Effect of pH Value on Stress Corrosion Cracking of X70 Pipeline Steel in Acidic Soil Environment

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The effect of pH value on the stress corrosion cracking (SCC) of API X70 pipeline steel in simulated acidic soil solutions was investigated by using slow strain rate test, electrochemical polarization curves, electrochemical impedance spectroscopy, and scanning electron microscopy. pH plays an important role in the susceptibility and electrochemical mechanism of SCC. The pH higher than 5 has no significant effect on electrochemical processes. By contrast, the pH lower than 5 intensifies cathodic hydrogen evolution reactions, thus increasing the cathodic current and corrosion potential. Under different pH values, the SCC mechanism of X70 pipeline steel varies among anodic dissolution (AD), hydrogen embrittlement (HE), and the combination of AD and HE (AD + HE) with variations of applied potential. At $-850 \text{ mV}_{\text{SCE}}$, the SCC mechanism is HE if pH is less than 4 or AD + HE if pH value is more positive.

KEY WORDS: X70 pipeline steel; Soil environment; pH; Stress corrosion cracking

1. Introduction

The construction of high-strength steel pipes has been increasing in China, thus arousing unprecedented concern on pipeline security against corrosion damage in soil environments. According to international investigations, stress corrosion cracking (SCC) is one of the most destructive deteriorations of oil or gas pipelines. Two types of SCC are recognized in soil environments: high-pH (pH of approximately 9) SCC and low-pH SCC, including near-neutral-pH and acidic-pH SCC^[1–7]. The mechanism of high-pH SCC is anodic dissolution (AD) for passive films at the crack tip between grain boundaries^[8]. However, no widely acceptable mechanism of low-pH SCC exists. Although considerable research has focused on the detailed mechanism of SCC in near-neutral-pH soil environments, few efforts have been made to investigate the same mechanism in acidic solutions. Parkins

et al.^[3] regarded the mechanism of near-neutral-pH SCC as the cooperation of AD and the ingress of hydrogen in steel. Park *et al.*^[9] indicated that SCC in a near-neutral-pH bicarbonate solution initiates a pit-to-stress corrosion crack transition mode. On the contrary, Chen *et al.*^[10] recognized that near-neutral-pH SCC follows a dissolution mechanism in the crack initiation and initial growth stages and that hydrogen facilitates the dissolution rate of steel, thus leading to high SCC susceptibility. Beavers *et al.*^[11] revealed that SCC occurs because of AD and is propagated by hydrogen-induced cracking. Wang *et al.*^[12] indicated that SCC is controlled by hydrogen embrittlement (HE) below $-800 \text{ mV}_{\text{SCE}}$ and by AD between -700 and $-500 \text{ mV}_{\text{SCE}}$. In acidic soil solutions, hydrogen evolution reactions are intensively promoted owing to the low pH, which increases the SCC susceptibility of pipeline steels. Liu *et al.*^[6,7,13–16] investigated the SCC of pipeline steels in acidic soil environments and concluded that the property of SCC is similar to that of near-neutral-pH environments. However, higher SCC susceptibility causes the SCC mechanism to vary within different potential ranges

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Table 1 Chemical composition of the X70 pipeline steel (wt.%)

C	Si	Mn	Nb	Ni	Cr	Cu	Al	Ti	V	S	P	Fe
0.073	0.22	1.52	0.054	0.18	0.17	0.20	0.029	0.017	0.026	0.0022	0.0035	Balance

Table 2 Mechanical data of the X70 pipeline steel

Yield strength $\sigma_{0.5}$ (MPa)	Ultimate tensile strength (MPa)	Elongation δ_0 (%)	Reduction-in-area ψ_0 (%)
565	739	15.5	58.4

Note: Measured according to standard GB/T 228.1-2010

Table 3 Chemical composition of the test solution ($\text{g}\cdot\text{L}^{-1}$)

CaCl_2	NaCl	Na_2SO_4	$\text{MgSO}_4\cdot 7\text{H}_2\text{O}$	KNO_3	NaHCO_3
0.222	0.936	0.284	0.394	0.586	0.302

in acidic soil solutions, and strain rate plays a dominant role in affecting SCC behavior because of the effect of the dislocation movement. Increasing evidence confirms the effect of hydrogen on the SCC of pipeline steel in soil environments. As demonstrated in a previous study^[6], SCC may occur in soil environments; thus, investigation of the behavior and main effect factors of SCC in acidic soil in Southeast China is crucial. However, no report has focused on the effect of pH value on SCC in acidic soil environments to demonstrate clearly the relationship between SCC in acidic and near-neutral-pH media. Such a study would be very helpful in developing adoptive protection techniques for the SCC of pipelines in acidic soil areas.

