below 10 bar [14]. Therefore, the dissolved CO_2 concentration at a CO_2 partial pressure of 8 bar can be calculated using Henry's law:

$$[CO_{2,aq}] = K_{Hen,353} \cdot [CO_{2,gas}] \quad (13)$$

where $K_{Hen,353}$ is Henry's constant for carbon dioxide at 353 K, 0.115 M/bar [15]; and $[x]$ is the concentration of "x" in M, the same below.

The equilibrium constant K_{hyd} for carbon dioxide hydration was obtained from Hu [15]. K_{hyd} does not change substantially within the temperature range of 20 °C to 100 °C [16]. Since it is not pressure-dependent, the equilibrium constant of carbon dioxide hydration, having the value of 1.67×10^{-3} (which is used in normal temperature and pressure environment models) is applicable at 80 °C and a CO_2 partial pressure of 8 bar.

$$[H_2CO_3] = K_{hyd} \cdot [CO_{2,aq}] \cdot [H_2O] \quad (14)$$

The first-order ionization constant of carbonic acid, K_a , is a function of the temperature and pressure, and can be expressed by the following equation, which is valid for a temperature range of 0 °C to 100 °C and pressure range of 1 bar to 3000 bar [17]:

$$\ln K_a = 273.5159304 - 11794.38348 \cdot T^{-1} - 36.506335 \cdot \ln T \\ + (-45.08004597 \cdot T^{-1} + 2131.318848 \cdot T^{-2} + 6.714256299 \cdot T^{-1} \ln T)(P - P_s) \\ + (0.008393915212 \cdot T^{-1} - 0.4015441404 \cdot T^{-2} - 0.00124018735 \cdot T^{-1} \ln T)(P - P_s)^2 \quad (15)$$

where T is the temperature, K; P is the pressure, bar; and P_s is the saturation pressure of water, bar. The relationship between P_s and T was obtained through nonlinear regression fitting of data acquired from the literature [18].

$$\ln P_s = 11.76791 - 3875.982/(T - 42.99) \quad (273 \leq T \leq 483) \quad (16)$$

$$\ln P_s = 13.13588 - 5203.362/(T - 32.28) \quad (483 \leq T \leq 643) \quad (17)$$

The second-order ionization constant of carbonic acid, K_b , was calculated from 0 °C to 100 °C and 1 bar to 3000 bar by using the following equation [17]:

$$\ln K_b = -151.1815202 - 0.088695577 \cdot T - 1362.259146 \cdot T^{-1} + 27.79798156 \cdot \ln T \\ - (29.51448102 \cdot T^{-1} + 1389.015354 \cdot T^{-2} + 4.419625804 \cdot T^{-1} \ln T)(P - P_s) \\ + (0.003219993525 \cdot T^{-1} - 0.1644471261 \cdot T^{-2} - 0.0004736672395 \cdot T^{-1} \ln T)(P - P_s)^2 \quad (18)$$

According to Eqs. (10) and (11), the HCO_3^- and CO_3^{2-} concentrations in the solution can be expressed as:

$$\lg[\text{HCO}_3^-] = \text{pH} + \lg(K_{a,353} \cdot [\text{CO}_{2,\text{aq}}] \cdot [\text{H}_2\text{O}]) \quad (19)$$

$$\lg[\text{CO}_3^{2-}] = 2 \cdot \text{pH} + \lg(K_{b,353} \cdot K_{a,353} \cdot [\text{CO}_{2,\text{aq}}] \cdot [\text{H}_2\text{O}]) \quad (20)$$

The equilibria of CO_2 -saturated solutions at 353 K and a CO_2 partial pressure of 8 bar were derived from the calculations depicted in Fig. 5. At $\text{pH} = 4.7$, the HCO_3^- concentration was 1.19 M, which was much higher than the H_2CO_3 concentration (0.0015 M). Moreover, the HCO_3^- concentration could increase exponentially with the pH , whereas the H_2CO_3 concentration remained unchanged. Therefore, the reaction expressed in Eq. (4) was probably the dominant cathodic reaction at $\text{pH} > 4.7$.

