Corrosion Law of Metal Pipeline in Tahe Oilfield and Application of New Materials

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Abstract: Frequent corrosion perforation of metal pipes severely restricts oil and gas fields’ safety production and increases maintenance costs. Therefore, it is imminent to change the characteristics of metal materials fundamentally. In this paper, taking the metal pipe of Northwest Oil and Gas Field in China as an example, for the corrosion environment with high concentrations of H2S, CO2, H2O, Cl−, and O2, the main factors leading to corrosion are analyzed, the corrosion rules and optical materials of the pipe under different environmental and operating conditions are figured out, and the corrosion resistance of new pipes materials is evaluated. The main conclusions are as follows: (1) In the environment of the CO2−H2O−Cl− strong scouring system, electrochemical corrosion dominates, and the corrosion morphology is mainly groove-like corrosion and ulcer-like corrosion; (2) The H2S content affects the incubation period and development period of pipe corrosion; (3) Through the two optimization directions of 20# steel refining and material alloying, BX245-1Cr pipe material has been developed. At present, the application of this pipe material has relatively better results.

Keywords: pipe material; oil and gas field; corrosion resistance; corrosion environment; uniform corrosion; pitting corrosion

1. Introduction

The frequent perforation of metal pipes severely restricts the safe production of oil and gas fields and increases maintenance costs. The leakage of oil and gas causes many energy losses and more serious environmental pollution, which limits the maximization of the benefit of oil and gas field development [1–5]. In the Northwest Oil and Gas Field, with the addition of dissolved oxygen in the CO2−H2O−Cl− coexisting corrosion environment, the original harsh corrosion environment system is more complicated, and the loss caused by corrosion increases year by year [6]. In 2015, 428 corrosion perforations occurred in the pipes of Tahe Oilfield (subordinate units of the Northwest Oil and Gas Field), representing an increase of 174% over 2014 and accounting for 69.8% of the total four-year perforation; the typical corrosion morphology of the pipe is shown in Figure 1. Therefore, it is necessary to study the corrosion mechanism of the pipe in this kind of corrosion environment and to develop a new anti-corrosion pipe material.

In 1955, Walter F. Rogers and A. Rowe Jr. studied the electrochemical corrosion experiment in oil field brines with CO2 or H2S, and they proposed the corrosion theory of sulfide [7]. In 2001, Bijan Kermani et al., studied a new type of material resistant to CO2 corrosion and analyzed the effect of different elements in the alloy on corrosion [8]. In 2006, Bijan Kermani et al., introduced the application of low-carbon 3% Cr steel, compared with the corrosion resistance of traditional carbon steel, which shows that low-carbon 3% Cr steel is an economical choice for well completions [9]. In 2007, Liu Hexia et al., analyzed
the corrosion behavior of 16Mn, X60, 20#, and X70 steel in CO$_2$-saturated brine solution. The analysis results show that the uniform corrosion rates of 16Mn, X60, and 20# steel are lower. Although X70 steel has a higher uniform corrosion rate at the beginning of the experiment, the pitting phenomenon is reduced. With the increase of the corrosion time, the uniform corrosion rate of X70 steel is decreasing [10]. In 2013, Ding Jinhu et al., investigated the effect of H$_2$S and Cl$^-$ on the pitting and stress corrosion cracking (SCC) of stainless steels. The results indicated that higher H$_2$S-CO$_2$ pressure could accelerate the anodic dissolution process, deteriorate the passivation film, and increase the sensitivity of SCC [11]. In 2014, Li Dapeng et al., studied the effect of H$_2$S concentration on the corrosion behavior of pipeline steel under the coexistence of H$_2$S and CO$_2$. They obtained that under the H$_2$S and CO$_2$ coexistence environment, the corrosion process of steel, the morphological structure, and the stability of the corrosion product film are related to the concentration of H$_2$S [12,13]. In 2010, Zhou Jianlong et al., explored the electrochemical behavior and corrosion behavior of X80 pipeline steel in NaHCO$_3$ solution. The corrosion products and corrosion mechanism were deeply understood and analyzed in detail [14]. In 2007, Xia Xiangming studied the stress corrosion of 20# steel in saturated H$_2$S solution and the preventive measures, which indicated that there is a high sensitivity to stress corrosion when 20# steel is soaked in saturated aqueous H$_2$S solution; however, when it is subjected to a certain degree of anodic or cathodic polarization, it can correspondingly reduce its stress corrosion cracking sensitivity, and relative to the cathodic polarization, the effect of anodic polarization is more pronounced [15]. In 2010, Lu Jinzhu et al., studied the corrosion behavior of 20G steel in a high Cl$^-$ concentration and glycol. The results show that in the formation of 20G thin film in ethylene glycol solution, its main composition is Fe$_3$O$_5$; in the occluded area, when the current density dissolved in the pores is greater than the dissolved product, the corrosion resistance of 20G steel began to increase gradually [16].

