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# The Initial Stage Corrosion of X80 Steel in Saturated Sandy Soil Containing Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>

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The corrosion differences of X80 steel are exhibited by electrochemical impedance spectroscopy, polarization curves, and scanning electron microscopy in saturated sandy soil containing different concentrations of NaCl and Na<sub>2</sub>SO<sub>4</sub> under indoor simulation conditions. The corrosion rate of X80 steel is minimal with NaCl and Na<sub>2</sub>SO<sub>4</sub> concentrations of 0.5% and 0.3%, respectively. Additionally, the corrosion morphologies are mainly shallow and small pits. However, the corrosion rates are hindered due to the accumulation of oxide films on the surface of X80 steel. The increase in sodium salt content accelerates the overall corrosion rate until 1.0%. Meantime, the oxide films are eroded by Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> and re-accelerate the electrochemical corrosion process, so the pits evidently deepen and expand.

Keywords: X80 steel, saturated soil, corrosion, polarization curves, EIS

# **1. INTRODUCTION**

With the current rapid advancement of China's industrialization construction, the demand for oil and natural gas resources is growing in various districts. However, since the regional energy supplement cannot suffice daily necessity, the current situation induces the urgent arrangement of oil and natural gas resource distribution and promotes the large-scale application and vigorous development of long-distance pipeline construction to transport oil and natural gas. Among them, the west-to-east gas transportation project in China is a typical case. The west-east natural gas pipeline is connected by underground and overhead laying in the complex and harsh desert soil environment of northwest China. The pipeline steel and soil media constitute an electrochemical system influenced by environment and climate underground, which causes the emergence of corrosion reactions and presents a challenge to the long-distance transportation quality and service life of oil and natural gas pipelines [1]. The failure of pipeline steel results in oil and natural gas leakage caused by corrosion damage, which will generate

serious resource loss and waste many human strength [2]. Therefore, the corrosion damage of pipeline steel has become a problem that cannot be ignored in the future. The study and analysis of the corrosion regularity and mechanism of pipeline steel to provide a basis for the anti-corrosion work of oil and natural gas pipelines have practical significance to avoid oil and natural gas leakage accidents and protect people's lives and property safety [3].

In recent years, scholars internal and external have conducted many studies on soil corrosion of pipeline steel. At present, pipeline steel models in oil and natural gas transportation include X52, X60, X70, X80, and Q235; the preservative quality of pipeline steel greatly varies in complex soil environment. The product film formed by X52 steel corrosion in acid sour media will constantly evolve to cover the steel surface, which results in poor protective property during the corrosion process [4]. X60 steel has a relatively higher corrosion rate than X52 steel when we compare the corrosion behaviour of X52 and X60 steel in acid NaCl solution containing  $CO_2$  [5]. Among the corrosion factors such as soil moisture content, clay content and plastic index, the moisture content has the governing effect on the corrosion rate of X70 steel, and other engineering factors may be more dominant in influencing the underground engineering corrosion [6]. The corrosion rate of Q235 steel in a simulated soil solution is closely related to its pH value. The corrosion rate decreases with increasing pH from 3.0 to 7.0 [7].

X80 steel has been widely used in long-distance oil and natural gas transportation projects due to its excellent strength and toughness. For the corrosion research of X80 pipeline steel, researchers mainly adopt various test methods based on the soil simulation solution and typical soil environment. In the soil simulation solution, research mainly focuses on the analysis of the electrochemical corrosion mechanism of the steel surface by  $Cl^{-}$ ,  $SO_4^{2-}$ ,  $HCO_3^{-}$  and other anions. A protective corrosion film that appears to be n-type semi-conductive is formed on the X80 pipeline steel surface in the soil simulation solution, and the protective effect of the corrosion film on the steel increases with increasing solution pH [8]. A superimposed AC degrades the passivity of the steel, negatively shifts the corrosion potential, and accelerates the corrosion rate in chloride-containing alkaline environments. AC and Cl<sup>-</sup> generate a synergistic effect on the corrosion behaviour of the pipeline steel; in particular, the corrosion rate greatly increases, and corrosion becomes more localized [9-10]. The synergistic effect of CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> on the corrosion behaviour of X80 pipeline steel in simulated solution with high pH is investigated to indicate that HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> have great impact on the corrosion process [11]. Currently, the electrochemical corrosion of X80 steel in typical soil media such as clay, slurry and sand has been studied by electrochemical measurement methods, which combine the polarization curve, EIS, buried weight loss and electrochemical noise [12]. Fe oxide obviously improves the corrosion process of X80 steel in the red clay soil and red soil slurry [13-14]. The corrosion of X80 steel in saline sandy soil with different concentrations of soluble salt anions (Cl<sup>-</sup>,  $SO_4^{2-}$ ,  $HCO_3^{-}$ ) reveals that  $SO_4^{2-}$  mainly affects the corrosion potential, Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> mainly affect the corrosion current density, and SO<sub>4</sub><sup>2-</sup> is the most important factor that affects the initial corrosion behaviour of the X80 steel [15]. The corrosion effect of X80 steel in different types of clay is random, which can be attributed to different microstructures in the steels. It is pitting corrosion in low-moisture soil and uniform corrosion in high-moisture soil [16-17]. In summary, the large difference in effect of complex structural properties on steel corrosion in different soil environments introduces certain difficulties to the study of X80 steel corrosion problems. To

improve and unify the evaluation criteria of pipeline steel corrosion, more basic research and data accumulation remain necessary.