At the lower pH level ($\text{pH} < 3.9$), q was 0.66, indicating that the cathodic reaction at $\text{pH} < 3.9$ was related to H^+ . By contrast, the hydrogen ion concentration increased exponentially while bicarbonate ion concentration decreased with the pH . Therefore, the dominant cathodic reaction was Eq. (5) if the pH decreased to approximately 3.9 or less.

As previously mentioned, the intermediate pH level ($4.7 > \text{pH} > 3.9$) was an apparent transition area for q and b_c . Based on the known dominant cathodic reactions for $\text{pH} > 4.7$ and $\text{pH} < 3.9$, the cathodic process in the intermediate pH range could be described as follows: both Eqs. (4) and (5) occurred in this pH range, and Eq. (5) became increasingly stronger, whereas Eq. (4) became increasingly weaker when the pH decreased from 4.7 to 3.9. Therefore, the two critical pH values were 4.7 and 3.9 for the cathodic reaction process of 3Cr steel in a CO_2 environment.

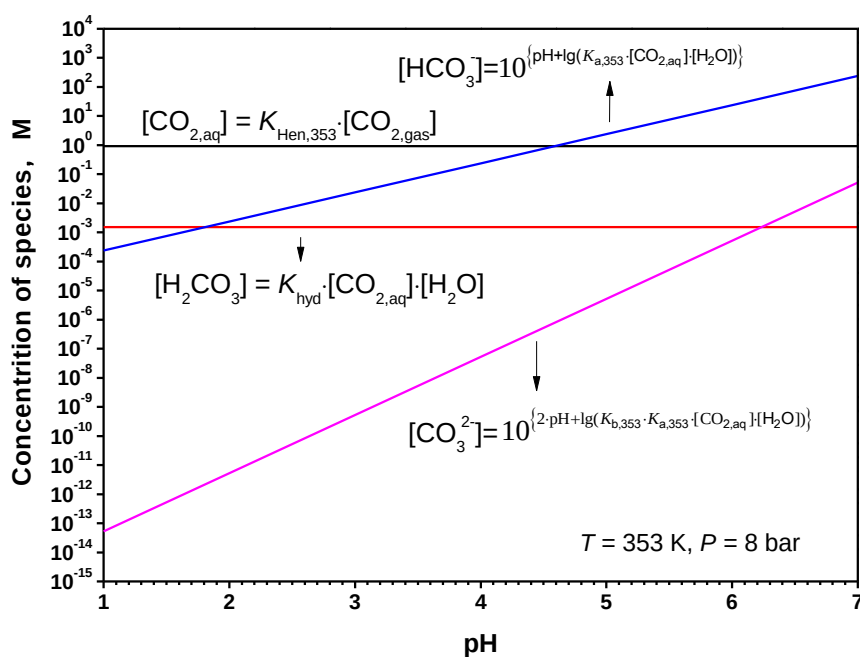


Figure 5. Equilibria of a CO₂-saturated solution (open system)

3.3 In situ pH monitoring

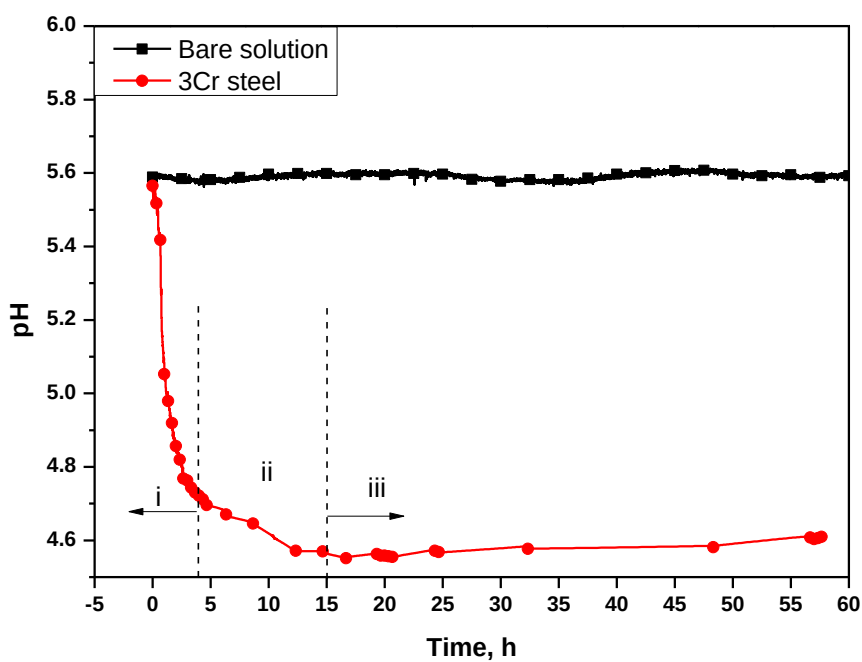


Figure 6. pH-Time curves of the bare solution (without steel in it) and the solution near the 3Cr steel surface in a CO₂ environment