This work aims to investigate the SCC behavior of X70 pipeline steel under various pH levels to obtain a detailed understanding of SCC mechanisms and predict SCC susceptibility within varying pH ranges.

2. Experimental

All samples in this work were made from a hot-rolled X70 pipeline steel plate. The chemical composition and mechanical properties of the X70 pipeline steel are listed in Tables 1 and 2, respectively.

The microstructure of the as-received steel, which is composed of polygonal ferrite with small martensitic–austenitic particles distributed along the grain boundaries, is shown in Fig. 1.

The compositions of the simulated solution of acidic soil (named “red soil” in Southeast China) prepared in this work are shown in Table 3^[6,13]. The pH value ranged from 3.5 to 6.5 according to the pH examination in the field; an acetic acid solution (5% in mass) was introduced to change the pH values^[13].

Potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) were employed to investigate the effect of the dynamic process of electrochemical reactions under varying pH values and their influence on the occurrence of SCC. Specimens were polished by using 800-grade emery paper and then coated with epoxy, thus leaving a working

Fig. 1 Microstructure of the rolling plate

area of 1 cm^2 . All polarization curve measurements were conducted within a potential range from -800 mV to 1200 mV against open-circuit potential (OCP). EIS were performed at both OCP and constant cathodic potentials. Prior to each test, the solution was de-aerated by using high-purity N_2 gas for 2 h, whereas the samples were pre-immersed for 0.5 h. The administration of N_2 gas was interrupted at the beginning to avoid the effect of solution disturbance.

Specimens for slow strain rate testing (SSRT) were created according to GB T15970.6 specification. The specimens were processed into flat samples with a working length of 25 mm, width of 6 mm, and thickness of 2 mm. SSRT was performed with a strain rate of $0.5 \times 10^{-6}\text{ s}^{-1}$ both in air and in solutions with various pH values under cathodic potential to investigate the relationship between SCC susceptibility and the pH values of the solutions. SSRT was conducted by using a WDML-30KN Materials Test System (Xi'an, China). Specimens were polished sequentially to 800 grade by using waterproof emery paper with the burnishing direction of the SSRT samples parallel to the tension direction. Prior to each SSRT in the solution, the specimen was immersed in the solution for 24 h without loading. Pure N_2 gas was used during the whole test to remove dissolved oxygen.

A three-electrode system was used for both electrochemical tests and SSRT: X70 steel samples served

Fig. 2 Variation of OCP against pH value

as the working electrodes, a saturated calomel electrode was the reference electrode, and a Pt plate was the counter electrode. All tests were performed at ambient temperature (approximately 22 °C).

3. Results

3.1 Effect of pH Value on Electrochemical Reactions

Fig. 2 shows the variation of OCP under different acidic-pH values. OCP decreases as the pH value of the solution increases from 3.5 to 6.5. A sharp decrease in OCP is observed between pH 4.5 and 5,

which is approximately 100 mV; thus, the electrochemical reaction mechanism within this pH range changes greatly when the pH value shifts. This change results from the effect of pH value on reaction dynamics, which is discussed in detail in subsequent sections of the paper.

Fig. 3 shows the effect of pH value on EIS curves under various cathodic potentials. The shape of the curve is altered greatly when the potential shifts negatively from OCP to -1200 mV_{SCE} or when the pH values increase from 3.5 to 6.5. For all curves under cathodic potentials, two time constants can be observed. However, under different pH conditions, the curves indicate different electrochemical corrosion processes. Under pH of 3.5 and 4.5 (Fig. 3(a) and Fig. 3(b)), the high-frequency semicircle reflects the electrode reactions on the interface and electric double-layer processes at OCP; the secondary semicircle (*i.e.*, the inductive loop) is related to the hydrogen evolution and absorption processes. Under cathodic potentials, such as -850 and -1200 mV_{SCE}, the high-frequency semicircle is related to the electric double-layer process or electrode reactions at the interface. The low-frequency part (the inclined line) is attributed to the diffusion processes of hydrogen evolution. By contrast, under pH of 5.5 to 6.5 (Fig. 3(c) and Fig. 3(d)), the high-frequency semicircle at OCP reflects the electrode reactions at the interface; the secondary semicircle is related to the resistance of the

Fig. 3 EIS plots under various potentials in test solutions with pH of 3.5 (a), 4.5 (b), 5.5 (c) and 6.5 (d)

Fig. 4 Effect of pH values on electrochemical curves with scanning rate of 50 (a) and 0.5 mV/s (b)

corrosion product layer (*i.e.* Warburg impedance). When applied potential is conducted at $-850 \text{ mV}_{\text{SCE}}$, only one semicircle can be observed with respect to the reduction of oxide layer as well as the hydrogen evolution. When the applied potential significantly negatively decreases (*e.g.*, $-1200 \text{ mV}_{\text{SCE}}$), the electrochemical processes are the same as that under lower pH conditions. The reason for this consistency is because some anodic reaction still exists within the localized area^[17] and some reactions of hydrogen evolution occur in other places^[18] within a weak cathodic potential range, such as from OCP to $-850 \text{ mV}_{\text{SCE}}$.