![Figure 1. The typical corrosion morphology of the pipes in Tahe Oilfield.](image)

This study analyzed the main factors leading to metal pipe corrosion in Northwest Oil and Gas Field, where the corrosion environment H$_2$S, CO$_2$, H$_2$O, Cl$^-$, and O$_2$ are highly concentrated. The corrosion rules and optical pipe material of different environmental and operating conditions were figured out. The corrosion resistance of new pipe materials was evaluated.

2. Analysis of Main Corrosion Factors

According to the partial pressure ratio of H$_2$S and CO$_2$, when $P_{CO_2}/P_{H_2S} > 500$, the main factor of pipe corrosion is CO$_2$; when $20 < P_{CO_2}/P_{H_2S} < 500$, the main factors of pipe corrosion are CO$_2$ and H$_2$S; when $P_{CO_2}/P_{H_2S} < 20$, the main factor of corrosion is H$_2$S [17]. Laboratory experiments (Corrosion coupons experiment) were carried out by the single-factor analysis method to determine the effect of different factors on the corrosion of 20# steel pipe. The equipment required are a high-temperature and high-pressure reactor, FEI Quanta 250 scanning electron microscope (SEM, FEI Company, Hillsboro, OR, USA), and laser scanning confocal microscope. The working pressure and temperature of the pipe in the field are 1.6 MPa and 70 °C, respectively, and the medium’s velocity in the pipe is 1.0 m/s.
2.1. Experimental Conditions

In order to make the experimental results more practical, it is necessary to investigate
the corrosion conditions of the field and the working conditions of the pipeline before de-
termining the experimental conditions. The corrosive medium’s content and the formation
water’s composition are shown in Tables 1 and 2, respectively.

Table 1. The content of the corrosion medium in the field.

| Medium | Minimum Value | Maximum Value | Average Value |
|--------|---------------|---------------|---------------|
| H₂S    | 2.4 mg/m³     | 170,571 mg/m³ | 38,962 mg/m³  |
| CO₂    | 4.88%         | 27.2%         | 8.07%         |
| Cl⁻    | 60,929 mg/L   | 150,325 mg/L  | 113,316 mg/L  |

Table 2. Composition of the formation water.

| Cl⁻ (mg/L) | SO₄²⁻ (mg/L) | Ca²⁺ (mg/L) | Mg²⁺ (mg/L) | HCO₃⁻ (mg/L) | Total Mineralization | PH Value |
|------------|--------------|-------------|-------------|--------------|----------------------|----------|
| 113,316    | 302.7        | 16,460.3    | 955.4       | 620.4        | 189,287              | 6.0      |

Experimental conditions 1: In the H₂S corrosion environment, by changing the CO₂
concentration, the effect of CO₂ on the material of 20# steel was analyzed. The experimental
parameters are shown in Table 3.

Table 3. Experimental conditions 1.

| Partial Pressure of CO₂ (MPa) | Partial Pressure of H₂S (MPa) | P_CO₂/P_H₂S | Concentration of Cl⁻ (mg/L) | Temperature (°C) | Total Pressure (MPa) | Test Cycle (days) |
|-------------------------------|-------------------------------|-------------|-----------------------------|------------------|----------------------|-------------------|
| 0.01                          | 0.25                          | 0.04        | 3.75                        | 110,000          | 1.6                  | 30                |
| 0.15                          | 0.04                          | 0.04        | 3.75                        | 110,000          | 1.6                  | 30                |
| 0.45                          | 0.04                          | 0.04        | 3.75                        | 110,000          | 1.6                  | 30                |

Experimental conditions 2: In the H₂S-CO₂ corrosion environment, by changing the
H₂S concentration, the effect of H₂S on the material of 20# steel was analyzed. The experimental
parameters are shown in Table 4.

Table 4. Experimental conditions 2.

| Partial Pressure of CO₂ (MPa) | Partial Pressure of H₂S (MPa) | P_CO₂/P_H₂S | Concentration of Cl⁻ (mg/L) | Temperature (°C) | Total Pressure (MPa) | Test Cycle (days) |
|-------------------------------|-------------------------------|-------------|-----------------------------|------------------|----------------------|-------------------|
| 0.15                          | 0.003                         | 0.003       | 50                          | 110,000          | 1.6                  | 30                |
|                               | 0.0008                        | 0.0008      | 200                         | 110,000          | 1.6                  | 30                |
|                               | 0.0003                        | 0.0003      | 450                         | 110,000          | 1.6                  | 30                |

Experimental conditions 3: In the H₂S-CO₂ corrosion environment, by changing the Cl⁻
concentration, the effect of Cl⁻ on the material of 20# steel was analyzed. The experimental
parameters are shown in Table 5.