Since the desert saline sandy soil is the main output of Northwest China, in this paper, the electrochemical reaction process and mechanism of X80 steel in saturated sandy soil containing different concentrations of NaCl and Na<sub>2</sub>SO<sub>4</sub> are analysed using indoor simulation with electrochemical impedance spectroscopy (EIS), polarization curves (PCs), open circuit potential curves (OCP) and scanning electron microscopy (SEM), which provide a reference for the study of buried pipeline steel and underground steel structures.

#### 2. EXPERIMENTAL PROCEDURE

## 2.1 Test and Characterization



Figure 1. Test instruments and moulds

The size of the test mould for this experiment was  $7.07 \text{ cm} \times 7.07 \text{ cm} \times 7.07 \text{ cm}$  (Figure 1), which was covered with a watertight and breathable membrane. The temperature and humidity were controlled at  $20 \pm 5^{\circ}$ C and  $45\% \pm 5\%$  RH, respectively. The electrochemical impedance spectroscopy and polarization curve of X80 steel were acquired by the CS350 electrochemical workstation via a three-electrode system. Three test electrodes are the working electrode WE (X80 steel), auxiliary electrode CE (copper electrode), and reference electrode RE (saturated calomel electrode). The test frequency range of electrochemical impedance spectrum was  $10^{-2} \sim 10^5$  Hz, and the amplitude of AC sinusoidal excitation signal was 5 mV. The EIS data was analysed through ZSimDemo software. In the polarization curve test, the scan rate was 2 mV/s under the self-corrosion potential, and the scan range was -300~1000 mV relative to the self-corrosion potential. In the Open circuit potential curve test, the sampling frequency is 5 Hz. The PC data was analysed through Cview software. The microscopic corrosion morphology of X80 steel in this experiment was observed by TM3000 scanning electron microscopy.

## 2.2 Experimental Materials and Pretreatment

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The material in this experiment was X80 pipeline steel. Its main chemical composition and content are shown in Table 1. The sample is a round X80 steel sheet with a diameter of 15 mm and a thickness of 2 mm. The working face of the steel sample was polished by step with sandpapers #600~#2000 until there was no obvious scratch on the surface before the test; then, we cleaned the working face with acetone, alcohol, deionized water and air dried after polishing. Finally, the steel sheet and silicone wire with built-in copper wire were sealed with epoxy resin into a square working surface of  $1.0 \times 1.0$  cm<sup>2</sup>.

 Table 1. Chemical composition of X80 steel

Chemical composition	С	Si	Zn	В	Mn	Cu	Cr	Mo	Ni
Content/%	0.091	0.003	0.020	0.017	7.860	0.010	0.300	0.065	0.022

The sandy soil was selected from Xiamen, China ISO standard sand with good gradation and medium dense degree ( $1/3 < Dr \le 2/3$ ), and the silica content was more than 98%.

After measurement: the maximum dry density  $\rho_{max}$  of the test sand is 1.86 g/cm<sup>3</sup>, the minimum dry density  $\rho_{min}$  is 1.56 g/cm<sup>3</sup>, and the relative density G<sub>s</sub> of the sand is 2.66. According to the relationship between dense degree and dry density:

$$D_{r} = \frac{(\rho_{d} - \rho_{d\min})\rho_{d\max}}{(\rho_{d\max} - \rho_{d\min})\rho_{d}} = \frac{(\rho_{d} - 1.56)1.86}{(1.86 - 1.56)\rho_{d}}$$
(1)  
So,  $\rho_{d} = 1.65 \sim 1.75 \text{g/cm}^{3}$   
 $1.65 < \rho_{d} = \frac{G_{s}\rho_{w}}{1 + e} < 1.75 \rightarrow e = 0.52 \sim 0.61$ (2)  
 $S_{r} = \frac{\omega_{s}G_{s}}{e}$ (3)

When the saturation is  $Sr \ge 80\%$ , the sandy soil is saturated. Given Sr = 80%, the calculation is  $16\% < \omega_s < 18\%$ . In this test, determined intermediate value  $\omega_s = 17\%$ . Then, we configured 450 g of standard sand and 76.5 g of distilled water as saturated sand with a moisture content of 17%.

$$\rho_{\rm d} = \frac{\rm m_s}{\rm V} = \frac{450}{7.07 \times 7.07 \times \rm h}$$
(4)

According to  $D_r=0.5$ ,  $\rho_d=1.70$  g/cm<sup>3</sup>, and the sand height can be controlled to h=5.30 cm. The mass fractions (relative to sand) of this test configuration were 0.3%, 0.5%, 0.75% and 1.0% NaCl and Na<sub>2</sub>SO<sub>4</sub> reagent dissolved in 76.5 g of distilled water by stirring (Table 2). The prepared NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions were mixed with 450 g sandy soil and stored in a fresh bag for 24 h to enable adequate mixing. Finally, the X80 steel sheet was embedded in compacted and stable saturated sandy soil containing four concentrations of NaCl and Na<sub>2</sub>SO<sub>4</sub> for 24 hours, and the height was approximately 2 cm from the bottom of the moulds.

Sodium saline reagent	$m_{sand}/g$	m <sub>water</sub> /g	Salt content/g	Salinity/%
	450	76.5	1.35	0.3
N <sub>2</sub> Cl	450	76.5	2.25	0.5
INACI	450	76.5	3.38	0.75
	450	76.5	4.50	1.0
	450	76.5	1.35	0.3
No SO	450	76.5	2.25	0.5
INa2504	450	76.5	3.38	0.75
	450	76.5	4.50	1.0

Table 2. Test sandy soil formulas

#### **3. RESULTS AND DISCUSSION**

3.1 Open circuit potential Curves of X80 Steel in Saturated Sandy Soils Containing Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>



(a) Open circuit potential-time curves of X80 steel in saturated sandy soils with 0.3, 0.5, 0.75, 1% NaCl content



- (b) Open circuit potential-time curves of X80 steel in saturated sandy soils with 0.3, 0.5, 0.75, 1% Na<sub>2</sub>SO<sub>4</sub> content
- **Figure 2.** Open circuit potential-time curves of X80 steel in saturated sandy soils containing Cl<sup>-</sup> (a) and SO<sub>4</sub><sup>2-</sup> (b)

The open circuit potential curves of X80 steel in saturated sandy soils are shown in Figure 2. The change rule of open circuit potential in the two conductive mediums is substantially the same, which shows a short-term decline and gradually keeps stable over time. This phenomenon results from the oxide film covering the electrode surface hindering the electrochemical reaction.