In this case, the total charge transfer impedance (Z_{tT}) depends on the anodic impedance (Z_{ta}) and cathodic impedance (Z_{tc}). Thus, we obtain the following equation^[19]:

$$\frac{1}{Z_{\text{tT}}} = \frac{1 - \theta}{Z_{\text{ta}}} + \frac{\theta}{Z_{\text{tc}}} \quad (1)$$

where θ is the coverage of the cathodic reaction zone, which increases with decreasing cathodic potential. Under a weak cathodic range, the anodic effect cannot be neglected. However, Z_{ta} and θ increase and Z_{tc} decreases when the potential shifts negatively, thus making $\frac{1 - \theta}{Z_{\text{ta}}}$ decrease and $\frac{\theta}{Z_{\text{tc}}}$ increase when applied potentials decrease negatively. Z_{tT} increases first if $\frac{\partial(\frac{1 - \theta}{Z_{\text{ta}}})}{\partial E} > \frac{\partial(\frac{\theta}{Z_{\text{tc}}})}{\partial E}$ (Eq. (1)). Z_{tT} reaches its maximum only if $\frac{\partial(\frac{1 - \theta}{Z_{\text{ta}}})}{\partial E} = \frac{\partial(\frac{\theta}{Z_{\text{tc}}})}{\partial E}$. The anodic reactions are almost diminished when the potential decreases further; thus, Z_{tT} becomes closer to Z_{tc} and decreases along with the potential. Hydrogen evolution reaction dominates the electrochemical processes with the potential lower than -850 mV (Fig. 3). However, anodic reaction is present above the potential, particularly in solutions with higher pH.

Fig. 4 shows the changes of the electrochemical polarization curves with shifting pH values. Fast-scanning rate plots (Fig. 4(a)) reflect the electrochemical reaction at the crack-tip area, and the slow-scanning rate curves exhibit the electrochemical characteristics at the non-crack-tip zone^[20]. When pH is

higher than 4, a small difference exists among fast-scanning rate curves, and the zero current potential for each curve is approximately $-1000 \text{ mV}_{\text{SCE}}$; thus, the electrochemical processes are the same in the crack tip, and the anodic reaction is dominant when the applied potential is above $-1000 \text{ mV}_{\text{SCE}}$ (Fig. 4(a)). However, when pH is less than 4, the zero current potential of the fast-scanning rate curves shifts positively; thus, the reduction of pH intensifies the cathodic processes in the crack tip. For the non-crack-tip area, a change in pH primarily affects the cathodic processes but not the anodic reactions (Fig. 4(b)). The increase of the cathode currents when pH is less than 5 is related to the reduction of H_2CO_3 and HCO_3^- ^[6,15]; thus, OCP changes significantly at pH of approximately 4.5 when the pH value varies from 3.5 to 6.5. The increase of the cathodic current with a pH of less than 5 is due to the intensification of hydrogen evolution, which can cause high concentrations of hydrogen to permeate into the bulk steel, thus leading to hydrogen-induced cracking or embrittlement.

To investigate the relationship between the pH value and SCC of the X70 pipeline steel, currents measured at the potential of $-850 \text{ mV}_{\text{SCE}}$ by both fast- and slow-scanning rate polarization curves are plotted in Fig. 5. The potential of $-850 \text{ mV}_{\text{SCE}}$ is chosen because it is within the proper cathodic protection potential range for pipeline steels in soil environments. When pH is lower than 4, the currents of the fast- and slow-scanning rate curves are both negative, indicating that both the crack-tip and non-crack-tip areas of the X70 pipeline steel are under the cathodic conditions during the occurrence of SCC (*i.e.*, the mechanism for this case is HE)^[6]. Similarly, when pH is higher than 4, the current of the fast-scanning rate curve at $-850 \text{ mV}_{\text{SCE}}$ is positive and that of the slow-scanning rate curve is negative; this result indicates that the effect of AD at the crack tip and the effect of AD caused by hydrogen evolution and diffusion into the steel, as well as their synergistic effect, simultaneously propagate cracking (*i.e.*, $-850 \text{ mV}_{\text{SCE}}$ is located in the AD + HE potential range). However,