Table 5. Experimental conditions 3.

| Partial Pressure of CO₂ (MPa) | Partial Pressure of H₂S (MPa) | P_CO₂/P_H₂S | Concentration of Cl⁻ (mg/L) | Temperature (°C) | Total Pressure (MPa) | Test Cycle (days) |
|-------------------------------|-------------------------------|-------------|-----------------------------|------------------|----------------------|-------------------|
| 0.15                          | 0.04                          | 0.04        | 3.75                        | 110,000          | 1.6                  | 30                |
|                               | 0.04                          | 0.04        | 3.75                        | 150,000          | 1.6                  | 30                |
2.2. Experimental Results

According to NACE RP0075 [18], the grade of corrosion, as shown in Table 6, can be used to evaluate the experimental results.

Table 6. Corrosion grade for the oil production system.

| Grade   | Uniform Corrosion Rate (mm/year) | Maximum Pitting Rate (mm/year) |
|---------|----------------------------------|--------------------------------|
| Low     | <0.025                           | <0.13                          |
| Moderate| 0.025–0.12                       | 0.13–0.20                      |
| High    | 0.13–0.25                        | 0.21–0.38                      |
| Severe  | >0.25                            | >0.38                          |

2.2.1. The Effect of CO₂ on the Material of 20# Steel

Maintaining the partial pressure of H₂S unchanged, the effects of the partial pressure of CO₂ on the uniform corrosion and pitting were investigated. The experimental results are shown in Table 7.

Table 7. Experimental results of the experimental conditions 1.

| Partial Pressure of CO₂ (MPa) | Partial Pressure of H₂S (MPa) | Uniform Corrosion Rate | Pitting Rate |
|--------------------------------|-------------------------------|------------------------|--------------|
| 0.01                           | 0.04                          | 0.4605 Severe          | 0.6765 Severe |
| 0.15                           | 0.04                          | 0.6572 Severe          | 0.8835 Severe |
| 0.45                           | 0.04                          | 0.8913 Severe          | 1.2435 Severe |

It can be seen from Table 5 that with the increase of the partial pressure of CO₂, the uniform corrosion rate and pitting rate increase. There are two reasons for this: with the increase of the partial pressure of CO₂, the concentration of CO₂ dissolved in the solution increases and the corrosivity increases. When the CO₂ concentration is increased, the corrosion products on the material’s surface will change, resulting in the corresponding changes of its protective properties.

Scanning electron microscope (SEM) was used to study the microsurface morphology of the specimen. As shown in Figure 2, there are apparent pits on the surfaces of the specimens, and the pit becomes larger with the increase of the partial pressure of CO₂. According to the observation of the 3-D morphology of the pits by laser scanning confocal microscope, with the increase of the partial pressure of CO₂, the opening size of the pit on the surface of the specimen shows little change, but the depth is increased. In summary, the content of CO₂ has a high degree of influence on the corrosion form of 20# steel.

2.2.2. The Effect of H₂S on the Material of 20# Steel

Maintaining the partial pressure of CO₂ unchanged, the effects of the partial pressure of H₂S on the uniform corrosion and pitting were investigated. The experimental results are shown in Table 8.

It can be seen from Table 8 that with the increase of the partial pressure of H₂S, the uniform corrosion rate and pitting rate increase, but the increases are not noticeable and far less than the corrosion of CO₂ on the 20# steel.

The scanning electron micrographs are shown in Figure 3. It can be seen from Figure 3 that in the H₂S/CO₂ coexistence environment, with the rapid increase of the H₂S concentration, the opening size of the corrosion pit gradually becomes larger. Results of laser scanning confocal microscope also indicated that the pitting depth is gradually deepened with the increase of the concentration of H₂S. In conclusion, the content of H₂S has a specific influence on the corrosion morphology and corrosion tendency of 20# steel.
2.2. Experimental Results

According to NACE RP0075 [18], the grade of corrosion, as shown in Table 6, can be maintained at the partial pressure of CO$_2$.

![Figure 2. Scanning electron micrographs of pits (×25 times) (a) $P_{CO_2} = 0.01$ MPa; (b) $P_{CO_2} = 0.15$ MPa; (c) $P_{CO_2} = 0.45$ MPa.](image)

Table 8. Experimental results of experimental conditions 2.

| Partial Pressure of CO$_2$ (MPa) | Partial Pressure of H$_2$S (MPa) | Uniform Corrosion Rate | Pitting Rate |
|----------------------------------|---------------------------------|------------------------|--------------|
|                                  |                                 | Value (mm/year)        | Grade of Corrosion | Value (mm/year) | Grade of Corrosion |
| 0.15                             | 0.0003                          | 0.5984                 | Severe         | 0.7166            | Severe              |
| 0.15                             | 0.008                           | 0.6105                 | Severe         | 0.7324            | Severe              |
| 0.15                             | 0.003                           | 0.6235                 | Severe         | 0.8877            | Severe              |