The open circuit potential rises with the increase of salinity in the two conductive mediums. On the one hand, the increase in NaCl and  $Na_2SO_4$  concentrations causes the electrode surface to be covered with more sodium ions. On the other hand, the higher the salinity, the more intense the electrochemical reaction on the electrode surface, which promotes the oxide film more dense and stable covering on the electrode surface. These two factors lead to the increase of open circuit potential.

3.2 Polarization Curves of X80 Steel in Saturated Sandy Soils Containing  $Cl^{-}$  and  $SO_4^{2^{-}}$ 



(a) Polarization curves of X80 steel in saturated sandy soils with 0.3, 0.5, 0.75, 1% NaCl content



(b) Polarization curves of X80 steel in saturated sandy soils with 0.3, 0.5, 0.75, 1% Na<sub>2</sub>SO<sub>4</sub> content

**Figure 3.** Polarization curves of X80 steel in saturated sandy soils containing  $Cl^{-}(a)$  and  $SO_4^{2-}(b)$ 

The polarization curves of X80 steel in saturated sandy soils are shown in Figure 3. The curves show the obvious passivation zone in saturated sandy soil with all concentrations of NaCl and Na<sub>2</sub>SO<sub>4</sub>. The polarization curves shift to the right with increasing concentrations of sodium saline in the environment. According to Faraday's law, the corrosion current density is proportional to the corrosion rate. The corrosion rate of X80 steel accelerates with the addition of NaCl and Na<sub>2</sub>SO<sub>4</sub> and most rapidly

increases when the concentration is 1.0%. The self-corrosion potential of X80 steel negatively shifts and subsequently positively shifts with the increase in NaCl and Na<sub>2</sub>SO<sub>4</sub> concentrations. In saturated sandy soil containing NaCl and Na<sub>2</sub>SO<sub>4</sub> concentrations of 0.75% and 1.0%, because the surface of electrodes are covered with corrosion products, the dissolved  $Fe^{2+}$  from X80 steel cannot diffuse into the pore solution, so a large amount of  $Fe^{2+}$  ions accumulates in the anode area, which increases the self-corrosion potential [18].

The corrosion process of X80 steel is described in conjunction with the distribution regularity of the polarization curves in Figure 3: The increased salinity in the pore solution can promote the ability of ion exchange at the electrode interface to expedite the corrosion rate. However, when the salinity continues to increase, the electrode surface generates a dense and stable oxide film as a barrier to the electrochemical reaction [19]. With further increase in sodium saline concentration,  $Cl^-$  and  $SO_4^{2-}$  erode the oxide film on the electrode surface [20], which makes the electrode surface contact the pore solution, so the corrosion reaction reoccurs.

To quantitatively study the polarization curves of X80 steel in saturated sandy soils, we use the weak polarization resistance ( $R_p$ ) from the Cview software to fit the original data (Table 3), and the fitting interval is  $\pm 20$  mV (with respect to the open circuit potential).

The corrosion current density in this study is calculated based on Stern-Geary equation (5) [21]:

$$i_{corr} = \frac{b_a \times b_c}{2.303 \times (b_a + b_c)} \times \frac{1}{R_p} = \frac{B}{R_p}$$
(5)

 $b_a, b_c$  are the Tafel slopes of the anode and cathode; since Tafel slope cannot be measured by R<sub>p</sub> fitting, its value is generally set to 0.12 V/dec. B is Stern-Geary coefficient; the electrochemical workstation of this experiment is generally tested at 18 mV.

Sandy soil sample		$E_0/V$	$I_0/A \cdot cm^{-2}$	$R_P/\Omega \cdot cm^{-2}$	$C_R/mm \cdot a^{-1}$
	0.3%	-0.686	6.23E-4	3608	0.085
NoCl saturated and	0.5%	-0.740	6.01E-4	4338	0.070
Naci saturateu sanu	0.75%	-0.727	7.42E-4	1839	0.166
	1.0%	-0.671	7.20E-4	2212	0.159
	0.3%	-0.749	5.78E-5	4517	0.068
Na <sub>2</sub> SO <sub>4</sub> saturated	0.5%	-0.770	8.21E-5	3179	0.096
sand	0.75%	-0.752	6.74E-5	3499	0.073
	1.0%	-0.740	1.10E-4	2371	0.129

**Table 3.**  $R_p$  fitting results for polarization curves of X80 steel in saturated sandy soil containing Cl<sup>-</sup> and  $SO_4^{2-}$ 

In Table 3, the corrosion current density of X80 steel is in the order of magnitude of  $10^{-4} \sim 10^{-5}$  A/cm<sup>2</sup>, which is above the average degree of corrosion [22-23]. The corrosion current density of X80 steel in saturated sand containing NaCl is one order of magnitude larger than that in saturated sand containing Na<sub>2</sub>SO<sub>4</sub>, i.e., there is more serious corrosion. When the concentration of ions in the pore solution increases, the polarization resistance R<sub>p</sub> of the two types of saturated sand show an overall reduced trend, and the anti-corrosion decreases. The corrosion rate of X80 steel in saturated sandy soil

containing 0.75% and 1.0% NaCl is slightly higher than that containing 0.3% and 0.5% NaCl. The corrosion rate of X80 steel in saturated sandy soil containing 1.0% Na<sub>2</sub>SO<sub>4</sub> is one order of magnitude larger than those with the prior three concentrations. The corrosion rate  $C_R$  and current density I<sub>0</sub> are maximal when the NaCl and Na<sub>2</sub>SO<sub>4</sub> concentration is 1.0%. Thus, X80 steel has mightier corrosion ability at high concentration than at low concentration in two types of sodium saline saturated sandy soil. The R<sub>p</sub> fitting results and distribution of polarization curves substantially integrate.