Fig. 5 Currents of slow-scanning rate curve (i_s) and fast-scanning rate curve (i_f) obtained under varying pH values

when pH is more than 4.5, the cathodic current, *i.e.*, the current obtained with a slow-scanning rate, significantly decreases and close to zero at pH 5 because of the inhibition of cathodic reactions^[15]. This result is caused by the inhibition of the hydrolysis process of bicarbonate ions to carbonic acid and the formation of corrosion products as pH increases to more than 5 (Fig. 5). Thus, hydrogen evolution and diffusion into the metal matrix are significantly reduced, as well as the effect of AD and/or hydrogen-induced dissolution on SCC occurrence. Moreover, anodic reaction is dominant at the crack tip according to the current of the fast-scanning rate curves when the pH is more than 4. When the pH is approximately 4.5, the anodic reaction rate at the crack tip and hydrogen evolution rate at the non-crack-tip zone show relatively high values. These results indicate that it is only when AD and HE are in good synergistic effects, *i.e.* there is enough high hydrogen charging current in non-crack-tip zone and high anodic current around the crack-tip, that SCC occurs in high susceptibility.

3.2 Effect of pH values on SCC occurrence in acidic soil solutions

Fig. 6 shows the SSRT curves of X70 steel obtained under various pH at $-850 \text{ mV}_{\text{SCE}}$. A small difference exists among the tensile strengths of the material in the test media. The elongation obtained under pH of less than 4.5 is relatively lower than that examined in air. However, when pH is higher than 4.5, no clear difference exists among the elongations obtained in the solutions and in air.

To investigate the effect of pH variation on the SCC of X70 pipeline steel, the reduction-in-area loss ratio (I_Ψ) and elongation loss ratio (I_δ) were calculated as the SCC susceptibility ratio. I_Ψ and I_δ are defined as the following:

$$I_\Psi = \left(1 - \frac{\Psi_{\text{pH}}}{\Psi_0}\right) \times 100\% \quad (2)$$

Fig. 6 SSRT curves of X70 pipeline steel under varying pH values

Fig. 7 SCC susceptibility ratio of X70 steel obtained under various pH conditions

$$I_\delta = \left(1 - \frac{\delta_{\text{pH}}}{\delta_0}\right) \times 100\% \quad (3)$$

where Ψ_0 and Ψ_{pH} are the reduction-in-area loss ratios measured in air and in solutions, respectively; δ_0 and δ_{pH} are the elongation loss ratios in air and in solutions with various pH values, respectively.

The calculation of I_Ψ and I_δ is plotted in Fig. 7, which shows that I_Ψ and I_δ follow the same trend. However, I_Ψ is higher than I_δ under the same pH condition. Both variables have a maximum value near pH 4.5, and either an increase or decrease in pH value leads to a reduction of SCC susceptibility. This reduction of I_Ψ and I_δ under a pH value less than 4 is due to the HE mechanism (Fig. 5), which may also cause lower SCC susceptibility^[21]. However, when the pH value is higher than 4.5, the reduction of SCC susceptibility is due to the decrease of the hydrogen charging current under the AD + HE mechanism; this finding also conforms the result in Fig. 5.

To investigate the evolution of SCC behavior with pH variations further, the fractographies of the samples after SSRT were observed by scanning electron microscopy (SEM) (Fig. 8). The results show a shift trend in brittle surface area distribution. Under pH

Fig. 8 Fractographies of X70 steel through SEM after SSRT in solutions with pH 3.5 (a), 4 (b), 4.5 (c), 5 (d), 5.5 (e) and 6.5 (f)

3.5, a small area of brittle fracture surface exists on an edge of the fracture, and the rest of the area is covered with the dimples (Fig. 8(a)). When pH increases to 4, a larger SCC zone can be observed (Fig. 8(b)). Under pH 4.5, a considerably wider SCC-wall platform can be seen on the lower side of the fractography, as marked in Fig. 8(c) with a beautiful brittle pattern. Fig. 8(a) to Fig. 8(c) show the increase of SCC susceptibility by comparing the SCC-wall area; this finding is consistent with the SCC susceptibility ratio (Fig. 7) under pH 4.5. However, when pH is 5, 5.5, and 6.5 (Figs. 8(d) to Fig. 8(f)), all fracture surfaces exhibit dimple-fracture morphology, and no brittle fracture surface exists. Thus, if the HE effect (hydrogen charging current, shown in Fig. 5) is not strong enough, the considerable resistance to micro-SCC growth causes small SCC susceptibilities in these cases even though the effect of AD (anodic current, shown in Fig. 5) is large. This finding indicates that the effect of AD + HE on SCC susceptibility requires the matching of these two effects.

