Discussion on the Corrosion Mechanism of X65 Steel in NaCl Solution Containing Supercritical CO_2 (Postprint)

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Abstract

The corrosion behavior of X65 pipeline steel in 3.5% NaCl solution containing supercritical CO2 (SC CO2), deionized water, and supercritical CO2 phase containing dissolved NaCl was investigated using a high-temperature high-pressure autoclave. The results show that the presence of Cl- causes a significant increase in the corrosion rate of X65 steel in NaCl solution containing saturated SC CO2, and changes the grain morphology of the corrosion product film. The corrosion rate of X65 steel in the supercritical CO2 phase is far lower than that in NaCl solution, but localized corrosion occurs. The corrosion of X65 steel in NaCl solution containing SC CO2 proceeds in three stages: the first stage is rapid matrix dissolution, during which no FeCO3 forms on the surface; the second stage is the initiation of FeCO3 deposition, where the formed FeCO3 corrosion product film is incomplete, increasing the area for cathodic reduction reactions and leading to accelerated corrosion; the third stage is the protection by the corrosion product film, where the compactness of the formed film gradually increases, providing good protection, but Cl- can still penetrate through the corrosion product film to reach the film/substrate interface, thereby accelerating steel corrosion. A model for supercritical CO2 corrosion of conventional pipeline steel in Cl- containing solution was established.

Full Text

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Abstract

In recent years, the corrosion problem of steels under supercritical CO_2/H_2O systems in oil and gas production has received increasing attention. The temperature and pressure in some deep oil wells in China typically exceed 120 ℃ and 100 MPa, where CO_2 exists in a supercritical state. For easier transportation and cost reduction, oil and gas in pipelines are usually pressurized to high pressures, which typically causes CO_2 to reach supercritical conditions. The supercritical CO_2 corrosion environment includes CO_2-saturated water and H_2O-saturated CO_2 phases. Moreover, corrosive ions such as Cl^- usually exist in CO_2 corrosion environments; however, investigations on the influence of Cl^- on the corrosion of carbon steel in supercritical CO_2-saturated NaCl solution and NaCl solution-saturated supercritical CO_2 have been limited.

The corrosion behaviors and rates of X65 carbon steel exposed in supercritical CO_2-saturated 3.5% NaCl solution, supercritical CO_2-saturated deionized water, and NaCl solution-saturated supercritical CO_2 systems were investigated. SEM, EDS, and XRD were used to analyze the morphology and characteristics of the corrosion product scale on the steel surface. The results show that the addition of Cl^- in supercritical CO_2-saturated water significantly increased the corrosion rate of X65 steel and modified the $FeCO_3$ grain morphology. The average corrosion rate of X65 steel in NaCl solution-saturated supercritical CO_2 was much lower than in supercritical CO_2-saturated NaCl solution, but in the supercritical CO_2 phase, X65 steel suffered serious localized corrosion.

The corrosion process of X65 steel in supercritical CO_2-saturated NaCl solution could be divided into three stages: the first was the active dissolution stage, where the surface of X65 steel was corroded inhomogeneously due to competitive adsorption between Cl^- and H_2CO_3, HCO_3^-, and Fe_3C, as well as some lumpish matrix that remained on the steel surface; the second was the initiation stage of $FeCO_3$ precipitation, where Cl^- postponed the precipitation of $FeCO_3$, the $FeCO_3$ scale formed in this period was incomplete, and increased the area of cathodic reaction, subsequently increasing the corrosion rate; the last was the protective stage of $FeCO_3$ corrosion scale, where the corrosion product scale formed in this period was denser and provided better protectiveness to the X65 steel matrix, however, Cl^- could pass through this scale and reach the scale/matrix interface, resulting in the corrosion rate of X65 steel remaining at a higher value than in deionized water environment. The corrosion model of normal pipelines was developed to better understand the corrosion mechanism in supercritical CO_2-saturated Cl^--containing solution.