# 3.3 EIS of X80 Steel in Saturated Sandy Soils Containing $Cl^{-}$ and $SO_4^{2^{-}}$

# 3.3.1 Electrochemical characterization



(a) Nyquist diagrams of X80 steel in saturated sandy soil with 0.3, 0.5, 0.75, 1% NaCl content



(b) Bode diagrams of X80 steel in saturated sandy soil with 0.3, 0.5, 0.75, 1% NaCl content

Figure 4. Nyquist (a) and Bode (b) diagrams of X80 steel in saturated sandy soil containing Cl<sup>-</sup>

Figure 4 shows the Nyquist diagram and Bode diagram of X80 steel in saturated sandy soil containing NaCl. The Nyquist diagram of four concentrations consists of a small section of the capacitive arc in the high-frequency region and an entire section of the capacitive arc and inductive arc in the middle- to low-frequency region in Figure 4(a). The obvious radius changes of the capacitive arc in the middle-low frequency show that different concentrations of NaCl pore solution significantly affect the corrosion degree of X80 steel; the larger radius of the capacitive arc indicates the greater resistance to

the electrochemical reaction on the electrode surface [24]. The intersections of the high-frequency capacitive arc on the real axis move to the left when the sodium saline concentration increases, which indicates that the conductivity of the pore solution optimizes with increasing sodium saline concentration. The Bode diagram in Figure 4(b) shows two time-constants for the electrochemical reaction of X80 steel in saturated sandy soil containing four NaCl concentrations. The shape of the phase angle curves presents a significant "valley", which indicates the inductive property in the frequency domain of  $10^{-1} \sim 10^{-2}$  Hz; the value of the valleys is approximately 5°. The shape of the phase angle curves presents the significant "peak" show capacitive property in the frequency domain of  $10 \sim 10^{2}$  Hz, the peak values are approximately  $20 \sim 35^{\circ}$ . The position of the peaks and valleys shift to the right with the increasing concentration of NaCl.



(a) Nyquist diagrams of X80 steel in saturated sandy soil with 0.3, 0.5, 0.75, 1% Na<sub>2</sub>SO<sub>4</sub> content



(b) Bode diagrams of X80 steel in saturated sandy soil with 0.3, 0.5, 0.75, 1% Na<sub>2</sub>SO<sub>4</sub> content

**Figure 5.** Nyquist (a) and Bode (b) diagrams of X80 steel in saturated sandy soil containing  $SO_4^{2-}$ 

Figure 5 shows the Nyquist diagram and Bode diagram of X80 steel in saturated sandy soil containing Na<sub>2</sub>SO<sub>4</sub>. The Nyquist diagram of X80 steel in Figure 5(a) has a similar curve distribution as Figure 4(a). The corrosion process of X80 steel is affected differently in four concentrations of Na<sub>2</sub>SO<sub>4</sub> pore solution. The Bode diagram in Figure 5(b) also shows two time-constants for the electrochemical

reaction of X80 steel, and two time-constants have identical properties to the electrode reaction in NaCl saturated sandy soil. On one hand, the peak phase angle in Figure 5(b) is slightly higher than that in Figure 4(b). On the other hand, the impedance value in saturated sandy soil containing NaCl is lower than that in saturated sandy soil containing Na<sub>2</sub>SO<sub>4</sub>, which implies that the corrosion process of X80 steel in saturated sandy soil containing NaCl is more active, and Cl<sup>-</sup> has stronger mobility than SO<sub>4</sub><sup>2-</sup>.

## 3.3.2 Equivalent circuit model

In this experiment, the corresponding equivalent circuit model is established based on the electrochemical reaction process of X80 steel in sodium saline sandy soil. The electrochemical reaction information of X80 steel can be accurately explained using the equivalent circuit model in the corrosion environment. The experiment to establish the equivalent circuit model involves two aspects:

1. Multiphase composite conductive medium composed of sandy soil, saline solution and air

Except for the resistance of the sodium saline pore solution filled in the sandy soil, the content of clay particles in the sandy soil is low, and the adsorption of cations by the sandy particles is weak, so the particle surface cannot have the identical electrical double-layer structure to the clay particles. However, the mutual role is the characteristic adsorption similar in nature and strength to the chemical bond between the surface of sandy particles and the water molecules. Therefore, the equivalent circuit established by the conductive properties of the porous layer of sodium saline saturated sand soil is shown in Figure 6.



Figure 6. Equivalent circuit model of the porous layer of sandy soil in sodium saline solution

 $C_1$  is the electrical double-layer capacitance at the interface between sandy particles and pore solution.  $R_1$  is the interface transfer resistance at the interface between sandy particles and pore solution.  $R_s$  is the resistance of the pore solution.

2. The electrical double-layer capacitance and oxide film structure are originated at the interface from the reaction of X80 steel as the electrode with the conductive medium.

