Coupling Effect of Hydrostatic Pressure and Erosion on Corrosion Behavior of X70 Steel in Simulated Seawater

PengWei Ren, XingYing Tang,* Zu’an Qin, YingHui Wang, and Jianjun Cai

Cite This: ACS Omega 2022, 7, 44033−44046

ACCESS

ABSTRACT: The corrosion behavior of X70 steel under the coupling effect of pressure and erosion in simulated seawater was investigated by using corrosion loss, electrochemical tests, SEM, AFM, XPS, and Raman spectroscopy. The coupling effect of pressure and erosion could induce changes in the amounts and compositions of the corrosion products and increase pitting. The rate of the combined corrosion of X70 steel represents a downtrend, which still displays a higher corrosion rate than only immersion at the same pressure. This means that the coupling of pressure and erosion will accelerate corrosion, but the effect of erosion is weakened by pressure. The larger the pressure is, the more erosion is weakened. The pressure reduces the water cutting force by increasing the liquid viscosity and reduces the surface hardness changes under high pressure by generating magnetite, which is closely bound to the substrate.

1. INTRODUCTION

With the increasing exploration of marine resources, subsea pipeline steels are widely used in offshore oil and gas transportation. However, they inevitably suffer severe corrosion due to complex deep-sea environmental factors. Pipeline steel in service is prone to accidents resulting from water velocity, dissolved oxygen, temperature, salinity, microbiology, and hydrostatic pressure (HP). The corrosive failure of subsea steel pipes causes enormous economic losses and severe environmental pollution. Therefore, it is necessary to understand the influence of deep-sea environmental factor variations on the corrosion behavior of pipeline steel.

The corrosion behaviors of materials have significant differences between shallow and deep ocean conditions. Much research has been devoted to the influences of the hydrostatic pressure on the corrosion behavior of pipelines. Yang et al. reported that HP could accelerate corrosion by promoting the pitting initiation and propagation of X70 steel, and the stress corrosion cracking susceptibility could increase under elevated HP. Similarly, Sun et al. proposed that HP accelerates the cathode hydrogen evolution of X70 steel by changing the permeated hydrogen concentration. Furthermore, a report provided by Li et al. found that HP had a specific influence on the chemical and physical properties of the corrosion products of X65 steel, and the cracks on the corrosion product layer became wider and deeper. Xu et al. also reported that high pressure promoted the formation of magnetite (Fe₃O₄) on X80 steel.

In addition to HP, seawater erosion also plays an important role in the corrosion of pipeline steel. In the flowing environment of seawater, a great degradation of the subsea pipeline steel surface would be caused by erosion–corrosion (E-C). Significant synergism between corrosion and erosion of X70 pipeline steel has been observed in a flowing solution containing solids. Islam and Farhat reported that the corrosion losses of X42, X70, and X100 steels gradually increased with increasing flow speed. Tian and Lan observed that different flow rates would lead to different electrochemical corrosion processes. Moreover, a study revealed that the rotating speed changed the corrosion type of X65 steel from pure uniform electrochemical corrosion into a combination of uniform corrosion and local damage, which was aggravated by increasing the rotating speed. Xu et al. calculated the critical impact energy for the initiation of erosion–corrosion of X65 steel.

It cannot be ignored even though the velocity of water in a deep-sea environment is lower than that of surface water. According to statistics, approximately 9% of corrosion failures in the oil and gas industry are due to the scouring process.

Received: August 23, 2022
Accepted: November 9, 2022
Published: November 23, 2022
However, most of the hydrostatic pressure experiments adopt the static immersion test method, and the erosion tests are usually at atmospheric pressure, which is quite different from the real deep-sea environment. The influencing factors of marine corrosion are complicated and mutually coupled, so the actual corrosion mechanism of materials cannot be obtained by simulating only a single factor. Hence, it is necessary to combine erosion and hydrostatic pressure to simulate the deep sea state. The corrosion behavior of X70 pipeline steel under the coupling of these two factors has rarely been studied. Therefore, in this work, the coupling effect of pressure and erosion on corrosion was analyzed by weight loss, electrochemical testing, corrosion morphology observation, and element analysis to obtain a quantitative database of X70 pipeline steel corrosion in a simulated deep-sea environment, reveal the process of pit corrosion, and provide a reasonable basis for protective anticorrosion actions in the marine environment.

2. MATERIALS AND METHODS

2.1. Experimental Equipment. The experimental setup was designed by the authors to simulate the erosion–corrosion behaviors of X70 steel under the deep sea, as schematically illustrated in Figure 1. The device comprises three parts: a pressure system, a speed control system, and a temperature control system. The hydrostatic pressure is controlled by inputting different amounts of the electrolyte solution through a liquid booster pump. By adjusting the speed of the stirrer to change the flow rate of the solution in the autoclave, the range of stirrer speed is from 0 to 600 rpm (approximately 0 to 3.3 m/s). The temperature of the deep sea is simulated by the cold machine.

2.2. Materials and Electrolytes. The chemical composition of X70 steel is exhibited in Table 1. As shown in Figure 2, the microstructure of the X70 steel consists of pearlite (the dark phase) and ferrite (the bright phase). Specimens were cut into 10 mm × 10 mm × 3 mm sections for the electrochemical experiments. The copper wire was welded to one end, and then the other surfaces except the working surface were encapsulated in epoxy resin. In addition, specimens with dimensions of 20 mm × 30 mm × 4 mm were prepared for weight loss measurements and morphology analysis. Each specimen was mechanically polished to a 2000 # finish, degreased ultrasonically in acetone and anhydrous ethanol, and dried. The electrolyte in this work was 3.5% NaCl (wt %), comprised of analytical grade NaCl and deionized water. The experiments were carried out for 24 h at a rotational speed of 180 rpm (approximately 1.0 m/s), at a temperature of 4 °C ± 1 °C, and at pressures of 0.1, 2, 5, 10, and 15 MPa. All measurements were made three times.