Keywords: CO_2 corrosion, supercritical CO_2, X65 steel, Cl^-, corrosion mechanism

1. Introduction

CO_2 corrosion has long been one of the serious problems plaguing the development of the oil and natural gas industry [**?**, **?**]. CO_2 dissolved in H_2O forms H_2CO_3, which is highly corrosive to steel. At the same pH value, H_2CO_3 is more corrosive to steel than HCl and HNO_3. The CO_2 corrosion of carbon steel is an electrochemical reaction process, including the anodic dissolution of Fe and the cathodic reduction of H, with the overall reaction as follows [**?**]:

$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2$

The anodic reaction is the dissolution of Fe: $Fe \rightarrow Fe^{2+} + 2e^-$

The main cathodic reduction reactions are: $2H_2CO_3 + 2e^- \rightarrow 2HCO_3^- + H_2$

Nesic et al. [**?**, **?**] believed that under $pH < 4$ conditions, the cathodic reduction reaction is dominated by H^+ reduction (reaction (3)); under $pH > 4$ conditions, the cathodic reduction reaction is dominated by H_2CO_3 and HCO_3^- reduction (reactions (4) and (5)); while under $pH > 5$ and very low CO_2 partial pressure conditions, the direct reduction of H from H_2O becomes important.

When temperature and pressure exceed the critical temperature (31.1 ℃) and critical pressure (7.38 MPa) of CO_2, CO_2 transforms from gas to supercritical state [**?**]. With the development of deep oil and gas fields and the application of CO_2 injection for enhanced oil/gas recovery (EOR, EGR) technology, the corrosion problem of carbon steel in the presence of supercritical CO_2 (SC CO_2) and H_2O impurities has attracted increasing attention. In fact, in some deep oil wells in China (6000-7000 m), temperature and pressure exceed 120 ℃ and

100 MPa [?], where CO_2 is in a supercritical state and carbon steel faces serious corrosion problems.

During oil and gas transportation, to facilitate transport and save costs, CO_2 is often compressed to certain pressures (typically supercritical state) [?]. Therefore, common pipeline carbon steels such as X65 and X70 also face supercritical CO_2 corrosion problems, and the aqueous solutions containing aggressive ions (especially Cl^-) mixed in oil and gas further promote carbon steel corrosion. During natural gas extraction and transportation, the natural gas/CO_2 mixture contains small amounts of H_2O, and the corrosion environment for carbon steel is the supercritical CO_2 phase dissolved with H_2O; during crude oil extraction and transportation, which contains more H_2O, the corrosion environment at the bottom of carbon steel is the H_2O phase dissolved with supercritical CO_2. Additionally, in carbon capture and storage (CCS) processes, because captured CO_2 inevitably contains H_2O and other impurities, temperature and pressure fluctuations during transportation cause liquid water to form in low-lying pipeline sections, subjecting transport pipelines to supercritical CO_2 two-phase corrosion (H_2O is the main phase in liquid water condensation areas, while supercritical CO_2 is the main phase in other areas) [?].

Choi and Nesic [?] studied the mutual solubility of CO_2 and H_2O, finding that when CO_2 transforms from gas to supercritical state, the solubility of CO_2 in H_2O increases sharply, thereby increasing H_2CO_3, HCO_3^-, and H^+ concentrations in solution. At 8 MPa (supercritical CO_2), the pH value of pure H_2O is 3.14, while at 0.1 MPa (gaseous), the pH value of pure H_2O is 4.05. The lower pH value promotes the cathodic reduction reaction (3), thereby promoting steel corrosion. Strong acidic environments accelerate steel corrosion and are unfavorable for corrosion product film formation. At 8 MPa, the concentration of H_2CO_3 in pure H_2O is 2.68×10^{-3} mol/L, much greater than the H_2CO_3 concentration at 0.1 MPa (0.044×10^{-3} mol/L), leading to increased reaction rates for the cathodic reduction reaction (4). Therefore, under supercritical CO_2 conditions, the concentration of ions participating in cathodic reduction reactions in solution is much higher than under low-pressure CO_2 conditions.

Zhang et al. [?] found that in the early corrosion stage, the corrosion rate of X65 steel in deionized water containing supercritical CO_2 was three times greater than under low pressure (1 MPa). Choi et al. [?, ?] and Cui et al. [?, ?] also found that in supercritical CO_2 environments, steel corrosion rates exceeded 10 mm/a. When there is no H_2O or only small amounts of H_2O in supercritical CO_2 (content less than its solubility in the supercritical CO_2 phase), steel basically does not corrode [?, ?]; however, when the H_2O content in supercritical CO_2 exceeds its solubility in the supercritical CO_2 phase, in addition to H_2O dissolved in the supercritical CO_2 phase, independent liquid water phases exist in the supercritical CO_2/H_2O system, and this independent liquid water phase forms a water film on the steel surface, causing steel corrosion [?].