![Figure 3. Scanning electron micrographs of pits (×25 times) (a) $P_{H_2S} = 0.0003$ MPa; (b) $P_{H_2S} = 0.0008$ MPa; (c) $P_{H_2S} = 0.003$ MPa.](image)

2.2.3. The Effect of Cl$^-$ on the Material of 20# Steel

Maintaining the partial pressure of CO$_2$ and H$_2$S unchanged, the effects of the concentration of Cl$^-$ on the uniform corrosion and pitting were investigated. The experimental results are shown in Table 9.

Table 9. Experimental results of experimental conditions 3.

| Partial Pressure of CO$_2$ (MPa) | Partial Pressure of H$_2$S (MPa) | Content of Cl$^-$ (mg/L) | Uniform Corrosion Rate | Pitting Rate |
|----------------------------------|---------------------------------|--------------------------|------------------------|--------------|
|                                  |                                 |                          | Value (mm/year)        | Grade of Corrosion | Value (mm/year) | Grade of Corrosion |
| 0.15                             | 0.04                            | 60,000                   | 0.6438                 | Severe         | 0.7585            | Severe              |
|                                  |                                 | 110,000                  | 0.6572                 | Severe         | 0.8835            | Severe              |
|                                  |                                 | 150,000                  | 0.6760                 | Severe         | 1.0081            | Severe              |

It can be seen from Table 9 that with the increase of the content of Cl$^-$, the uniform corrosion rate and pitting rate increase. Among them, the increase of the uniform corrosion rate is not apparent, and the pitting rate increases.

The scanning electron micrographs are shown in Figure 4. It can be seen from Figure 4 that in the H$_2$S/CO$_2$ coexistence environment, the corrosion product films are loose and...
flaky. The corrosion pit can be seen in three kinds of solutions with different Cl\(^-\) concentrations. Obviously, the change of the Cl\(^-\) concentration does not change the microstructure of the corrosion products on the surface of the sample, indicating that the Cl\(^-\) content has little influence on the surface film. Results of laser scanning confocal microscope suggested that the depth of pitting deepens with the increase of the Cl\(^-\) concentration. Based on the above, the concentration of Cl\(^-\) has little effect on the surface film and the uniform corrosion rate and greatly influences the local corrosion rate.

![Figure 4. Scanning electron micrographs of pits ($\times$25 times): (a) Cl\(^-\) = 60,000 mg/L; (b) Cl\(^-\) = 110,000 mg/L; (c) Cl\(^-\) = 150,000 mg/L.](image_url)

3. Optimization of Corrosion-Resistant Metal Pipe Material

In the H\(_2\)S-CO\(_2\)-Cl\(^-\) coexisting corrosion environment system, the usual solution is to use a duplex stainless-steel pipe, but the cost of the pipe is high, and the cost of oilfield mining will be increased. Therefore, it is necessary to develop new pipe material. Steel components can be smelt using a vacuum furnace, and pipe material can be made through forging, rolling, and other processes. In addition, the mechanical properties, corrosion resistance, and welding performance of the new pipe were evaluated and compared with 20# steel.

3.1. Chemical Composition Optimization

According to the characteristics of electrochemical corrosion, the development of anticorrosive materials is mainly based on improving the potential of materials. Therefore, Cr, Cu, Mo, and other alloying elements were selected as the main objects of material optimization. The content of Cr varied from 0.5% to 2.2%. The proper addition of Cu, Mo, Nb, and other alloying elements can improve the strength and corrosion resistance. The optimized chemical composition of the material is shown in Table 10.

| Material | C (%) | Si (%) | Mn (%) | P (%) | S (%) | Cr (%) | Cu (%) | Nb (%) | Mo (%) | Carbon Equivalent (%) |
|----------|-------|--------|--------|-------|-------|--------|--------|--------|--------|-----------------------|
| 20#      | 0.23  | 0.26   | 0.49   | 0.014 | 0.009 | -      | -      | -      | -      | 0.31                  |
| 20J      | 0.20  | 0.30   | 0.51   | 0.009 | 0.001 | -      | -      | -      | -      | 0.29                  |
| XA       | 0.07  | 0.29   | 0.48   | 0.007 | 0.002 | 0.65   | -      | -      | -      | 0.25                  |
| XB       | 0.09  | 0.34   | 0.52   | 0.009 | 0.002 | 0.63   | 0.18   | -      | -      | 0.31                  |
| XC       | 0.07  | 0.33   | 0.51   | 0.006 | 0.002 | 1.09   | -      | -      | -      | 0.37                  |
| XD       | 0.09  | 0.31   | 0.51   | 0.009 | 0.003 | 1.11   | 0.23   | -      | -      | 0.41                  |
|XE        | 0.08  | 0.34   | 0.52   | 0.010 | 0.002 | 2.08   | -      | -      | -      | 0.58                  |
| XF       | 0.08  | 0.33   | 0.53   | 0.009 | 0.003 | 2.1    | 0.04   | -      | -      | 0.59                  |
| XG       | 0.08  | 0.35   | 0.50   | 0.009 | 0.002 | 1.09   | 0.21   | -      | 0.23   | 0.44                  |
| XH       | 0.09  | 0.33   | 0.51   | 0.008 | 0.002 | 2.11   | 0.21   | -      | 0.24   | 0.65                  |
3.2. Mechanical Properties of Optimized Materials