2.3. Electrochemical Measurements. Electrochemical tests were measured by using a three-electrode Gamry electrochemical workstation system (Reference 600+, USA), and the X70 steel specimen was used as the working electrode. A Ag/AgCl electrode was used as the reference electrode, and a Pt electrode was used as the counter electrode. Each specimen was put into the electrolytic cell after erosion–corrosion exposure and stabilized for 30 min prior to the electrochemical test. Electrochemical impedance spectroscopy (EIS) measurements were conducted with a 5 mV sinusoidal signal over a frequency range from 10⁵ to 10⁻² Hz around the open circuit potential (OCP). The experimental data were fitted by ZSimpWin software after the measurements. Potentiodynamic polarization was performed over a potential range of −500 mV to 500 mV (vs the OCP), and the scanning direction was from the cathode potential to the anode potential with a scan rate of 1 mV/s.
2.4. Surface Morphology Observations and Composition Analyses. The surface morphologies of the exposed X70 steel specimens were observed by scanning electron microscopy (SEM, Hitachi SU5000, Japan) and atomic force microscopy (AFM, 5100N, Japan). The elemental distributions on the steel surfaces were identified using energy dispersive spectroscopy (EDS, FEI TeN-Cai G2 f20 s-twin, 200 kV, USA). The compositions of the corrosion products were determined by X-ray photoelectron spectroscopy (XPS, Ultima IVX, JAPAN) and Raman spectroscopy (RS, Invia, UK) with a range of 150 to 1600 cm\(^{-1}\) at 633 nm.

3. RESULTS AND DISCUSSION

3.1. Corroded Morphology Analysis of X70 Steel under the Coupling of Pressure and Erosion. Figure 3a.1–e.1 illustrate the macroscopic corrosion morphologies of X70 steel after exposure to different erosion–corrosion conditions. Significant outer layer spallation of the X70 steel was observed, exposing the subsurface layer to a corrosive environment. In addition, several pinhole-like rust points were found on the X70 steel, and it is reasonable to assume that the corrosion type combines uniform corrosion with pitting corrosion during the erosion–corrosion exposure. The colors of the corrosion products are related to their physical phases, and the X70 steel generated new corrosion products at 15 MPa because the colors appeared green. The corrosion areas of the X70 steel were reduced, and the pinhole-like rust points increased with increasing pressure.

Figure 3. Surface morphologies of the specimens after 24 h of exposure to erosion–corrosion in 3.5% NaCl solution at (a) 0.1 MPa, (b) 2 MPa, (c) 5 MPa, (d) 10 MPa, and (e) 15 MPa. (1) Macrograph; (2) the areas of uniform corrosion; (3) the areas of scratch; (4) the areas of pitting.

Figure 3a.2–e.2 present the SEM images of the uniform corrosion areas on the X70 steel after 24 h of exposure to erosion–corrosion. The outer layers with apparent holes and voids are composed of spherical corrosion products that are not smooth. In the inner layer, corrosion products have flower–flake morphologies with dense connections, which gradually increase in size as the pressure increases. The corrosion products of the bottom layer were observed by selecting the areas where scratches could still be distinguished, as shown in Figure 3a.3–e.3. The number and volume of corrosion products of the X70 steel gradually increased, and the agglomeration phenomenon appeared at higher pressures. Furthermore, there were needle-like corrosion products with a uniform distribution at 15 MPa. These results signify that pressure promotes the formation and growth of corrosion products and changes the morphologies of the corrosion products.

The pitting area corrosion morphologies of the X70 steel were significantly different from the surrounding uniform corrosion areas, and there were distinct demarcations among all of the test conditions (Figure 3a.4–e.4). The products in the uniform corrosion areas were mainly spherical, and the pitting corrosion areas were surrounded by band-shaped corrosion products with obvious cracks, which are likely due to dehydration of the corrosion product layer in the air after erosion–corrosion exposure. The erosion–corrosion products inside the pit had tremendously different morphologies and gradually increased as the pressure increased. It may be related to erosion and will be discussed in section 3.7.
3.2. Electrochemical Test Results of X70 Steel under the Coupling of Pressure and Erosion.

According to the Nyquist diagram presented in Figure 4a, X70 steel exhibits a single capacitive reactance arc after 24 h of exposure to erosion−corrosion under different pressures, and the radii of the arcs increase gradually with pressure, which reveals that the impedance value of X70 steel increases and enhances the corrosion resistance. All of the arcs are incomplete semicircles with their centers deviating from the real axis, so there is a dispersion effect caused by the roughness and inhomogeneity of the electrode surface. The results of the Bode-phase angle study of X70 steel are presented in Figure 4b, and the curves have a single time constant in the low-frequency region. Therefore, the equivalent circuit of $R(QR)$ was selected to fit the EIS data, as shown in Figure 4e. The fitting results are listed in Table 2. The $R_{ct}$ values gradually increase as the pressure increases, and it is reasonable to consider that the denser corrosion product layer hinders the charge transfer process. $n$ is the frequency dispersion factor and varies from 0 to 1. It represents the surface roughness of the electrode, the uneven distribution of the corrosion current density, and the deviation from the ideal capacitance, reflecting the strength of the dispersion effect. The value of $n$ was as low as 0.6 in the experiment, and one possible reason is that it is a porous electrode. The smallest value of $n$ at 15 MPa demonstrates that the electrode surface is the most uneven, resulting from the increase in pits.