During high-pressure oil and gas transportation (CO_2 in supercritical state), oil and gas usually contain aqueous solutions dissolved with aggressive ions. When

CO_2 is injected into underground aquifers and other storage sites through CCS technology, groundwater containing NaCl enters the interior of carbon steel pipe walls, forming NaCl solution saturated with supercritical CO_2, which contacts the pipeline and causes supercritical CO_2 corrosion [**?**]. The influence of Cl^- on steel corrosion has always been a non-negligible issue in CO_2 corrosion processes. Liu et al. [**?**] found that the corrosion rate of carbon steel first increases then decreases with increasing Cl^- content, reaching a maximum at 25 g/L Cl^-; the presence of Cl^- destroys the corrosion product film and changes its morphology. Chen et al. [**?**] found that Cl^- affects both anodic and cathodic electrochemical reactions during CO_2 corrosion of steel; Cl^- enriches at the film/matrix interface on carbon steel surfaces, promoting pitting formation. The corrosion product film on steel surfaces has an important influence on the corrosion behavior of the steel matrix; dense corrosion product films reduce steel corrosion rates, while loose and porous corrosion product films promote steel corrosion. Schmitt [**?**] found that at room temperature, Cl^- inhibits CO_2 corrosion by reducing CO_2 solubility in solution. Therefore, studying the influence of Cl^- on steel corrosion behavior in CO_2 corrosion environments can better explore steel corrosion mechanisms and predict steel service life. However, research on the influence of Cl^- on steel corrosion has focused on low-pressure CO_2 conditions, and studies on steel corrosion behavior in supercritical CO_2 environments are still very scarce.

This work uses a high-temperature and high-pressure autoclave to study the corrosion behavior of X65 carbon steel in 3.5% NaCl (mass fraction) solution containing supercritical CO_2, deionized water, and supercritical CO_2 phase dissolved with NaCl solution, providing a basis for interpreting steel corrosion mechanisms under supercritical CO_2 conditions.

2. Experimental

The material selected for the experiments was X65 carbon steel with a chemical composition (mass fraction, %) of: C 0.1, Si 0.31, Mn 1.48, Fe balance. Sample dimensions were 10 mm × 10 mm × 3 mm. Before the experiment, sample surfaces were ground stepwise with SiC waterproof abrasive paper to 800 grit, degreased with acetone, dried with alcohol, weighed with an electronic balance, and then fixed on polytetrafluoroethylene fixtures. Only one 10 mm × 10 mm surface of each sample was exposed to the corrosion medium, while all other surfaces were sealed with 704 silicone rubber. Each experimental group had six parallel samples.

CO_2 corrosion experiments were conducted in a magnetically driven high-temperature and high-pressure autoclave at an experimental temperature of 80 ℃ and pressures of 1.0 and 9.5 MPa, with immersion times of 0.5, 2, 7, 12, 24, 50, 96, and 168 h. The experimental solutions were deionized water and 3.5% NaCl solution. Before the experiment, the solution was deoxygenated

with high-purity CO_2 for 8 h, then quickly poured into the autoclave, samples were installed and sealed, and deoxygenation continued with high-purity CO_2 for 2 h, after which temperature and pressure were increased to the specified experimental values and timing began. All CO_2 corrosion experiments were conducted under static conditions. Exposure experiments under supercritical CO_2 conditions were performed in both the liquid phase saturated with dissolved CO_2 and the supercritical CO_2 phase saturated with dissolved solution.

After the experiments, an Evo18 scanning electron microscope (SEM) was used to observe the surface and cross-sectional micro-morphology of the corrosion product scale on sample surfaces, a Bruker energy dispersive spectrometer (EDS) and D/MAZ-RB X-ray diffraction (XRD) were used to analyze the composition and structure of the corrosion product scale, and an MTS Nano Indenter XP nanoindenter was used to measure the elastic modulus E of the corrosion product scale. After each experimental group, three samples were taken to remove the surface corrosion product scale with a descaling solution, weighed with an electronic balance, and the uniform corrosion rate was calculated using the following formula:

$$v = (8.76 \times 10^4 \times \Delta m) / (S \times \rho \times t)$$

where v is the uniform corrosion rate of steel (mm/a), Δm is the weight loss (g), S is the exposed surface area (cm^2), ρ is the density of steel (g/cm^3), and t is the immersion time (h). SEM was used to observe the surface morphology after scale removal.