The mechanical properties of 20# steel and the optimized pipe materials were tested, including the yield strength, tensile strength, extensibility, impact energy, and yield ratio, as shown in Table 11.

Table 11. Mechanical properties of 20# steel and optimized steel.

| Material | Yield Strength (MPa) | Tensile Strength (MPa) | Extensibility (%) | Impact Energy (J @ 0°C) | Yield Ratio | Metallographic Structure |
|----------|----------------------|------------------------|-------------------|-------------------------|-------------|--------------------------|
| 20#      | 308                  | 469                    | 28.5              | 83, 90, 87              | 0.67        | F + P \(^1\)             |
| 20J      | 288                  | 454                    | 36.5              | 153, 177, 139           | 0.63        | F + P                    |
| XA       | 251                  | 390                    | 43.5              | 233, 240, 236           | 0.64        | F + P                    |
| XB       | 286                  | 446                    | 36.5              | 109, 109, 94            | 0.64        | F + P                    |
| XC       | 266                  | 404                    | 43.0              | 281, 274, 274           | 0.66        | F + P                    |
| XD       | 294                  | 491                    | 36                | 135, 120, 116           | 0.60        | F + P                    |
| XE       | 248                  | 501                    | 36.0              | 41, 34, 26              | 0.50        | F + B \(^1\)             |
| XF       | 367                  | 607                    | 25.0              | 28, 16, 23              | 0.60        | F + B                    |
| XG       | 366                  | 606                    | 25.5              | 15, 15, 16              | 0.60        | F + B + M \(^1\)         |
| XH       | 565                  | 851                    | 22                | 11, 9, 10               | 0.66        | B + M                    |

\(^1\) In Table 9, F represents ferrite, P represents pearlite, B represents bainite, and M represents martensite.

It can be seen in Table 11 that: (1) The strength of 20J steel (refined 20# steel) is similar to that of 20# steel, but the toughness is increased from the lowest 83 J to 139 J, which shows that the scouring effect is noticeable. (2) The Cr content of XA and XC is 0.6% and 1.1%, respectively, and the yield strength reaches 245 MPa, but the tensile strength is lower, and the impact energy is above 200 J. (3) After adding about 0.2% of Cu, the strength of the corresponding XB and XD increased, while the impact energy decreased by more than 100 J, indicating that the damage of the Cu to the toughness was apparent. (4) When the content of Cr is increased to 2%, that is, XE steel, the yield ratio decreases obviously, the bainite structure appears in the steel, and the impact energy is down to about 30 J. (5) The strength of XF steel with the addition of grain element Nb is increased, but the impact energy is not improved. (6) Mo element is added based on XD steel, that is, the XG steel. Compared with XD steel, the strength of XG increased, and the impact energy decreased significantly. (6) XH steel is an alloy adding Mo and Cu based on Cr content 2% in the material, and the strength reaches the X80 steel grade, but the impact energy is shallow, which is a composite structure of bainite and martensite. (7) The rank of the mechanical properties of these steel materials is: XA, XC > 20J, XB, XD > 20# > XE, XF, XG, XH.

3.3. Corrosion Resistance Comparison

Immersion experiments and pressure kettle experiments were used to evaluate the corrosion resistance of the optimized materials.

3.3.1. Immersion Experiment

Accelerated corrosion experiments include two parts: (1) Continuous access to CO\(_2\) under anaerobic condition; and (2) Aerobic condition.

Metal Coupons Were Immersed in a Solution of CO\(_2\) Partial Pressure of 0.1 MPa

According to the produced water test data of the oil field, the simulated solution (Table 12) was configured and continued to access to CO\(_2\) under the anaerobic condition, as shown in Figure 5. The duration of the experiment was 20 days, and each material had two coupons.
Metal Coupons Were Immersed in a Solution of CO₂ Partial Pressure of 0.1 MPa

According to the produced water test data of the oil field, the simulated solution (Table 12) was configured and continued to access to CO₂ under the anaerobic condition, as shown in Figure 5. The duration of the experiment was 20 days, and each material had two coupons.