The potentiodynamic polarization curves of X70 steels after 24 h of exposure to erosion−corrosion under different pressures are plotted in Figure 4c. The existence of the same corrosion mechanism is due to the similar shapes of the polarization curves under each condition. Pitting potential is defined as the potential at which the current density increases abruptly, such as that found in the rupture of the passivation film in stainless steel. Although the apparent pitting potential on the polarization curve was not observed, there is one inflection point, and the slope value of the curve after the inflection point is smaller than that before the inflection point. Wang et al. reported that pitting corrosion of steel occurs even under free-corrosion conditions and possibly during the whole anodic polarization. Therefore, it is speculated that before the inflection point, mainly uniform corrosion occurs with a low corrosion current value, and pitting increases after the inflection point. In addition, the potential range values of uniform corrosion on the anode polarization curve are broader at low pressure and decrease gradually with increasing pressure, but the corresponding range of pitting expands. At 15 MPa, the lower inflection point potential indicates that the tendency of pitting is higher than at other pressures. There are also inflection points in the cathode polarization curves, and the reaction may occur, that is, the depolarization of hydrogen and oxygen. Ma et al. reported that HP reduced the equilibrium electrode potential of the hydrogen evolution reaction and enhanced the equilibrium electrode potential of the oxygen uptake reaction. The equilibrium potential difference ($\varphi_{e,C} - \varphi_{e,A}$) of the cathode and anode is a thermodynamic parameter that reflects the electrochemical affinity of the corrosion reactions. According to the Gibbs free energy change, X70 steel becomes more prone to corrosion resulting from the large variation. Therefore, in this research, the reduction reaction of oxygen occurs preferentially, while

![Figure 4. Electrochemical test and weight loss diagrams of X70 steel after 24 h of exposure to erosion−corrosion at different pressures: (a) Nyquist, (b) Bode-phase angle, (c) polarization curves, (d) weight loss and corrosion current density, (e) equivalent circuit model used to fit EIS.](https://doi.org/10.1021/acsomega.2c05435)

| Pressure (MPa) | $R_s$ ($\Omega \cdot \text{cm}^2$) | $Q_0$ | $Y_0$ (S·sn·cm$^{-2}$) | $n$ | $R_{ct}$ ($\Omega \cdot \text{cm}^2$) |
|---------------|-------------------------------|-------|----------------------|-----|-----------------------------|
| 0.1 MPa       | 9.23                          | 0.003497 | 0.6770 | 819 |                             |
| 2 MPa         | 14.12                         | 0.004813 | 0.7007 | 859 |                             |
| 5 MPa         | 10.28                         | 0.002280 | 0.6831 | 1250 |                             |
| 10 MPa        | 13.24                         | 0.005689 | 0.7082 | 1452 |                             |
| 15 MPa        | 13.13                         | 0.002834 | 0.6480 | 1886 |                             |
the reduction reaction of hydrogen starts under the condition of low oxygen content or hypoxia. The hypoxic environment will easily form in the corrosion pits.

The corrosion weight loss results of the specimen are shown in Figure 4d. The weight loss data are expressed as the weight loss per unit of surface area. With increasing pressure, the corrosion weight loss gradually decreases. Meanwhile, the fitting corrosion current density has the same trend, indicating that the erosion–corrosion rate is decelerated by increasing pressure.

3.3. Corrosion Product Analysis of X70 Steel under the Coupling of Pressure and Erosion. Figure 5a shows the EDS diagram of the uniformly corroded area of X70 steel. In this area, O is enriched in the outer layer, while Fe is more concentrated in the inner layer. The adsorption of Cl on the corrosion products may cause the enrichment of Cl on the surface. The pitting area of X70 steel of erosion–corrosion is shown in Figure 5b. The corrosion products at the edge of the pit are rich in O and Cl, while Fe is more concentrated in the middle area where pitting and uniform corrosion are connected. Moreover, the energy spectrum identified Si and Mn, which primarily exist in the inclusion phase and are nucleation points that induce pitting corrosion.

The atomic ratios of several main elements in corrosion products under different pressures are shown in Figure 6. The sum of the O and Fe accounts for approximately 90% of the corrosion products, demonstrating that most of the corrosion products are iron oxides or hydroxides. At 0.1 MPa, Fe accounts for 52%, and O accounts for 34%. The proportion of C is also as high as 12%, which may be the residual C in situ after the preferential dissolution of the Fe in the pearlite being incorporated into the corrosion products. With increasing pressure, the proportion of C decreased sharply and then remained stable under high pressure. The proportion of O in the product increased continuously while the proportion of Fe decreased. However, the content of Cl stayed at a low level in the above experiments because chloride cannot stably remain on the specimen.

Raman spectroscopy and XPS were used to analyze the compositions of the corrosion products of X70 steel under various conditions (see Figure 7 and Figure 8). The corrosion products mainly consisted of γ-FeOOH and α-Fe₂O₃ at 0.1 MPa and γ-FeOOH, α-Fe₂O₃, and Fe₃O₄ at 2 to 10 MPa. However, when the pressure reached 15 MPa, β-FeOOH appeared based on the 2 to 10 MPa. Furthermore, the peak areas of α-Fe₂O₃ and γ-FeOOH decreased with increasing pressure, while that of Fe₃O₄ increased, so more iron oxide particles were present on the surface in the form of Fe₃O₄. It manifests that the compositions of the corrosion products and the transformation of product types were changed by the variation of pressure under exposure to erosion–corrosion.

3.4. Pitting Corrosion Morphology Analysis of X70 Steel under the Coupling of Pressure and Erosion. As shown in Figure 9 and Table 3, the diameters, depths, and
amounts of corrosion pits of X70 steel increased after erosion−corrosion exposure with increasing pressure. When the metal is immersed in seawater, there is a potential difference due to the inhomogeneity of the composition and stress distribution, and the metal surface will form numerous corrosion galvanic cells. The low potential region loses electrons to be the anode region, which is the active point of corrosion. X70 steel is composed of pearlite and ferrite (see Figure 2), and pearlite will preferentially dissolve with a lower electric potential. In addition, with the growth and accumulation of corrosion products, the accumulation areas have oxygen concentrations that are different from other places, thus forming an oxygen concentration battery that becomes the anode, then gradually evolves into a corrosion pit. Under the coupling of pressure and erosion, the number and size of pits increased, which is related to the physical and chemical effects of pressure and erosion on the longitudinal and horizontal growth of pits, see section 3.7.