When X80 steel is measured by electrochemical impedance spectroscopy in a conductive medium, the current density on the electrode surface originates from two parts: faradic current of electrode reaction; non-faradaic current of electrical double-layer charge and discharge cycles at the interface of electrode and pore solution [25]. The electrochemical reaction occurs at the interface between X80 steel and pore solution. The Fe<sup>2+</sup> ions dissolved from the surface combine with H<sub>2</sub>O or OH<sup>-</sup> ions adsorbed on the surface of X80 steel to form the metal oxide film, which covers the electrode

surface. The Fe<sup>2+</sup> ions dissolved from the anode are hindered by this process into the pore solution, which suppresses the electrochemical reaction on the surface of X80 steel. However, the erosion of Cl<sup>-</sup> and  $SO_4^{2-}$  on the oxide film causes pitting. Therefore, the equivalent circuit established by this series of reactions from the electrode and pore solution at the interface is shown in Figure 7.



**Figure 7.** Equivalent circuit model of the X80 steel electrode-pore solution contact interface in saturated sandy soil containing sodium saline

Q is the electrical double-layer capacitance at the interface between the electrode and the pore solution. Capacitance C is replaced by the constant-phase angle element CPE in the equivalent circuit model to signify the electrical double-layer capacitance at the interface of the electrode and pore solution to avoid the "dispersion effect" caused by the roughness of the electrode surface in the actual test. CPE includes two parameters CPE-T and CPE-P: CPE-T is the ability of electrical double-layer capacitance to store electric charge; CPE-P is the similarity between a constant-phase angle element and a pure capacitance, and the value range is 0~1 [26]. R<sub>t</sub> is the interface transfer resistance at the interface between electrode and pore solution [27]. R<sub>L</sub> and L are the resistance and inductance of the oxide film on the electrode surface, respectively [28].

According to the introduction to electrochemical impedance spectroscopy, when the electrode reaction speed is determined by another state variable in addition to electrode potential E, the state variable is the oxide film thickness *l* on the surface of X80 steel in this experiment. Faraday current  $I_F$  through the oxide film decreases when the oxide film thickens, so that  $m = \left(\frac{\partial I_F}{\partial l}\right)_{re} < 0$ . The dissolution

rate of oxide film at the pitting position enriched by Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> on the electrode surface is much higher than that in the normal state, i.e., the impedance of the pitting position is much lower than the impedance of the remainder of the electrode surface. Therefore, the EIS measured in the experiment mainly reflects the electrochemical properties of the pitting position. At the pitting location,  $b = (\partial l/\partial E)_{ss} < 0$ , B = mb > 0, and B > 0.

Thus, Faraday admittance is [29]

$$Y_{F}^{0} = \frac{1}{R_{t}} + \frac{1}{\frac{a}{B} + j\omega\frac{1}{B}} = \frac{1}{R_{t}} + \frac{1}{R_{L} + j\omega L}$$
(6)

R<sub>t</sub> is the interface transfer resistance at the interface between the electrode and the pore solution;  $a = -(\partial \Xi / \partial X)_{ss}$ ; *x* is the surface state variable of the electrode reaction;  $\Xi$  is the rate of change of state variable *x*; subscript ss denotes the stationary state; R<sub>t</sub> and *a* are both positive numbers.

The inductive reactance appears in Faraday impedance.  $R_L = a/B > 0, L = 1/B > 0$ . This formula shows that the Faraday impedance is formed in parallel by interface transfer resistance R<sub>t</sub>, composite

element  $R_LL$ , equivalent resistance  $R_L$  and equivalent inductance L in series with composite element  $R_LL$ .

By unifying these two aspects, the circuit description code of the equivalent circuit model is R(C(R(QR(RL)))) (Figure 8).



Figure 8. Equivalent circuit model of X80 steel in saturated sandy soil containing sodium saline

Sodium saline	Salinity	$\frac{R_s}{/\Omega\!\cdot\!cm^2}$	$C_1$ /F·cm <sup>-2</sup>	$R_1$ $/\Omega \cdot cm^2$	Q CPE-T/S⋅s <sup>-</sup> <sup>n</sup> ⋅cm <sup>-2</sup>	CPE-P	$\begin{array}{c} R_t \\ /\Omega\!\cdot\!cm^2 \end{array}$	L /H·cm <sup>2</sup>	$\begin{array}{c} R_L \\ /\Omega\!\cdot\!cm^2 \end{array}$
NaCl	0.3%	24.05	8.01E-8	73.01	4.45E-4	0.75	243.8	661.2	579.7
	0.5%	28.7	1.67E-7	42.66	6.38E-3	0.79	1350	6701	3348
	0.75%	16.29	2.86E-7	27.15	3.88E-3	0.75	254.7	458.2	563.9
	1.0%	10.93	2.63E-8	20.67	7.79E-4	0.75	142.5	467	408.1
Na <sub>2</sub> SO <sub>4</sub>	0.3%	42.66	7.44E-9	105.5	5.84E-3	0.74	1256	4043	1728
	0.5%	46.33	1.12E-7	54.44	4.84E-3	0.77	631	1317	1181
	0.75%	27.85	1.85E-7	41.24	2.42E-3	0.79	1074	5646	2300
	1.0%	36.06	4.98E-7	14.84	2.82E-3	0.77	495.4	3021	1161

Table 4. Fitting results of EIS of X80 steel in saturated sandy soils containing Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>