2.1 Results and Discussion

2.1.1 Uniform Corrosion Rates of X65 Steel Under Different Conditions The corrosion rates of X65 steel immersed in deionized water [**?**] and 3.5% NaCl solution under supercritical CO_2 (9.5 MPa) and low CO_2 partial pressure (1.0 MPa) conditions for 0.5 and 96 h are shown in Table 1. The corrosion rates of X65 steel immersed in NaCl solution were much greater than those in deionized water, indicating that the presence of Cl^- caused a significant increase in the corrosion rate of steel in supercritical CO_2 environments. When NaCl was present in deionized water, even at 1.0 MPa, the corrosion rate of X65 steel after 0.5 h immersion was much greater than that in deionized water at 9.5 MPa, indicating that the addition of large amounts of Cl^- promoted carbon steel corrosion more than the corrosion acceleration caused by increased CO_2 partial pressure.

Under conditions with Cl^- present, the anodic reaction of bare steel was not the simple reaction process described by equation (2), but followed the anodic reaction mechanism proposed by Ikeda et al. [**?**]:

$$Fe + Cl^- + H^+ \quad [FeCl] \, d + H \, d$$

[FeCl] d + H_2O → FeClOH + H^+ + e^-
FeClOH → $FeOH^+$ + Cl^- + e^-
$FeOH^+$ + H^+ Fe^{2+} + H_2O

Cl^- competes with H_2CO_3 and $HCO_3{}^-$ for adsorption, and large amounts of Cl^- preferentially adsorb on the steel matrix surface, catalyzing the anodic active dissolution of steel through reactions (7)-(9), thereby accelerating corrosion. Additionally, the presence of Cl^- also affects the cathodic reduction reaction: on one hand, because excess Cl^- occupies the steel surface, reducing the area for H_2CO_3 and $HCO_3{}^-$ to participate in reduction reactions, the cathodic reduction reaction rate decreases; on the other hand, the addition of Cl^- increases the ionic strength of the solution, reducing CO_2 solubility in water [**?**, **?**], thereby decreasing the concentrations of H_2CO_3, $HCO_3{}^-$, and H^+ in solution, inhibiting the cathodic reduction reaction and reducing the corrosion rate. However, comparing the corrosion rates of steel in deionized water and NaCl solution after 0.5 h immersion under either 1.0 or 9.5 MPa conditions shows that the catalytic effect of Cl^- on anodic active dissolution far exceeds its inhibiting effect on cathodic reduction reactions. Therefore, with the addition of Cl^-, the corrosion rate of X65 steel increased significantly.

The corrosion rate patterns of X65 steel after 96 h immersion under different pressures and in different solutions were similar to those after 0.5 h immersion, but the corrosion rates were lower than after 0.5 h immersion, which is related to the formation of protective corrosion product scales on the sample surfaces.

2.1.2 Corrosion Product Morphology of X65 Steel in Deionized Water The microstructure of X65 steel is shown in [Figure 1: see original paper], consisting mainly of polygonal ferrite and a small amount of granular bainite. The surface morphologies of X65 steel after 0.5 h immersion in deionized water under 1.0 and 9.5 MPa pressures [**?**] and the surface and cross-sectional micro-morphology of the corrosion product scale formed after 96 h immersion in deionized water under 1.0 MPa pressure are shown in [Figure 2: see original paper].

As can be seen from Figures 2a and 2b, after 0.5 h immersion under two different pressures, the sample surfaces were smooth with clear scratches, and under 9.5 MPa conditions, slight corrosion traces could be observed on the matrix surface. After 96 h immersion, the sample surfaces under both pressure conditions were covered with a layer of regularly shaped polyhedral granular corrosion product $FeCO_3$. The surface corrosion product scale formed under low pressure had higher density than that formed under supercritical CO_2. From the cross-sectional morphology of the corrosion product scale (Figure 2c), it can be seen that under low-pressure CO_2 conditions, the $FeCO_3$ corrosion product scale consisted of a double layer; while under supercritical CO_2 conditions, the corrosion product scale had indistinct layering and poor density [**?**]. This is mainly related to the $FeCO_3$ deposition rate and the pH value of the solution.