3.5. Effects of Hydrostatic Pressure and Erosion on the Corrosion Behavior. To explore the coupling effect of hydrostatic pressure and erosion, except the combination of two factors to carry out the test on X70 steel, first, it is essential to analyze the effect of the single factors of pressure or erosion on X70 steel.

3.5.1. Effect of Hydrostatic Pressure on the Corrosion Behavior. The macroscopic corrosion morphologies of X70 steel immersed at different hydrostatic pressures (0.1, 2, 5, 10, 15 MPa) at 4 °C for 24 h are shown in Figure 10. The area of the corrosion products at high hydrostatic pressure is significantly larger than that at atmospheric pressure. All conditions have pinhole-like rust points on the surface of the X70 steel except for the 0.1 MPa specimen. By observing the anodes and cathodes of the polarization curves, it is found that the polarization curve shapes at 2 to 15 MPa are similar to those of the erosion−corrosion experiment, which is a combination of uniform corrosion and pitting (Figure 11). The anodic polarization curve with a lower slope has no inflection point at 0.1 MPa; the cathode polarization curve hardly changes in the potential range of −0.64 V to −0.7 V. The diffusion of oxygen is considered the key to controlling the corrosion rate. In addition, the open circuit potential is much higher than other conditions at 0.1 MPa, indicating that the metal has higher thermodynamic stability and a lower tendency for corrosion.

Pressure increases the corrosion rate of the X70 steel not only by affecting the thermodynamic stability of the material but also by promoting corrosion kinetics of the material. Using molecular dynamics modeling, Liu et al. revealed that pressure-promoted anodic dissolution mainly amplifies the Ψ1 effect by decreasing the thickness of the Helmholtz layer on the metal surface. Xiong et al. Figure 7. Raman spectroscopy analysis of the corrosion products from X70 steel after 24 h of exposure to erosion−corrosion at different pressures.

Figure 8. XPS analyses of the corrosion products of X70 steel after 24 h of exposure to erosion−corrosion at different pressures.
showed that hydrostatic pressure increases the capacity of the electric double layer (stern layer and diffusion layer), resulting in an increase in the current density of both oxidation and reduction reactions near the equilibrium potential through measurements of potentiodynamic polarization and electrochemical impedance spectroscopy. Luck and Latz simulated the effect of the electric double layer on the electrochemical reaction and found that higher capacitance produced more charges, which increased the potential gradient between the electric double layer. The potential difference in the electric double layer directly affected the kinetics of the electrode reaction, increasing the charge transfer rate. Thus, the corrosion rate gradually increases as the pressure increases, as shown in Figure 13a. Raman spectroscopy (Figure 12) shows that $\gamma$-FeOOH and $\beta$-FeOOH were generated under the five conditions, but Fe$_3$O$_4$ only forms at high pressure. With increasing pressure, the content of $\beta$-FeOOH gradually increased, and the contents of $\gamma$-FeOOH and Fe$_3$O$_4$ decreased, possibly due to more Fe$^{2+}$ being converted into $\beta$-FeOOH at high pressure.

$\beta$-FeOOH, which often exists between the iron matrix and the rust layer, has an orthorhombic structure that can adsorb Cl$^-$ on the surface, and its morphology can be needle-like or rod-like, loose, and porous. Moreover, it can alter the structure of the rust layer to provide channels for the diffusion and penetration of corrosive elements, thereby deteriorating the protective effect of the rust layer and accelerating the corrosion process. $\beta$-FeOOH has a significant

| pressure (MPa) | diameter ($\mu$m) | depth ($\mu$m) | number (mm$^{-2}$) |
|---------------|------------------|--------------|------------------|
| 0.1           | 32.3             | 0.381        | 42               |
| 2             | 60.2             | 1.162        | 47               |
| 5             | 70.4             | 1.159        | 59               |
| 10            | 81.1             | 1.161        | 109              |
| 15            | 123.0            | 1.166        | 119              |
surface area, which can create a favorable condition for pitting. β-FeOOH is generated by the hydrolysis and oxidation of FeCl₂ (the intermediate products include FeCl₃ and FeOCl) or Fe₂(OH)₃Cl (the intermediate products include green rust) under conditions with higher contents of Cl⁻ and Fe²⁺, so it usually arises in pitting and crevice corrosion areas as shown in the following reactions:

\[ 4\text{FeCl}_2 + O_2 + 6\text{H}_2\text{O} \rightarrow 4\beta\text{-FeOOH} + 8\text{HCl} \quad (1) \]

First, anodically dissolved Fe²⁺ is combined with Cl⁻ to form FeCl₃. The oxidation of FeCl₃ is the main pathway for generating β-FeOOH. FeOCl is the product of the initial hydrolysis of FeCl₃, and β-FeOOH is the product of further hydrolysis. Fe₂(OH)₃Cl is slowly oxidized to green rust (GR(Cl⁻)), which is a general term for a series of compounds containing both Fe(II) and Fe(III). Then, β-FeOOH is generated by further oxidation, including a dissolution-recrystallization process.

3.5.2. Effect of Erosion on the Corrosion Behavior. The effect of erosion of X70 steel is analyzed to compare the

Figure 10. Macromorphologies of X70 steel following 24 h of immersion in 3.5% NaCl solution at (a) 0.1 MPa, (b) 2 MPa, (c) 5 MPa, (d) 10 MPa, and (e) 15 MPa.

Figure 11. Polarization curves of X70 steel following 24 h of immersion in 3.5% NaCl solution at different pressures.

Figure 12. Raman spectroscopy analysis of the corrosion products from X70 steel after 24 h of immersion at different pressures.