To verify the proposed cathodic mechanism, the pH of the solution near the 3Cr steel surface was monitored and recorded as a function of the corrosion time. The pH of the bare solution (without steel in it) served as a reference. As shown in Fig. 6, the 3Cr-pH curve could be divided into three stages: initial rapid acidification (stage i), a transition area (stage ii), and a late stable period (stage iii). The pH of the bare solution was maintained constant at approximately 5.6. Moreover, after 2, 8, and 96 h during the corrosion period, which were within stages i, ii, and iii, respectively, immersion tests were performed. The corrosion rates of 3Cr steel were obtained using the weight loss method, and the cross-sectional morphologies of the corrosion films were observed using the SEM and QBSD techniques.

Fig. 7(a)–(c) show the cross-sectional morphologies of the corrosion films formed on 3Cr low alloy steel after 2, 8, and 96 h, respectively. In Fig. 7(a), no film formed on the 3Cr steel. This was related to the supersaturation (S), which was defined as the ratio of the crystallizing substance concentration to the solubility product for FeCO_3 (K_{sp}) (Eq. (21)). Only when the product of $[\text{Fe}^{2+}]$ and $[\text{CO}_3^{2-}]$ exceeds K_{sp} of FeCO_3 (i.e. $S > 1$), can FeCO_3 begin to nucleate. Therefore, stage i remained a no-film period. The bare steel without any protective covering exhibited a high corrosion rate. As shown in Fig. 8, the corrosion rate of 3Cr steel reached 16.42 ± 0.90 mm/y at 2 h, causing much chromium to be continually released into the solution and hydrolyzed, decreasing the pH considerably. As mentioned in Section 3.2, the dominant cathodic reaction was Eq. (4) at pH = 5.6. The reduction of HCO_3^- would have increased the pH slightly. Therefore, the pH would have decreased sharply because of the joint effect of the hydrolysis of Cr^{3+} and Eq. (4) in stage i.

$$S = [\text{Fe}^{2+}] \cdot [\text{CO}_3^{2-}] / K_{\text{sp}} \quad (21)$$

In stage ii, when the pH fell to approximately 4.7, the reaction in Eq. (5) began. Apparently, the direct reduction of H^+ increased the pH of the solution. In addition, an incomplete coverage film began to form on the steel surface (Fig. 7(b)), protecting the substrate. As shown in Fig. 8, the corrosion rate of 3Cr steel dropped to 8.56 ± 0.58 mm/y, which was much lower than the rate in stage i. Therefore, the rate of Cr added to the solution decreased and the acidification effect weakened. Consequently, the decline rate of the pH in the vicinity of 3Cr steel in stage ii decreased.