At pH < 4, H^+ reduction is the main cathodic reduction reaction, and the pH value directly affects the corrosion rate of carbon steel. However, the more important role of pH value is its indirect effect on the formation conditions of $FeCO_3$ corrosion product scale. Dugstad' s research [**?**] showed that with increasing pressure and decreasing pH value, the concentration of Fe^{2+} required to reach $FeCO_3$ saturation increases. Tanupabrungsun et al. [**?**] found that at 80 ℃ and pH = 4, no $FeCO_3$ formed on carbon steel surfaces, while at pH = 6, a relatively dense $FeCO_3$ corrosion product scale formed on carbon steel surfaces. This is because $FeCO_3$ solubility is high in low pH solutions, ultimately leading to reduced $FeCO_3$ deposition rates; meanwhile, $FeCO_3$ is unstable under low pH conditions and easily decomposes according to the following reaction:

$$FeCO_3 + H^+ \quad Fe^{2+} + HCO_3{}^-$$

Therefore, in deionized water saturated with SC CO_2, due to its lower pH value compared to low pressure, the $FeCO_3$ deposition rate is low, resulting in the formation of less dense corrosion product scales on carbon steel surfaces.

2.1.3 Corrosion Product Scale Morphology of X65 Steel in 3.5% NaCl Solution The surface and cross-sectional morphologies of X65 steel after immersion in NaCl solution under 9.5 and 1.0 MPa conditions for 0.5 and 96 h are shown in [Figure 3: see original paper]. XRD results ([Figure 4: see original paper]) indicate that the corrosion products formed after 96 h immersion were all $FeCO_3$. After 0.5 h corrosion, both pressure conditions showed different degrees of corrosion on X65 steel surfaces, more severe than in deionized water. From the cross-sectional morphology, the matrix surface after corrosion under 9.5 MPa was more uneven, which may be related to competitive adsorption between Cl^- and H_2CO_3, $HCO_3{}^-$. Under 1.0 MPa conditions, because fewer particles (H_2CO_3, $HCO_3{}^-$, and H^+) participate in cathodic reduction reactions in the solution, the matrix surface was mainly covered by Cl^- adsorption, resulting in relatively uniform corrosion. Under 9.5 MPa conditions, the number of particles participating in cathodic reduction reactions in the solution increased significantly, leading to more intense competitive adsorption with Cl^-, reducing the adsorption area of Cl^- on the steel surface and increasing its concentration in adsorbed areas, thereby accelerating local active dissolution and causing increased non-uniformity of matrix surface corrosion.

After 96 h corrosion, compared with the corrosion product scale formed in deionized water, the $FeCO_3$ grains formed in NaCl solution were larger, irregularly shaped, but more tightly packed. As shown in Figure 3h, the corrosion product scale formed in 9.5 MPa NaCl solution was an obvious double-layer scale: the outer layer was pure $FeCO_3$ scale; the inner layer morphology differed from that formed in NaCl solution under low pressure and in deionized water, with blocky materials the same color as the matrix interspersed within the dense $FeCO_3$ scale. Comparing EDS analysis results of the blocky materials with the X65 steel matrix revealed that both had identical elemental compositions and contents (mass fraction) (blocky materials: Fe 88.45%, C 8.64%, Mn 2.91%; matrix:

Fe 88.55%, C 8.62%, Mn 2.83%), indicating these blocky materials were matrix spalled after local dissolution of X65 steel. In the early stage of supercritical CO_2 corrosion, because areas of the matrix with adsorbed Cl^- corroded faster, undissolved Fe_3C and areas of the matrix with slower corrosion (covered by H_2CO_3, HCO_3^-, and H^+) spalled off. $FeCO_3$ easily nucleated and grew on the spalled blocky materials, gradually encapsulating the spalled portions, reducing their dissolution rate, and ultimately preserving them in the inner product scale.

Comparing the morphologies of corrosion product scales formed in deionized water and NaCl solution under supercritical conditions shows that the corrosion product scale formed in NaCl solution was denser, which is closely related to the effect of Cl^- on $FeCO_3$ deposition rate. The $FeCO_3$ deposition process includes nucleation and growth. Generally [**?**], grain nucleation and growth are related to the relative supersaturation s of $FeCO_3$: the nucleation rate of grains has an exponential relationship with relative supersaturation; the growth rate of grains has a linear relationship with relative supersaturation. Therefore, at lower supersaturation, $FeCO_3$ growth is controlled by growth; at high supersaturation, $FeCO_3$ growth is controlled by nucleation. In the early stage of CO_2 corrosion, due to the low supersaturation of $FeCO_3$, the deposition rate of $FeCO_3$ corrosion product scale on carbon steel surfaces is often controlled by the grain growth rate [**?**].