Figure 13. Corrosion results of X70 steel after 24 h exposure at different pressures. (a) Corrosion rates under immersion and erosion-corrosion conditions. (b) The contributions of the hydrostatic pressure and erosion-corrosion conditions.

\[ \text{FeCl}_3 + 2\text{H}_2\text{O} \rightarrow \beta\text{-FeOOH} + 3\text{HCl} \quad (2) \]

\[ \text{FeCl}_3 + \text{H}_2\text{O} \rightarrow \text{FeOCl} + 2\text{HCl} \quad (3) \]

\[ \text{FeOCl} + \text{H}_2\text{O} \rightarrow \beta\text{-FeOOH} + \text{HCl} \quad (4) \]

\[ 2\text{Fe}_2(\text{OH})_3\text{Cl} + \text{O}_2 \rightarrow 4\beta\text{-FeOOH} + 2\text{HCl} \quad (5) \]

The effect of erosion of X70 steel is analyzed to compare the
immersion and erosion–corrosion tests at atmospheric pressure. It is evident that the specimens have some corrosion pits after erosion and have larger corrosion areas than immersion. Tafel fitting of the polarization curves shows that the corrosion rate is 1.058 mpy under immersion conditions and 3.473 mpy under erosion–corrosion conditions, and the rate of erosion is approximately 3 times that of immersion.

Uniform corrosion occurred and generated γ-FeOOH and β-FeOOH after immersion, which can remain on the surface and prevent contact between the corrosive solution and the metal matrix, thus providing efficient protection for the matrix. Nevertheless, in the γ-FeOOH accumulation layer, oxygen will be limited rather than Cl⁻ due to the competitive adsorption of Cl and O, indicating that the existence of a high concentration of Cl⁻ would promote the formation of β-FeOOH. The formation process is shown in eqs 1–5.

Under erosion–corrosion conditions, the corrosion products are α-Fe₂O₃ and γ-FeOOH, and γ-FeOOH is loose with poor adhesion to the matrix, showing significant spallation under the action of gravity and erosion. The γ-FeOOH partially converts into stable α-Fe₂O₃, which can enhance the resistance to erosion. However, according to the adsorption theory, the metal ions of the oxide film can form high-energy complexes with Cl⁻, and the complexes can readily separate from the oxide ions in the lattice once it is formed, causing the dissolution of the passivation film and an autocatalytic effect to induce pitting. This is the reason that Cl⁻ can trigger pitting of the matrix, although α-Fe₂O₃ and γ-FeOOH accumulate on the specimen surface. It is vital that the effect of erosion behavior is related not only to the mechanical and chemical damage but also to the surface state of the specimen. In the erosion test, electrochemical corrosion promotes damage to the specimen by increasing the roughness and reducing the hardness of the specimen, thus accelerating corrosion.

Erosion affects the corrosion behavior and characteristics of X70 steel on the hydrodynamic level. On the one hand, erosion reduces the oxygen diffusion layer and shortens the cathode reaction time, leading to corrosion product generation being fast and abundant; on the other hand, when the fluid shear stress is greater than the bonding force between the product and the matrix, the corrosion products, even the passivation layer, can be spalled off and washed away from the surface, which weakens the corrosion resistance of the product deposition and aggravates corrosion. The metal matrix is exposed to the corrosive medium after the old corrosion product layer is broken, forming new active sites and generating a new corrosion product layer.

3.6. Coupling Effect of Hydrostatic Pressure and Erosion on Corrosion Behavior. Fe₂O₃ is generated at high pressure. It exists in the inner layer and has an excellent protective effect on the matrix, so the impedance of the specimen is still increasing with increasing pressure. Moreover, γ-FeOOH can be mechanically washed off by the shear stress of the fluid, which grows faster on the surface of X70 steel. Therefore, this could explain the fact that the solution appears turbid yellow after the experiment. Figure 13a shows the corrosion rates of erosion–corrosion and immersion corrosion under different pressures, and it is apparent that the erosion–corrosion condition has a higher corrosion rate than immersion at the same pressure, indicating that the coupling of pressure and erosion will accelerate corrosion. It is interesting that there is a decreasing trend of X70 steel at erosion–corrosion with increasing pressure.

Corrosion is normally a phenomenon having anodic and cathodic processes and a strong coupling with several competing reactions. Both pressure and erosion affect the cathodic and anodic processes. It is rarely possible to accurately and quantitatively analyze which reactions at the cathode or anode are caused by pressure or erosion under the coupling effect. Therefore, the contribution, which is the sum of the anodic and cathodic corrosion effects from one factor, is used here. The results of the immersion condition are taken as the contribution of hydrostatic pressure in the coupling condition. Due to erosion being introduced based on pressure, the portion of the corrosion rate, which is higher than that of pure pressure, contributes to erosion. As shown in Figure 13b, the contribution of erosion decreases with increasing pressure, and it only accounts for 5% when the pressure is 15 MPa. It is likely that the corrosion kinetics of the steel are mainly dominated by pressure in the coupling environment.

To clarify the corrosion effect of pressure and erosion in the coupling, we also measured the pure erosion of X70 steel under atmospheric pressure. The corrosion rate of pure erosion under atmospheric pressure is used here as the pure erosion rate in all of the experiments because of the same flow velocity. The total corrosion rate can be calculated as follows:

\[ R_{CT} = R_{Cp} + R_{Ce} = R_{Cp} + \Delta R_{Cp} + R_{Ce} + \Delta R_{Ce} \]  

where \( R_{Cp} \) is the total corrosion rate, \( R_{Ce} \) is the corrosion rate caused by pressure, \( R_{Cp} \) is the corrosion rate caused by erosion, \( R_{Ce} \) is the pure corrosion rate under atmospheric pressure, \( \Delta R_{Cp} \) is the corrosion rate promoted by pressure, \( R_{Ce} \) is the pure corrosion rate caused by erosion under atmospheric pressure, and \( \Delta R_{Ce} \) is the coupling effect of pressure and erosion. Because the flow velocity is the same under all conditions while the pressure changes, the influence of erosion on the pressure is not considered here, and the coupling effect refers to the effect of pressure on erosion. As shown in Figure 14a, \( \Delta R_{Ce} \) shows a gradually increasing trend with increasing pressure, but the values of \( \Delta R_{Ce} \) decrease and change from positive to negative. This means that the pressure increases corrosion and weakens the erosion effect.