Table 12. Simulated solution of the oil field.

| Icon Content (mg/L) | CO₂ Partial Pressure (MPa) | Experimental Duration (h) |
|---------------------|---------------------------|--------------------------|
| K⁺, Na⁺             | Mg²⁺                      | Cl⁻                      |
| Ca²⁺                | SO₄²⁻                     | HCO₃⁻                    |
| 71,993              | 1298                      | 134,345                  |
| 15,000              | 300                       | 113                      |
| 1298                | 300                       | 113                      |
| 0.1                 | 480                       |                           |

The average corrosion rate of the different materials is shown in Figure 6, and the specific experimental data are shown in Table A1. The morphology of coupons after the experiment can be seen in Figure 7. It can be seen from Figures 6 and 7 that pitting corrosion occurred obviously in both 20# and 20J steel, and the XA and XD steel with Cr content of 0.6% and 1.1%, respectively, had a better anti pitting effect. The anti-pitting effect of XE and XF with a Cr of 2% is the best, but the corrosion loss is small, and the corrosion rate is low in this experiment.

Metal Coupons Were Immersed in a Solution of pH Value of 1.5

The pH value of the produced water in the oil field is 5.8. In order to accelerate the experimental process, the pH value was adjusted to 2.5 with hydrochloric acid and soaked for 27 days. The corrosion rate of different materials is shown in Figure 8, and the specific experimental data are shown in Table A2. The morphology of coupons after the experiment can be seen in Figure 9. It can be seen from Figures 8 and 9 that obvious pitting corrosion occurred in 20# and 20J steel, but the corrosion rate was not much different from that of XA, XB, XC and XD, XE, and XF steel with a 2% Cr content only containing bainite, and the corrosion rate is low. XG and XH steel with Mo element produce martensite and the corrosion rate is larger. The pitting is more serious, indicating that the harm of unbalanced martensite tissue is greater.
Figure 6. Average corrosion rate of different materials.

Figure 7. Morphology of coupons after the experiment.

Figure 8. Corrosion rate of different materials.
Based on two immersion experiments, XG, XH, 20#, and 20J have noticeable pitting, while XA, XB, XC, and XD with a Cr content of 0.6% and 1.1% show a pitting tendency. However, compared with other steels, they have better pitting corrosion resistance.

3.3.2. Medium Pressure Kettle Experiment

Experiments were carried out using the simulated solution (Table 13). Oxygen was removed, and CO₂ was introduced and maintained at a partial pressure of 1 MPa. The experimental temperature was 80 °C, the rotation speed was 1 m/s, and the experiment duration was 10 days. The corrosion rate of different materials can be seen in Figure 10, the specific experimental data of uniform corrosion are shown in Table A3, and specific experimental data of pitting corrosion are shown in Table 14. The morphology of coupons after the experiment can be seen in Figure 11.

Table 13. Formulation of simulated solution.

| Composition | NaCl  | KCl   | MgCl₂ | CaCl₂ | Na₂SO₄ | NaHCO₃ | PH Value |
|-------------|-------|-------|-------|-------|--------|--------|----------|
| Content (g/L) | 154.93 | 20.97 | 5.14  | 41.63 | 0.44   | 0.156  | 4.5      |

Figure 9. Morphology of coupons after the experiment.

![Morphology of coupons after the experiment](image)

Figure 10. Corrosion rate of different materials.

![Corrosion rate of different materials](image)
Table 14. Pitting rate in the case of CO₂ partial pressure of 1 MPa and 80 °C.

| Material | Maximum Pitting Depth (mm) | Average Pitting Depth (mm) | Maximum Pitting Rate (mm/year) | Average Pitting Rate (mm/year) |
|----------|---------------------------|-----------------------------|-------------------------------|-------------------------------|
| 20#      | 2.990                     | 2.914                       | 109.135                      | 106.361                      |
| 20J      | 0.690                     | 0.578                       | 25.185                       | 21.097                       |
| XA       | 0.440                     | 0.152                       | 16.060                       | 5.548                        |
| XB       | 0.430                     | 0.302                       | 15.695                       | 11.023                       |

No pitting phenomenon

![Figure 11. Morphology of coupons after the experiment.](image)

It can be obtained from Figure 10 and Table A3 that the corrosion rates of XA and XB steel with the Cr content of 0.6% are 2.51 and 2.341 mm/year, respectively, while the corrosion rates of XC and XD steel with the Cr content of 1.1% are 1.52 mm/year, and it can be seen that the addition of a small amount of Cu (XB and XD steel) has little effect on the corrosion rate. Compared with XC steel and XD steel, the corrosion rates of XF and XF steel with a Cr content of 2.1% decrease to 1.35 mm/year, indicating that adding 1% Cr element does not substantially affect the corrosion rate. However, the corrosion rate of XG and XH steel with Mo element is lower than that of XD and XE steel; especially, the corrosion rate of XH steel is only 0.15 mm/year, which shows that Mo significantly affects CO₂ corrosion resistance.