The supersaturation S and relative supersaturation s of $FeCO_3$ are calculated as follows:

$$S = [Fe^{2+}][CO_3{}^{2-}] \,/\, Ksp$$
$$s = S - 1$$

where Q is the instantaneous concentration of $FeCO_3$ in solution, Qeq is the equilibrium solubility of $FeCO_3$ in solution, Ksp is the solubility product constant of $FeCO_3$, which is related to solution temperature and ionic strength [**?**]:

$$\log Ksp = -59.3 - 0.041T + 24.6\log T + 2.5I^{0 \cdot 5} - 2.2I$$

where T is thermodynamic temperature (K), and I is ionic strength (mol/L).

Different scholars have proposed different formulas for calculating $FeCO_3$ deposition rate [**?**, **?**]:

$$Rprec = A \times \exp(54.8 - 123000/RT) \times (S - 1)$$
$$Rprec = A \times \exp(52.4 - 119800/RT) \times (S - 1)^2$$

where Rprec is the $FeCO_3$ deposition rate ($kmol/(m^2 \cdot s)$), A is the surface area available for $FeCO_3$ deposition per unit volume (m^{-1}), and R is the ideal gas constant ($J/(mol \cdot K)$).

At 80 ℃, Rprec is jointly affected by S and I, increasing with increasing S and I. Cl^- increases the ionic strength of the solution (3.5% NaCl: I = 0.6 mol/L; deionized water: I = 0.0006 mol/L), thereby increasing Ksp. However, Cl^- has a greater effect on S. As can be seen from Table 1, in the early corrosion

stage, the corrosion rate of X65 steel in NaCl solution was three times that in deionized water, which led to large amounts of Fe^{2+} being released into the solution. To maintain electrical neutrality in the solution, more $CO_3{}^{2-}$ was generated. Therefore, the supersaturation of $FeCO_3$ in NaCl solution was much greater than in deionized water. These two reasons increased the deposition rate of $FeCO_3$ in NaCl solution, promoting the formation of dense corrosion product scales.

Because the presence of Cl^- increased the ionic strength of the solution, reducing CO_2 solubility in the solution, the pH value of the solution increased, and the increase in Fe^{2+} also increased the solution pH value [**?**]. Therefore, the increased $FeCO_3$ deposition rate on the solution surface made the outer layer of the corrosion product scale formed in NaCl solution dense with large grain size.

XRD analysis ([Figure 4: see original paper]) shows that the corrosion products formed under different conditions were all $FeCO_3$. Additionally, matrix diffraction peaks can be observed in the XRD spectra, which is related to the thickness of the corrosion product scale.

Furthermore, $FeCO_3$ corrosion product scale has anion-selective permeability [**?**], and Cl^- easily passes through the corrosion product scale to the scale/matrix interface and enriches there (EDS analysis after 96 h immersion showed Cl content of about 10% (mass fraction) at the scale/matrix interface), promoting matrix corrosion to produce more Fe^{2+}. Under the concentration gradient, Fe^{2+} diffuses into the solution and combines with $CO_3{}^{2-}$ in the micro-channels of the $FeCO_3$ corrosion product scale to form $FeCO_3$, making the $FeCO_3$ corrosion product scale denser.

2.2 Corrosion Behavior of X65 Steel in Supercritical CO_2 Phase and Liquid Solution

The uniform corrosion rate of X65 steel placed in the H_2O-containing supercritical CO_2 phase for 96 h (0.8 mm/a) was only about 1/15 of that in the liquid solution (14 mm/a), but it still demonstrated that X65 steel did corrode in the water-containing SC CO_2 phase. [Figure 5: see original paper] shows the surface and cross-sectional morphologies of the corrosion product scale formed on X65 steel after 96 h immersion in the H_2O-containing supercritical CO_2 phase. As can be seen from Figure 5a, the basic surface was covered with a dense crystalline corrosion product. The XRD spectrum ([Figure 4: see original paper]) indicates this corrosion product was $FeCO_3$. Additionally, matrix diffraction peaks can be observed in the XRD spectrum, which is related to the thickness of the corrosion product scale.

In fact, due to temperature or pressure fluctuations, even when no separate liquid water exists in the H_2O-containing supercritical CO_2 phase, water can condense and precipitate out in the SC CO_2 phase [**?**]. Once precipitated H_2O

condenses and adheres to the steel matrix surface, it immediately forms a water-rich film saturated with SC CO_2, causing matrix corrosion. However, due to the small volume of the water-rich film, $FeCO_3$ easily reaches saturation and nucleates and grows on the matrix surface, forming a relatively dense corrosion product scale (Figure 5a). However, from the cross-sectional morphology (Figure 5b), it can be seen that the corrosion product scale was not uniform, and corrosive solution could permeate through thin or loose areas of the corrosion product scale to the scale/matrix interface, further corroding the matrix and causing localized corrosion. From the surface morphology after scale removal of samples immersed in the SC CO_2 phase ([Figure 6: see original paper]a), localized corrosion pits can be clearly observed; while the surface morphology after scale removal of samples immersed in NaCl solution, although non-uniform, still exhibited uniform corrosion characteristics, as shown in Figure 6b.