EIS data were further analysed using the equivalent circuit R(C(R(QR(RL)))) through the ZSimDemo software. The measured curve and fitting curve are compared in Figure 9, and the fitting electrochemical parameters are listed in Table 4. The electrical double-layer capacitance  $C_1$  and interface transfer resistance  $R_1$  of the sandy particle surface greatly fluctuate, possibly since the content of clay particles in the sandy soil is low, and the adsorption of cations by sandy particles is weak. The soil particles are encompassed by the obvious electrical double layer in the viscous soil, which affects the conductive property of the soil. Pore solution resistance  $R_s$  decreases with increasing salinity; the

addition of ions aims to promote the conductivity of the pore solution. Additionally, interface transfer resistance  $R_t$  results from the oxide film on the electrode surface, and the erosion of  $Cl^-$  and  $SO_4^{2-}$  presents high and low changes. The changes of these two parameters indicate that the corrosion ability of X80 steel in saturated sandy soil containing NaCl and Na<sub>2</sub>SO<sub>4</sub> is weak at low concentrations and strong at high concentrations, which coincides with the distribution rule of the electrochemical impedance spectrum.



(a) Fitting figures of EIS of X80 steel in saturated sandy soils with 0.3, 0.5, 0.75, 1% NaCl content





(b) Fitting figures of EIS of X80 steel in saturated sandy soils with 0.3, 0.5, 0.75, 1%  $Na_2SO_4$  content

**Figure 9.** Fitting figures of EIS of X80 steel in saturated sandy soils containing  $Cl^{-}$  (a) and  $SO_4^{2-}$  (b)

As shown in Figure 4 and Figure 5, the capacitive arc in the first quadrant of the Nyquist diagram and the "peak" in the Bode diagram are reflected by the  $(QR_t)$  section; the inductive arc in the fourth quadrant of the Nyquist diagram and the "valley" in the Bode diagram are reflected by the  $(R_t(R_LL))$  section.

The radius of the capacitive arc in the middle- to low-frequency region first expands when the concentration of sodium saline increases. The increase in salinity can promote the conductivity of the pore solution, which makes the electrochemical reaction on the surface of X80 steel easily occur. Meanwhile, it also promotes the throughput of the oxide film on the surface of X80 steel. The oxide film covering the surface of X80 steel hinders the electrochemical reaction process on the electrode surface, which reflects the larger radius of the capacitive arc in Nyquist diagrams. With increasing Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> contents in the pore solution, the penetrability of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> may destroy the oxide film, so that the surface of X80 steel contacts the pore solution again to accelerate the electrochemical reaction on the electrode surface. The Nyquist diagrams show the smaller radius of the capacitive arc, and this process can easily cause pitting on the surface of X80 steel [30].

The radii of the inductive arc in the middle- to low-frequency region reduce when the concentration of sodium saline increases, since the inductive arc in the middle- to low-frequency region in EIS is caused by the formation of pore core from the pitting corrosion of the oxide film due to  $Cl^{-}$  and  $SO_4^{2-}$  on the X80 steel surface. The surfaces of X80 steel are continuously covered with corrosion products from  $Cl^{-}$  and  $SO_4^{2-}$ , and the sand particles adhered to the electrode surface promote the uneven coverage of the oxide film. The resulting dispersion effect strengthens on the electrode surface, which forms scattered points in the measured middle- to low-frequency inductive arc, and the radius of the inductive arc decreases with the increase in salinity.

As shown in Figure 4(b) and Figure 5(b), the frequency positions of the peak and valley move towards the high-frequency direction with increasing sodium saline concentration. The reason is that with higher concentrations of  $Cl^{-}$  and  $SO_4^{2^-}$  in the pore solution, more  $Cl^{-}$  and  $SO_4^{2^-}$  are adsorbed on the electrode surface, and there is less time for the electrode surface to complete the "relaxation process".

Time constant  $\tau$  decreases. A negative correlation between time constant  $\tau$  and frequency positions of the peak and valley on the Bode diagrams makes the positions move in the high-frequency direction with increasing salinity. After the calculation, the (QRt)'s phase angle is  $\Phi = \arctan(\omega R_t Q)$ . Moreover, the phase angle of the "peak" in saturated sandy soil containing NaCl is slightly lower than that in saturated sandy soil containing NaCl is lower than Rt in saturated sandy soil containing Na<sub>2</sub>SO<sub>4</sub>. Rt in saturated sandy soil containing NaCl is lower than Rt in saturated sandy soil containing Na<sub>2</sub>SO<sub>4</sub> because Cl<sup>-</sup> is more destructive to the oxide film on the steel sample surface than SO<sub>4</sub><sup>2-</sup>. Meanwhile, perhaps because Cl<sup>-</sup> is easier to adsorb on the electrode surface than SO<sub>4</sub><sup>2-</sup>, CPT-T in saturated sandy soil containing NaCl is lower than Z<sub>0</sub> in saturated sandy soil containing Na<sub>2</sub>SO<sub>4</sub>. Finally, the phase angle value of the "peak" in the saturated sandy soil containing NaCl is slightly lower than that in the saturated sandy soil containing Na<sub>2</sub>SO<sub>4</sub> in the Bode diagrams.

# 3.4 Macroscopic and Microscopic Corrosion Morphologies of X80 Steel



Table 5. Macroscopic morphologies of X80 steel in saturated sandy soils containing Cl<sup>-</sup> and SO4<sup>2-</sup>

Table 5 shows the macroscopic corrosion morphologies of X80 steel in saturated sandy soil containing NaCl and Na<sub>2</sub>SO<sub>4</sub>. The surfaces of X80 steel lose metallic luster and have serious local corrosion after corrosion in saturated sand soil containing NaCl. In this neutral-pH environment, one cathode reaction and one anode reaction are included in the corrosion process of X80 steel in sodium saline saturated sandy soil with different concentrations [31].

The cathode process is the depolarization reaction of oxygen, as shown in equation (7).