It can be seen from Table 11 that the maximum pitting depths of 20# and 20J steel are 2.99 and 0.69 mm, respectively, and the maximum pitting rates are up to 25 mm/year. The maximum pitting rates of XA and XB steel with a Cr content of 0.6% are up to 15 mm/year. Other types of steel do not show pitting corrosion, showing more typical uniform corrosion characteristics.

3.3.3. High-Pressure Kettle Experiment

The components of the simulated solution are still shown as Table 13. After oxygen was removed, CO₂ (partial pressure is 1 MPa) and H₂S (partial pressure is 0.1 MPa) were introduced into the high-pressure kettle at a temperature of 60 °C. Experiments were conducted using XA, XB, XC, and XD steel with a higher corrosion resistance, and the experiment duration was 10 days. The corrosion rate of different materials can be seen in Figure 12, and the morphology of coupons after the experiment can be seen in Figure 13.
1. The corrosion resistance of 20J steel is higher than that of ordinary 20# steel, but the pitting tendency is still high, and the maximum pitting rate is up to 25 mm/year.
2. The XE and XF steel with a Cr content of 2.1% have better corrosion resistance, but the carbon equivalent of the two steels reaches 0.58. During the welding process, preheating or subsequent heat treatment is necessary, which will increase the difficulty and cost of construction.
3. Mo can effectively improve the hardenability of materials. The XH steel containing Mo exhibits an unbalanced bainitic structure and martensite structure. Although it does not affect the corrosion resistance of CO₂, it is very sensitive to the corrosion of dissolved oxygen, and the tendency of pitting corrosion is pronounced.
4. The XC and XB steel with a Cr content of 0.6% and the XC and XD steel with a Cr content of 1.1% all have uniform corrosion characteristics. The uniform corrosion resistance of XA and XB relative to 20# is improved by 50%, and the uniform corrosion resistance of XC and XD relative to 20# is improved by 70%. XA and XB steel have obvious pitting corrosion problems and a maximum pitting rate of 15 mm/year. Moreover, XC and XD steel do not have a pitting corrosion tendency, so they can be used as potential pipe materials for corrosion resistance.
5. The corrosion resistance of these steel materials is: XE, XF, XC, XD > XA, XB, 20J > 20# > XG, XH.

3.4. Comparison of Welding Performance

The welding performance of steel material generally refers to whether cracks are easily formed in the weld and heat-affected areas and whether the welded joints are brittle. The “carbon equivalent” is usually used to measure the quality of the welding performance.
The greater the carbon equivalent, the more efficiently the weld zone produces cracks. The formula for calculating carbon equivalent $C_{eq}$ is:

$$C_{eq} = \omega_C + \frac{\omega_{Mn}}{6} + \frac{\omega_{Ni} + \omega_{Cu}}{15} + \frac{\omega_{Cr} + \omega_{Mo} + \omega_{V}}{5}$$ (1)

where $\omega_C$, $\omega_{Mn}$, $\omega_{Ni}$, $\omega_{Cu}$, $\omega_{Cr}$, $\omega_{Mo}$, $\omega_{V}$ represent the mass fraction of C, Mn, Ni, Cu, Cr, Mo, and V in the alloy, respectively, %.

Field experience shows that when the $C_{eq}$ is less than 0.45%, the cold cracking tendency of the steel is not obvious, and the weldability is good. When the $C_{eq}$ is between 0.45% and 0.6%, the steel tends to have a more pronounced cold cracking tendency and poor weldability, and it is necessary to preheat the steel and take other technical measures to prevent cracks in the welding; when the $C_{eq}$ is greater than 0.6%, the cold cracking tendency of steel welding is pretty obvious, and the welding performance is poor, basically not suitable for welding, or only under strict process measures and high preheating temperatures for welding operation.

From Table 8, it can be concluded that the rank of weldability of these steel materials is: XA, 20J, 20#, XB, XC, XD > XG, XE, XF, XH.

### 3.5. Determination of New Pipe Material

Based on the evaluation of the mechanical properties, corrosion resistance, and other aspects of the new material, XC steel was selected and named as BX245-1Cr, and its chemical composition is shown in Table 15.

#### Table 15. Chemical composition of BX245-1Cr steel.

| Composition | C   | Si  | Mn  | P    | S    | Cr  |
|-------------|-----|-----|-----|------|------|-----|
| Mass fraction (%) | 0.06–0.09 | 0.25–0.35 | 0.4–0.6 | \(\leq 0.015\) | \(\leq 0.003\) | 0.01–0.012 |

### 4. Laboratory and Field Evaluation of the New Pipe Material

In this paper, the corrosion resistance of the new material was evaluated by two methods: laboratory evaluation and field evaluation. The 20# steel and BX245-1Cr steel were used for comparison experiments. The components of the actual products of 20# steel and BX245-1Cr steel made by Baosteel company are shown in Table 16 and Figure 14, respectively.