4. Discussion

4.1 Analysis of electrochemical Reactions of X70 steel in acidic soil environments

In this study, the solution containing HCO_3^- , H_2CO_3 , and H^+ ions has a pH of less than 7. The presence of H_2CO_3 is due to the hydrolysis of HCO_3^- , and a lower pH corresponds to a higher H_2CO_3 distribution. H_2CO_3 is the highest-contributing species to the SCC of pipeline steels^[15,22]. The primary cathodic reactions involving these species are as follows:

However, some of these reactions are inhibited by the diffusion effect in an unsteady status. For the reactions defined in Eq. (4) and Eq. (5), the reductant diffusion from the bulk solution limits the reduction rate. Thus, if the scanning rate of the polarization curve is slow, such as 0.5 mV/s (Fig. 4(b)), the time between two potential steps to reach a quasi-equilibrium reaction condition is much longer than that of the recovery time for the transmission of cathodic reactants. However, if the potential scanning rate is significantly increased, such as 50 mV/s (Fig. 4(a)), no reaction occurs between the reagents on the metal/solution interface. This effect inhibits cathodic reactions, thus resulting in the occurrence of anodic reactions at the crack tip under such a low potential (Fig. 4(a)). The anodic reactions of X70 steel in de-aerated low-pH solutions are expressed as follows^[23]:

Mass diffusion plays a key role in affecting electrochemical reactions above approximately $-1000 \text{ mV}_{\text{SCE}}$, thus inhibiting cathodic reactions under high potential scanning rates and promoting the occurrence of anodic reactions within the usual cathodic potential range (Fig. 4 and Fig. 5).

4.2 Relationship between the property of SCC and electrochemical reactions of X70 steel under varying pH conditions

In the crack tip, the metal surface is covered without a polarizing layer or just with a half-baked electric double layer because of the continuous onset of fresh metal surfaces caused by SCC growth. When the newly generated metal surface is exposed to a solution under applied potentials, the electric double layer will be formed immediately and charged under the applied potential. For this case, the electrochemical processes can be simulated via electrochemical examinations by using a fresh-surface sample under non-equilibrium status. The AD can occur in a fresh metal at a far lower potential than the OCP obtained under non-equilibrium conditions (Fig. 4(a)) because the electrode surface remains quasi-fresh when polarized at 50 mV/s^[20]. However, electrochemical reactions on a non-cracking surface occur in a quasi-equilibrium status, which can be simulated *via* electrochemical examinations by using a sample exposed in a solution under slow-scanning rate polarization (Fig. 4(b)). For this case, a sufficient cathodic reactant supply is available for hydrogen evolution reactions; as a result, diffusive hydrogen is introduced to the crack-tip area to increase the SCC growth rate caused by the synergistic effect of hydrogen on HE^[24] and/or hydrogen-induced dissolution^[4,25]. Thus, the SCC mechanism within the pH value range of 4 to 6.5 is AD + HE (Fig. 5, Fig. 7 and Fig. 8). Moreover, SCC susceptibility under the HE mechanism is less than that under the AD + HE mechanism in some cases, such as SCC susceptibility ratios with pH values of 3.5 to 4.5 (Fig. 7), which result from the highest synergistic effect of AD and HE with a pH of 4.5. This result confirms that the AD effect can sharpen the crack tip to accelerate crack growth, and HE can both intensify the rate of AD at the crack tip and generate micro-cracks to help the main crack grow faster. AD and HE are able to accelerate the initiation and propagation of SCC; thus, SCC susceptibility decreases because of the weakening of the AD (in lower pH media) and HE effects (in higher pH solutions).

5. Conclusions

The pH value significantly affects SCC susceptibility and its electrochemical mechanism. The pH higher than 5 has no significant effect on electrochem-

ical processes. However, when the pH is lower than 5, the reduction in pH value intensifies the cathodic hydrogen evolution reactions, thus increasing the cathode current and corrosion potential. Under varying pH values, the SCC mechanism of X70 pipeline steel varies among AD, HE and AD + HE. At -850 mV_{SCE} , the SCC mechanism is HE if pH is less than 4 and is AD + HE when pH is more than 4. The X70 pipeline steel exhibits the highest SCC susceptibility under pH 4.5 because of the strongest synergistic effect of AD and HE. A weakening AD effect reduces SCC susceptibility when pH is lower than 4.5, whereas a weakening HE effect reduces SCC susceptibility when pH is higher than 4.5.

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