2.3 Corrosion Mechanism of X65 Steel in Cl^--Containing Solution

The surface morphologies of X65 steel samples after immersion in NaCl aqueous solution saturated with SC CO_2 for different times are shown in Figures 3c and g and [Figure 7: see original paper]. It can be seen that after 0.5 h immersion, most areas of the matrix surface showed obvious unevenness, with a small portion of the surface being relatively smooth (Figure 3c). After 12 h immersion, no $FeCO_3$ had formed on the matrix surface, but a layer of corrosion product covered the surface (Figure 7a). From Figure 7b, it can be seen that after 24 h immersion, large amounts of $FeCO_3$ grains formed on the matrix surface, and the corrosion product scale formed at this time was incomplete with many pores and defects. Previous research [**?**] showed that $FeCO_3$ began to deposit after 7 h immersion in deionized water, earlier than the deposition start time of $FeCO_3$ on X65 steel surface immersed in NaCl solution, possibly because Cl^- adsorption on the matrix surface reduced the nucleation sites for $FeCO_3$, delaying $FeCO_3$ deposition. Starting from 24 h immersion, the density and integrity of the $FeCO_3$ corrosion product scale increased rapidly with immersion time.

Figures 3d and h and [Figure 8: see original paper] show the cross-sectional morphologies of corrosion product scales formed on X65 steel after immersion in NaCl aqueous solution saturated with SC CO_2 for different times. It can be seen that after 12 h immersion (Figure 8a), although no $FeCO_3$ corrosion product scale had formed on the X65 steel surface, there was a loose corrosion product layer composed of blocky materials with colors similar to the matrix. Combined with XRD spectrum analysis ([Figure 9: see original paper]), this corrosion product layer was determined to be Fe_3C and spalled undissolved matrix. From the cross-sectional morphology of the corrosion product scale formed after 24 h immersion (Figure 8b), it can be seen that $FeCO_3$ particles did not form a complete corrosion product scale, leaving large amounts of matrix directly exposed to the solution. This type of corrosion product scale not only lacked protectiveness but also increased the cathodic area, leading to increased

corrosion rates. Additionally, $FeCO_3$ did not form at the interface adjacent to the matrix but formed in the loose corrosion layer containing Fe_3C and spalled matrix materials, as shown in Figure 8c. This indicates that on one hand, $FeCO_3$ grains easily nucleate and grow in Fe_3C and spalled matrix areas, and on the other hand, proves that Cl^- adsorption on the matrix surface makes $FeCO_3$ nucleation on the matrix surface difficult. Dugstad' s research [**?**] showed that only when $FeCO_3$ nucleates and grows at the matrix interface to form a dense corrosion product scale can it provide good protectiveness to the matrix, and when the adhesion between the corrosion product scale and matrix is poor, the protectiveness is also poor. Subsequently, with increasing immersion time, the density and protectiveness of the corrosion product scale increased, while the undissolved matrix inside the corrosion product scale gradually dissolved.

Ramachandran et al.' s calculations [**?**] showed that the elastic modulus E of $FeCO_3$ corrosion product scale decreases with increasing porosity in the scale, meaning the elastic modulus can reflect the density of the corrosion product scale. From the relationship between E and immersion time shown in [Figure 10: see original paper], it can be seen that E gradually increased with immersion time, indicating that the porosity of the corrosion product scale decreased with immersion time, the scale became denser, and its protectiveness improved.

[Figure 11: see original paper] shows the EDS analysis of Cl^- distribution areas at the scale/matrix interface and the corresponding relationship between Cl^- content and immersion time after X65 steel was immersed in NaCl solution saturated with SC CO_2 for 50, 96, and 168 h. It can be seen that Cl^- gradually accumulated at the scale/matrix interface with increasing immersion time. These accumulated Cl^- at the scale/matrix interface kept the corrosion rate of X65 steel at a relatively high level. Although there were tiny localized corrosion pits in Cl^- accumulation areas, they were not the deepest corrosion areas of the matrix, meaning that Cl^- enrichment at the scale/matrix interface did not cause obvious pitting or localized corrosion, and the matrix still exhibited overall uniform corrosion.