 $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$  (7)

The anode process is the dissolution reaction of iron, as shown in equation (8).

 $Fe+nH_2O \rightarrow Fe^{2+} \cdot nH_2O+2e^{-}$  (8)

Meanwhile, the  $Fe^{2+}$  dissolved by the anode reaction and the OH<sup>-</sup> produced by the oxygen reduction at the cathode combine to form  $Fe(OH)_2$  as shown in equation (9).

 $Fe^{2+}+2OH^{-} \rightarrow Fe(OH)_2$  (9)

Fe(OH)<sub>2</sub> is extremely unstable and easily oxidized to Fe(OH)<sub>3</sub>, as shown in equation (10). 4Fe(OH)<sub>2</sub> + O<sub>2</sub> + 2H<sub>2</sub>O  $\rightarrow$  4Fe(OH)<sub>3</sub> (10) One part of  $Fe(OH)_3$  is decomposed into brown-red product  $Fe_2O_3$ ; another part of  $Fe(OH)_3$  is decomposed into FeOOH [32-33], as shown in equations (11)-(12).

 $2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \tag{11}$ 

 $Fe(OH)_3 \rightarrow FeOOH+H_2O$  (12)

Simultaneously, FeOOH reacts with the  $Fe^{2+}$  dissolved by the anode reaction to generate black products  $Fe_3O_4$ ,  $Fe(OH)_3$  and  $Fe(OH)_2$ , which combine to form  $Fe_3O_4$ , as shown in equations (13)-(14).

 $2FeOOH+Fe^{2+} \rightarrow Fe_3O_4+2H^+ \qquad (13)$ 

 $2Fe(OH)_3+Fe(OH)_2 \rightarrow Fe_3O_4+4H_2O$  (14)

Finally, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> cover a dense and stable oxide film on the surface of X80 steel and hinder the electrochemical reaction on the electrode surface [34]. In particular, marco-morphologies display the surfaces cover black Fe<sub>3</sub>O<sub>4</sub> and brown-red Fe<sub>2</sub>O<sub>3</sub> corrosion products. The surface of the steel sample is most severely corroded at the concentration of 1.0%. The surfaces of X80 steel are uniformly covered with black and little brown-red corrosion products after corrosion in the saturated sandy soil containing Na<sub>2</sub>SO<sub>4</sub>. In general, the corrosion morphologies of X80 steel are notably different in saturated sandy soil containing different concentrations of sodium saline. When the salinity increases, the corrosion of X80 steel deteriorates.

After cleaning the surface impurities of the steel sheet with alcohol, we magnify the scanning electron microscopy by 500 times to observe the corrosion morphologies of X80 steel (Table 6).

Sodium saline Salinity	0.3%	0.5%	0.75%	1.0%
NaCl				
Na <sub>2</sub> SO <sub>4</sub>			and the second sec	

**Table 6.** Microscopic morphologies of X80 steel in saturated sandy soils containing Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>

X80 steel has significant differences in degree of corrosion in saturated sandy soil containing different concentrations of NaCl. Dense and shallow corrosion pits appear on the surface of the steel sheet at the concentration of 0.3%. However, the corrosion degree develops, and the corrosion pits are contiguous with increasing salinity. Steel sheet corrosion is more serious at the concentrations of 0.75% and 1.0%, where large and deep corrosion pits appear on the surface, and corrosion products are loose and cracked. The surface of X80 steel has similar corrosion morphologies in Na<sub>2</sub>SO<sub>4</sub>-saturated sandy soil with concentrations of 0.3~0.75%, and the degree of corrosion is relatively milder, the surface of steel sheets with three prior concentrations show fragmented pitting and attached black substance. Steel sheet corrosion is the heaviest at the concentration of 1.0%: the corrosion area significantly increases, and the surface is covered by a large amount of black substance.

With the increase in concentration of NaCl and Na<sub>2</sub>SO<sub>4</sub>, the corrosion degree of X80 steel corresponds to the distribution of polarization curves. The corrosion products covering the surfaces of X80 steel generate a strong protective effect, but the area on the surface that is not covered by corrosion products is severely corroded. Pitting corrosion occupies a dominant position through the corrosion process [35], and the increase in such corrosion phenomena will cause pipeline leakage accidents in practical engineering [36].

# **4. CONCLUSIONS**

In this paper, the electrochemical corrosion behaviours of X80 steel in saturated sandy soil containing different concentrations of NaCl and Na<sub>2</sub>SO<sub>4</sub> were studied using electrochemical impedance spectroscopy, polarization curves and scanning electron microscopy. The following conclusions are obtained.

(1) X80 steel has significantly different corrosion behaviours in saturated sandy soil containing NaCl and Na<sub>2</sub>SO<sub>4</sub>. With the increase in concentration of NaCl and Na<sub>2</sub>SO<sub>4</sub> in the pore solution, the corrosion rate  $C_R$  of X80 steel shows an accelerating trend; the corrosion rates are maximal at the salinity of 1.0%. The polarization resistance  $R_p$  of X80 steel shows a decreasing trend overall, and the anti-corrosion property is weakened.

(2) X80 steel in sandy soil containing NaCl and Na<sub>2</sub>SO<sub>4</sub> has notably different corrosion morphologies. The corrosion products of black  $Fe_3O_4$  and brown-red  $Fe_2O_3$  are generated from the electrochemical reaction on the surface of X80 steel. The corrosion type of X80 steel in low-concentration sodium saline saturated sandy soil is pitting with shallow and small corrosion pits. The corrosion degree develops, and the corrosion pits are deep and contiguous with increasing salinity. The transportation pipelines of oil and natural gas buried in practical saline soil will leak due to pitting corrosion.