According to the relationship between the viscosity of the liquid and the pressure:

\[ U_p = U(1 + 0.003 \times 10^{-5}P) \]  

where \( U_p \) (Pa/s) is the kinematic viscosity when the pressure is \( P \) (Pa), and \( U (Pa/s) \) is the kinematic viscosity of the liquid when the pressure is 0.1 MPa.

The viscosity of the liquid is \( 1.5674 \times 10^{-3} \) Pa/s under atmospheric pressure at 4 °C. When the pressure rises to 15 MPa, the viscosity of water is \( 2.2821 \times 10^{-3} \) Pa/s, according to eq 7. The viscosity of water increases with increasing pressure. Hence, at high pressure, the kinetic energy of water caused by the rotating shaft decreases, which reduces the actual flow velocity and the disturbance of the water to reduce the material transfer velocity on the sample surface. Figure 14b shows the relationship between pressure and erosion, which fits the following equation:

\[ y = 0.20913 - 0.29587 \times \ln(x - 0.08926) \]  

According to the equation calculation, there is no synergistic effect between pressure and erosion when the pressure is 2.01
MPa (1 m/s). Moreover, the downward trend of the curve is obvious at low pressure, indicating that the effect of erosion is still important. In contrast, the fact that the curve is flat under high pressure means that the effect of erosion is weakened. However, the pressure is only 15 MPa in the test. The equation predicts that the fitting curve is infinitely close to a specific value for the condition of ultrahigh pressure, and the effect of erosion is minimal. Nevertheless, the coupling effect of pressure and erosion still has a higher corrosion rate than when pressure exists alone.

Electrochemical corrosion increases the roughness of the sample surface and decreases the hardness of the sample, and the state of the sample surface has a significant influence on the corrosion—erosion. Lu et al.\textsuperscript{50} shows that the reduction of in situ surface hardness caused by corrosion is the main mechanism of corrosion enhancement of low carbon steel. According to the literature,\textsuperscript{53,54} the change in the surface strength is a linear function of the logarithm of the anodic current density.

\[
\frac{\Delta H_v}{H_v} = -b \log \frac{i}{i_{th}} \tag{9}
\]

where $\Delta H_v$ ($\Delta H_v < 0$) is the change in surface hardness caused by anodic dissolution, $H_v$ is the original surface hardness, $b$ is the experimental constant, $i$ is the anode current density, and $i_{th}$ is the threshold anode current density that induces a decrease in surface hardness.

With increasing pressure, the corrosion rate gradually decreases. Thus, the surface hardness of the sample under high pressure is greater than that under low pressure. The reason may be the increase in Fe$_2$O$_3$ under high pressure, which binds closely to the matrix and is not easily destroyed by water flow. The surface hardness of the sample is higher and is not easily destroyed.

### 3.7. Corrosion Mechanism of X70 Steel under the Coupling of Hydrostatic Pressure and Erosion

Under atmospheric pressure, the inner layer consists of $\alpha$-Fe$_2$O$_3$, and the outer layer is covered with $\gamma$-FeOOH. As a corrosive ion in the sea, Cl$^-$ can easily pass through the gaps and holes from the outer layer to the inner layer, acting on the $\alpha$-Fe$_2$O$_3$ and replacing the O to form chloride. Then, pitting occurs because of the high solubility of chloride. Cl$^-$ will be released when chloride dissolves in the solution, which acts as a catalyst to accelerate corrosion.\textsuperscript{46} Due to the debonding effect of Cl$^-$, the protective film is difficult to regenerate, and pitting easily develops. At high pressure, the inner corrosion product contains not only $\alpha$-Fe$_2$O$_3$ but also Fe$_3$O$_4$. According to a previous study, Fe$_3$O$_4$ has good electrical conductivity, and the matrix covered with Fe$_3$O$_4$ can still lose electrons and dissolve, thus forming pitting, as shown in Figure 15a. Moreover, some literature\textsuperscript{6,58} reported that hydrostatic pressure increases the activity and adsorption amount of Cl$^-$ on a specimen and accelerates the transmission of aggressive particles, which means that the high specific conductivity of the solution under high pressure\textsuperscript{6,58} and Cl$^-$ more easily penetrates the passivation film and induces pitting.

The Fe in the pit continues to dissolve after forming corrosion pits, while O$_2$ will repair it. The bottom of the pit, where it becomes the anode,\textsuperscript{57} has a lower potential with the depth of the pit, and the edge of the cathode is the cathode, where the reduction of O$_2$ takes place. Hence, iron oxide/hydroxide is generated at the edge of the pit. The unfavorable area ratio of the large cathode and small anode will make the corrosion go deeper along the bottom of the pit to the substrate, and the electrochemical reaction trend strengthens with the potential difference increase.\textsuperscript{38} However, when the outside of the pit is covered with dense corrosion products, the O$_2$ in the pit will be consumed at a faster speed,\textsuperscript{60} and now it is difficult for external O$_2$ and internal Fe$^{2+}$ to diffuse through the film. Meanwhile, part of the Fe$^{3+}$ hydrolyzes to generate H$^+$, and the accumulation of H$^+$ causes the acidification of the environment and the reduction of H. Cl$^-$ will flood into the pit to maintain the balance of anions and cations. Both the H$^+$ and the Cl$^-$ ions in the pit will enhance the corrosion tendency of the matrix, and it will reach a severe level, as shown in Figure 15b. The H generated in the pit can be absorbed by the metal matrix and will accumulate in the high-stress region of the metal crack tip under the action of stress, reducing the bonding force between the atoms and fracturing the surface energy of the matrix,\textsuperscript{56,61} which is then prone to cracking.