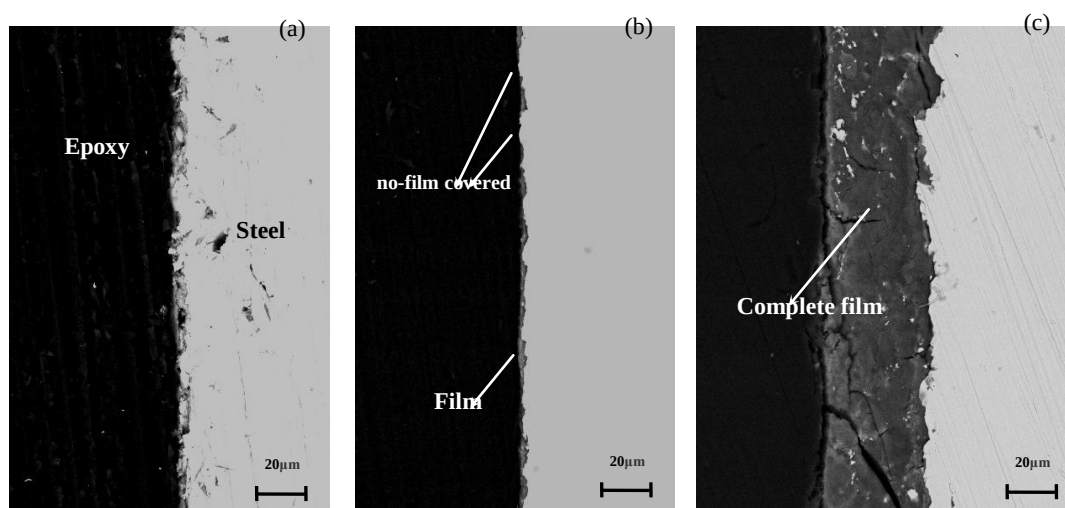


Figure 7. Cross-sectional morphologies of corrosion films formed on 3Cr low alloy steel at different times: (a) 2 h, (b) 8 h, and (c) 96 h

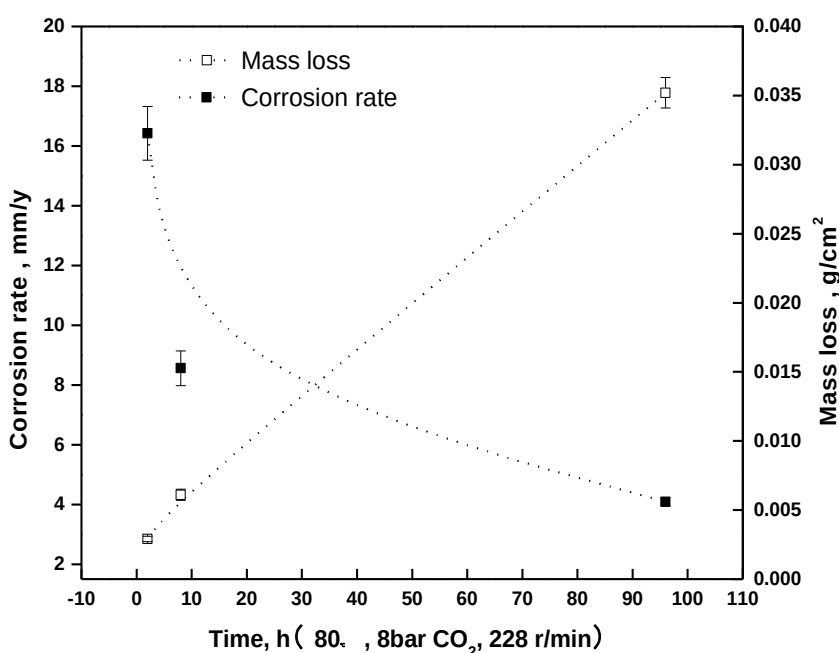


Figure 8. Mass loss and corrosion rate of 3Cr low alloy steel during various corrosion periods

Over time, a complete and thicker film formed on the 3Cr steel (Fig. 7(c)). Chen [19] found that the Cr-rich film that formed on Cr-containing low alloy steel was compact and showed selectivity to certain cations, which considerably lowered the HCO_3^- concentration at the interface compared with that in the solution media. Therefore, the reduction of HCO_3^- was suppressed in stage iii. In addition, the compact film led to a very low corrosion rate at 96 h, as shown in Fig. 8, and the Cr dissolution rate decreased. The reduction of H^+ was slightly stronger than the hydrolysis of Cr, and therefore, the pH increased slightly in stage iii.

According to the previous analysis, the cathodic reaction mechanism fits the pH-monitoring results effectively, indicating that the cathodic mechanism described in this paper is reliable.

4. CONCLUSION

In the corrosion process, the solution near the 3Cr steel surface appeared acidic, and two critical pH values were observed. At $\text{pH} > 4.7$, the direct reduction of HCO_3^- was the dominant cathodic reaction, while at $\text{pH} < 3.9$, the direct reduction of H^+ was the dominant reaction. The dominant cathodic reaction changed from the reduction of HCO_3^- to the reduction of H^+ during the early corrosion of 3Cr steel.

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