(3) The corrosion process of X80 steel in saturated sandy soil containing NaCl and Na<sub>2</sub>SO<sub>4</sub> shows the capacitive arc generated by the electric double-layer capacitance on the electrode surface and the inductive arc generated by the pitting corrosion of the oxide film on the electrochemical impedance spectroscopy. The coverage and dissolution of the oxide film on the surface of X80 steel changes the electrode conductivity, which is reflected in the expansion and reduction of the capacitive arc radius in the Nyquist diagrams. The oxide film pitted by Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> forms the pore core and expands the dispersion effect on the electrode surface, which creates the inductive arc and reduces the inductive arc radius.

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## References

- 1. T. M. Liu, Y. H. Wu, S. X. Luo and C. Sun, Materialwiss. Werkstofftech., 41(4) (2010), 228.
- 2. H. Guo and X. He, Corros. Pro., 27(5) (2006), 232.
- 3. T.J. Moore and C.T. Hallmark, Soil Sci. Soc. Am. J., 51 (1987), 1250.
- 4. A. Hernández-Espejel, M.A. Domínguez-Crespo, R. Cabrera-Sierra, C. Rodríguez-Meneses and E.M. Arce-Estrada, *Corros. Sci.*, 52(7) (2010), 2258.
- 5. R.O. Rihan, Mater. Res., 16(1) (2012), 227.
- M.N. Norhazilan, Y. Nordin, K.S. Lim, R.O. Siti, A.R.A. Safuan and M.H. Norhamimi, J. Appl. Sci. Res., 8(3) (2012), 1739.
- 7. Y.H. Wu, T.M. Liu, S.X. Luo and C. Sun, Materialwiss. Werkstofftech., 41(3) (2010), 142.
- 8. Q. Song, Y. Liu, X. Chen and C. Yang, Total Corros. Control., 22(4) (2008), 63.
- 9. M. Zhu and C.W. Du, J. Mater. Eng. Perform., 26(1) (2016), 221.
- 10. M. Zhu, C.W. Du, X.G. Li and Z.Y. Liu, Mater. Corros., 66(5) (2015), 494.
- 11. H. Xiao, F. Xie, M. Wu, D. Wang, W. Zhao and X. Luo, Mater. Pro., 50(8) (2017), 14.
- 12. J.N. Murray and P.J. Moran, Corros. Sci., 45(1) (1989), 34.
- 13. M. Yan, C. Sun, J. Xu, J. Dong and W. Ke, Corros. Sci., 80 (2014), 309.
- 14. S. Han, H. Sun, Z. Xu, L. Yu, M. Yan, C. Yu and C. Sun, Corros. Res., 30(11) (2016), 49.
- 15. F. Ma, R. Xie, P.J. Han and X.H. Bai, Int. J. Electrochem. Sci., 13 (2018), 5396.
- 16. L.M. Quej-Ake, J. Marín-Cruz and A. Contreras, Anti-Corros. Methods Mater., 64(1) (2017), 61.
- 17. S.Z. Yu, G.J. Xu, H.H. Song, X. Zhu, W.W. Lu and Y. Cheng, Adv. Mater. Res., 1015 (2014), 655.
- 18. P. Han, P. Han, R. Xie, B. He and X. Bai, Int. J. Electrochem. Sci., 13 (2018), 8694.
- 19. P. Pernice, M. Arpaia and A. Constantini, Mater. Chem. Phys., 26 (1990), 323.
- 20. J.L. Alamilla, M.A. Espinosa-Medina and E. Sosa, Corros. Sci., 51(11) (2009), 2628.
- 21. F. Mansfeld, Adv. Corros. Sci. Technol., (1976), 163.
- 22. H. Tang, G. Song, C. Cao and H. Lin, Corros sci Pro Technol., 7(4) (1995), 285.
- 23. H. Tang, G. Song, C. Cao and H. Lin, Corros sci Pro Technol., 8(3) (1996), 179.
- 24. H. Li, W. Kang, J. Hu and Y. Liu, Trans. Mater. Heat Treat., 32(10) (2011), 151.
- 25. A. Lasia, Mod. A. Electrochem., 32(10) (1999), 143.
- 26. K. Belmokre, N. Azzouz, F. Kermiche, M. Wery and J. Pagetti, Mater. Corros., 49 (1998), 108.
- 27. A. Benmoussa, M. Hadjel and M. Traisnel, Mater. Corros., 57(10) (2006), 771.
- 28. M. Li, H. Lin and C. Cao, J. Chin. Soc. Corros. Pro., 20(2) (2000), 111.
- 29. C. Cao and J. Zhang, An Introduction to Electrochemical Impedance Spectroscopy., Science Press, (2002) BeiJing, China.
- 30. L.J. Zhang, Z. Zhang, F.H. Cao, J.Q. Zhang, J.M. Wang and C.N. Cao, Acta Metall. Sinica., 17(6) (2004), 907.
- 31. M. Stratmann and J. Muller, Corros. Sci., 36(2) (1994), 327.
- 32. M. Sancy, Y. Gourbeyre, E.M.M. Sutter and B. Tribollet, Corros. Sci., 52(4) (2010), 1222.
- 33. M. Yan, C. Sun, J. Dong, J. Xu and W. Ke, Corros. Sci., 97 (2015), 62.
- 34. C. Ren, P. Han and W. Zhang, Corros. Pro., 36(12) (2015), 1137.
- 35. I.S. Cole and D. Marney, Corros. Sci., 56 (2012), 5.
- 36. Z.Y. Liu, X.G. Li and Y.F. Cheng, *Electrochim. Acta.*, 60 (2012), 259.

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