The accumulation of rust inside the pits could facilitate the longitudinal growth of the pits,\textsuperscript{62} which is mainly caused by electrochemical corrosion. Horizontal growth is controlled by not only electrochemical corrosion but also erosion. The boundary between the pits disappeared due to the cutting effect of erosion, and the edge of the pit is impacted and developed horizontally, which displays a uniform corrosion morphology, as shown in Figure 15c--f. In addition, at the edge of the hole at the cathode, where the reduction of oxygen occurs, the region is covered with sediment, and the oxygen diffusion path will be impeded, forming an oxygen concentration cell with the uncovered area. The change in the potential difference in this region causes an ohmic potential drop. The kinetics of corrosion always occur based on potential differences. Therefore, the combination of physics and chemistry advances corrosion. Wang et al.\textsuperscript{57} reported that the aggregation of Cl$^-$ promotes the horizontal development of
pits. \( \text{Cl}^- \) gathers toward the pit to maintain electrical neutrality, resulting in a higher \( \text{Cl}^- \) concentration near the pit mouth. Part of \( \text{Cl}^- \) forms iron chloride here with \( \text{Fe}^{2+} \), and then the chloride moves horizontally under the concentration difference, promoting the horizontal development of pitting. The stress intensity around the pit is much higher than in other areas and multiplies with increasing hydrostatic pressure, hence, the high-stress area preferentially corrodes or is disrupted after being impacted by water flow.\(^{3}\) This is also one of the reasons why the diameter of the pit increases with pressure. However, the effect of erosion is significantly reduced with increasing pressure, and the contribution of erosion is only 5% at 15 MPa. It can be demonstrated that the probability of corrosion pits developing from local corrosion to uniform corrosion is reduced, and many corrosion pits could be observed after corrosion at high pressure.

Although \( \text{Fe}_3\text{O}_4 \) has a spinel structure with a dense and stable organization that has a specific protective effect,\(^ {64} \) it can easily separate from the matrix after the electrode reaction.\(^ {65} \) Once the corrosion products separated from the matrix are impacted by the fluid, they will be broken and peeled off while the fresh substrate is exposed, and then a new round of corrosion starts (Figure 15e,f). Corrosion products undergo the cyclic process of formation–deposition–protrusion–shedding–regeneration.

4. CONCLUSIONS

Under erosion–corrosion, the corrosion of X70 steel is a combination of uniform corrosion and pitting. The corrosion products are \( \text{\gamma-FeOOH} \) and \( \text{\alpha-Fe}_2\text{O}_3 \) under atmospheric pressure, while the corrosion products contain \( \text{\gamma-FeOOH} \), \( \text{\alpha-Fe}_2\text{O}_3 \), and \( \text{Fe}_3\text{O}_4 \) under high pressure. In the immersion state,
the corrosion products consist of $\gamma$-FeOOH and $\beta$-FeOOH, and the corrosion is uniform corrosion at atmospheric pressure. Under other conditions, uniform corrosion and pitting occur, and the corrosion products include $\gamma$-FeOOH, $\beta$-FeOOH, and Fe$_3$O$_4$. Pressure and erosion can change the contents and compositions of the corrosion products, of which pressure promotes the formation of Fe$_3$O$_4$; Fe$_3$O$_4$ increases with increasing pressure; and erosion promotes the formation of $\alpha$-Fe$_2$O$_3$.

A corrosion pit is formed at the point where there is an uneven potential on the surface of the X70 steel. After the breaking of the corrosion product film in the outer layer, a new corrosion product film is formed, and pitting grows through the constant circulation of this process.

The erosion–corrosion results show that the corrosion products in the inner layer of X70 steel grow, and $R_{ct}$ increases with increasing pressure. The number, depth, and diameter of pits on the surface increased at high pressure, and the horizontal development of pitting increased gradually while the area of uniform corrosion decreased. Furthermore, the corrosion rate of erosion–corrosion of X70 steel decreases with increasing pressure. However, the condition of erosion–corrosion still has a higher corrosion rate than immersion at the same pressure. The coupling of pressure and erosion will accelerate corrosion, but the effect of erosion is weakened by the same pressure. The coupling of pressure and erosion will change the corrosion rate of erosion.

The work was supported by the National Natural Science Foundation of China (No. 22068003) and the science and technology major project of Guangxi (No. AA18242007).

**AUTHOR INFORMATION**

**Corresponding Author**

XingYing Tang — School of Marine Sciences, Guangxi Key Laboratory on the Study of Coral Reefs in the South China Sea, Guangxi University, Nanning 530004, China; orcid.org/0000-0003-1372-3948; Email: tangxingying@gxu.edu.cn

**Authors**

PengWei Ren — School of Marine Sciences, Guangxi Key Laboratory on the Study of Coral Reefs in the South China Sea, Guangxi University, Nanning 530004, China

Zu’an Qin — School of Marine Sciences, Guangxi Key Laboratory on the Study of Coral Reefs in the South China Sea, Guangxi University, Nanning 530004, China

YingHui Wang — School of Marine Sciences, Guangxi Key Laboratory on the Study of Coral Reefs in the South China Sea, Guangxi University, Nanning 530004, China

Jianjun Cai — School of Architecture and Traffic, Guilin University of Electronic Technology, Guilin 541004, People’s Republic of China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c05435

**Author Contributions**

P.R.: investigation, methodology, writing—original draft. X.T.: conceptualization, writing—review and editing, funding acquisition. Z.Q.: investigation, methodology. Y.W.: investigation, conceptualization, supervision. J.C.: validation, investigation.

**Notes**

The authors declare no competing financial interest.

---

**ACKNOWLEDGMENTS**

The work was supported by the National Natural Science Foundation of China (No. 22068003) and the science and technology major project of Guangxi (No. AA18242007).