[Figure 12: see original paper]a shows the relationship between the roughness measured on the X65 steel matrix surface after scale removal and immersion time (roughness can indicate the corrosion state of the matrix surface). It can be seen that before $FeCO_3$ corrosion product scale formation (before 12 h), the roughness gradually increased with immersion time, increasing the non-uniformity of the matrix surface morphology. The roughness decreased somewhat after 24 h immersion, then increased rapidly with immersion time. As can also be seen intuitively from Figure 12b, before $FeCO_3$ corrosion product scale formation, the matrix surface was relatively smooth; once $FeCO_3$ corrosion product scale began to cover the matrix surface, corrosion non-uniformity increased significantly, with the maximum height difference on the matrix surface after scale removal reaching 45 μm. This is because before $FeCO_3$ formation, the matrix was in a rapid dissolution stage with relatively uniform corrosion; at 24 h immersion, the formation of non-protective $FeCO_3$ grains significantly increased

the cathodic reduction reaction area of X65 steel, intensifying local corrosion of the matrix and thereby increasing the non-uniformity of the matrix surface.

[Figure 13: see original paper] shows the relationship between corrosion rate and immersion time for X65 steel in NaCl solution and deionized water [**?**] saturated with SC CO_2. It can be seen that the corrosion rate of X65 steel in NaCl solution was much greater than in deionized water. Based on the analysis of corrosion product scale surface and cross-sectional morphologies, combined with the corrosion rate variation trend, the corrosion process of X65 steel in NaCl solution saturated with SC CO_2 was divided into three stages, with the corrosion mechanism shown in [Figure 14: see original paper].

Stage I (0-12 h): Fast dissolution stage. No $FeCO_3$ film formed, most areas of the matrix surface were covered by Cl^-, the matrix dissolution rate was fast, and the corrosion rate of X65 steel was relatively high. Competitive adsorption between Cl^- and H_2CO_3, HCO_3^- made matrix surface corrosion non-uniform, causing Fe_3C and some undissolved matrix to remain on the steel surface, forming a residual product layer. The corrosion rate in this stage decreased rapidly with immersion time.

Stage II (12-24 h): $FeCO_3$ crystal deposition initiation stage. Due to Cl^- adsorption on the scale/matrix surface delaying $FeCO_3$ nucleation on the matrix surface, while Fe_3C and blocky matrix residues provided numerous nucleation sites for $FeCO_3$, $FeCO_3$ began to deposit and precipitate in the residual corrosion product layer, forming an incomplete, non-protective $FeCO_3$ corrosion product scale. This scale increased the cathodic reduction reaction area, thereby accelerating matrix corrosion, so the corrosion rate increased in this stage.

Stage III (24-168 h): Corrosion product scale protection stage. The corrosion product scale completely covered the matrix surface, and with increasing immersion time, its density and protectiveness increased, causing the corrosion rate to rapidly decrease to a relatively low level. However, due to the anion-selective permeability of the $FeCO_3$ scale, Cl^- could still pass through the $FeCO_3$ scale to the scale/matrix interface, promoting matrix corrosion, so the corrosion rate of X65 steel in NaCl solution remained much higher than in deionized water solution.

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3. Conclusions

1. In the water-saturated SC CO_2 phase, the corrosion rate of X65 steel was 0.8 mm/a, much lower than its corrosion rate in NaCl aqueous solution containing SC CO_2, but localized corrosion occurred.
2. The presence of Cl^- significantly increased the corrosion rate of X65 steel in SC CO_2 environments, changing the shape of $FeCO_3$ particles and the composition of the corrosion product scale.

3. The corrosion process of X65 steel in NaCl solution containing SC CO_2 could be divided into three stages: in the first stage, no $FeCO_3$ scale formed and the matrix was in a rapid dissolution stage, with competitive adsorption between Cl^- and H_2CO_3, HCO_3^- making matrix surface corrosion non-uniform; in the second stage, $FeCO_3$ began to deposit, with the initially formed $FeCO_3$ scale being incomplete and poorly adherent to the matrix and non-protective; in the third stage, the $FeCO_3$ corrosion product scale completely covered the matrix surface, with significantly increased protectiveness to the matrix, but Cl^- could still pass through the $FeCO_3$ scale to the scale/matrix interface, resulting in the corrosion rate of X65 steel in NaCl solution being much higher than in deionized water.

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Note: Figure translations are in progress. See original paper for figures.