**REFERENCES**

(1) Traverso, P.; Canepa, E. A review of studies on corrosion of metals and alloys in deep-sea environment. Ocean Eng. 2014, 87, 10–15.

(2) Yang, Z. X.; Kan, B.; Li, J. X.; Su, Y. J.; Qiao, L. J. Hydrostatic pressure effects on stress corrosion cracking of X70 pipeline steel in a simulated deep-sea environment. Int. J. Hydrogen Energy 2017, 42, 27446–27457.

(3) Yang, Z. X.; Kan, B.; Li, J. X.; Su, Y. J.; Qiao, L. J. Hydrostatic pressure effects on corrosion behavior of X70 pipeline steel in a simulated deep-sea environment. J. Electroanal. Chem. 2018, 822, 123–133.

(4) Yang, Z.; Kan, B.; Li, J.; Qiao, L.; Volinsky, A. A.; Su, Y. A Statistical Study on the Effect of Hydrostatic Pressure on Metastable Pitting Corrosion of X70 Pipeline Steel. Materials 2017, 10, 1307.

(5) Sun, F. L.; Ren, S.; Li, Z.; Liu, Z. Y.; Li, X. G.; Du, C. W. Comparative study on the stress corrosion cracking of X70 pipeline steel in simulated shallow and deep sea environments. Materials science & engineering. A, Structural materials: properties, microstructure and processing 2017, 685, 145–153.

(6) Li, Q. S.; Luo, S. Z.; Xing, X. T.; Yuan, J.; Liu, X.; Wang, J. H.; Hu, W. B. Effect of deep sea pressures on the corrosion behavior of x65 steel in the artificial seawater. Acta Metall. Sin. 2019, 32, 972–980.

(7) Xu, C. C.; Zhu, Y. X.; Liu, W. L.; Bao, F. H.; Liu, E. J.; Huang, F. F.; Wen, L.; Jin, Y.; Sun, D. B. Hydrostatic pressure effects on corrosion behaviour of X80 steel in artificial sea water. Corrosion engineering, science, and technology 2021, 56, 383–391.

(8) López, D.; Congote, J. P.; Cano, J. R.; Toro, A.; Tschiptschin, A. P. Effect of particle velocity and impact angle on the corrosion–erosion of AISI 304 and AISI 420 stainless steels. Wear 2005, 259, 118–124.

(9) Aguirre, J.; Walczak, M.; Rohwerder, M. The mechanism of erosion–corrosion of API X65 steel under turbulent slurry flow: Effect of nominal flow velocity and oxygen content. Wear 2019, 438-439, 203053.

(10) Yang, R. P.; Weng, Y. J.; Han, C. C. Comparison of corrosion behavior of X70 and 16Mn steels III. Corrosion-erosion. Corrosion Science and Protection Technology 2006, 1, 50–53.

(11) Aminul Islam, M.; Farhat, Z. N.; Ahmed, E. M.; Alfantazi, A. M. Erosion enhanced corrosion and corrosion enhanced erosion of API X-70 pipeline steel. Wear 2013, 302, 1592–1601.

(12) Islam, M. A.; Farhat, Z. Erosion-corrosion mechanism and comparison of erosion–corrosion performance of API steels. Wear 2017, 376-377, 533–541.

(13) Al-Yasiri, M.; Al-Khateeb, M.; Wen, D. S. Examination of drill pipe corrosion in water-based drilling fluids under wellbore conditions. Corrosion engineering, science, and Technology 2018, 53, 183–187.

(14) Tian, Y.; Lan, X. Influences of temperature and velocity on corrosion rate of x70 subsea pipelines. Total Corrosion Control 2018, 03, 62–68.

(15) Zheng, Q. B. Effect of rotating speed and hydrostatic pressure on erosion-corrosion behavior of x65 pipeline steel. Int. J. Electrochem. Sci. 2017, 3, 2593–2605.

(16) Xu, Y. Z.; Liu, L.; Xu, C. B.; Wang, X. N.; Tan, M. Y. J.; Huang, Y. Electrochemical characteristics of the dynamic progression of erosion–corrosion under different flow conditions and their effects on corrosion rate calculation. J. Solid State Electro. 2020, 24, 2511–2524.

(17) Kermani, M. B.; Harrop, D. The Impact of Corrosion on Oil and Gas Industry. Spe Production & Facilities 1996, 11, 186–190.
induced diffusion and corresponding fracture behaviour of a structural steel. *Mater. Sci. Technol.-London* **2017**, *33*, 1539−1547.

(61) Banerjee, K.; Chatterjee, U. K. Effect of applied potential on hydrogen embrittlement of weld simulated HSLA-80 steel in seawater. *British corrosion journal* **2000**, *35*, 273−278.

(62) Xu, Y.; Zhang, Q.; Zhou, Q.; Gao, S.; Wang, B.; Wang, X.; Huang, Y. Flow accelerated corrosion and erosion–corrosion behavior of marine carbon steel in natural seawater. *Npj Materials degradation* **2021**, *S*, 1−13.

(63) Yang, Y.; Zhang, T.; Shao, Y.; Meng, G.; Wang, F. New understanding of the effect of hydrostatic pressure on the corrosion of Ni−Cr−Mo−V high strength steel. *Corros. Sci.* **2013**, *73*, 250−261.

(64) Wang, Z. F.; Li, P. H.; Guan, Y.; Chen, Q. F.; Pu, S. K. The corrosion resistance of ultra-low carbon bainitic steel. *Corros. Sci.* **2009**, *51*, 954−961.

(65) Xie, F.; Wang, Y.; Wang, X. F.; Wang, J.; Guo, D. C.; Jiang, J. T.; Zhao, X.; Engineering, S. P.; University, L. S. Effect of dissolved oxygen on corrosion of X70 pipeline steel in Liaohe oilfield. *Surface Technology* **2018**, *3*, 60−64.