#### Table 16. The components of the actual products of 20# steel and BX245-1Cr steel.

| Steel     | C  | Si  | Mn  | P   | S   | Cr  | Ni | Cu |
|-----------|----|-----|-----|-----|-----|-----|----|----|
| 20#       | 0.21 | 0.32 | 0.52 | 0.032 | 0.035 | 0.21 | 0.23 | 0.22 |
| BX245-1Cr | 0.07 | 0.30 | 0.5  | 0.007 | 0.011 | 0.011 | -  | -  |

### 4.1. Laboratory Evaluation

The experimental parameters were designed according to the highest, average, and minimum values of the corrosion medium content in the oilfield so that the experimental results were more representative. The experimental parameters are shown in Table 17. The evaluation contents of the experiment include the rate of uniform corrosion and the rate of pitting.
Under different operating conditions, the uniform corrosion rate and pitting corrosion rate of the two metallic materials are shown in Figure 14. The microscopic corrosion morphology under different corrosive media conditions is shown in Figure 15.

From Figures 14 and 15, it can be seen that the uniform corrosion rate and pitting corrosion rate of BX245-1Cr steel are smaller than that of 20# steel in all operating conditions, and the pitting pit on the surface of 20# steel is more obvious, and the pits are large and deep. While the surface of BX245-1Cr steel is relatively flat, it is dominated by uniform corrosion. Although the pitting pit is localized, the pits are small and shallow. In the $\text{H}_2\text{S}-\text{CO}_2-\text{Cl}^-$ corrosion environment, the corrosion of 20# steel and BX245-1Cr steel is mainly caused by $\text{CO}_2$ and $\text{H}_2\text{S}$. $\text{Cl}^-$ participates in the whole electrochemical corrosion reaction process, but it does not constitute the corrosion product while $\text{Cl}^-$ only plays the role of catalyst. Under the simulated experimental conditions, the uniform corrosion resistance of BX245-1Cr steel is 30.25% higher than that of 20# steel, and the pitting corrosion resistance of BX245-1Cr steel is 29.66% higher than that of 20# steel.

### 4.2. Field Evaluation

Field evaluation still adopts the coupon (Size: $50 \text{ mm} \times 13 \text{ mm} \times 1.5 \text{ mm}$) experiment. In the oil, gas, water systems of Northwest Oil and Gas Field, 24 monitoring points were selected for real-time monitoring. The monitoring points are located in the more severe pipe corrosion areas in the northwest oil and gas fields, including where (1) corrosion perforation occurred; (2) the corrosion rate is moderate and above; (3) the corrosion environment is horrible; and (4) sewerage system monitoring points.
Under different operating conditions, the uniform corrosion rate and pitting corrosion rate of the two metallic materials are shown in Figure 14. The microscopic corrosion morphology under different corrosive media conditions is shown in Figure 15.

**Figure 14.** Corrosion rate of 20# steel and BX245-1Cr steel.

(a) (b) (c)  
(d) (e) (f)  
(g) (h) (i)

**Figure 15.** Microscopic corrosion morphology (× 25 times) (a) Partial pressure of CO$_2$ = 0.01 MPa; (b) Partial pressure of CO$_2$ = 0.15 MPa; (c) Partial pressure of CO$_2$ = 0.45 MPa; (d) Partial pressure of H$_2$S = 0.0003 MPa; (e) Partial pressure of H$_2$S = 0.0008 MPa; (f) Partial pressure of H$_2$S = 0.003 MPa; (g) Concentration of Cl$^{-}$ = 60,000 mg/L; (h) Concentration of Cl$^{-}$ = 110,000 mg/L; (i) Concentration of Cl$^{-}$ = 150,000 mg/L.

The total monitoring period was 240 days, which can be divided into Phase I (30 days), Phase II (90 days), and Phase III (120 days). In order to make the monitoring data more in line with the actual situation, the coupons of Phase I were brand new. In Phase II, after coupons’ data analysis of Phase I was completed, the original monitoring point was returned to. In Phase III, after coupons’ data analysis of Phase II was completed, and the original monitoring point was returned to. The corrosion rate was calculated from the average of 24 coupons’ corrosion rate. The experimental results are shown in Table 18.

### Table 18. Corrosion rate monitoring results.

| Phase | Uniform Corrosion Rate (mm/year) | Corrosion rate Decline (%) | Pitting Corrosion Rate (mm/year) | Corrosion Rate Decline (%) |
|-------|----------------------------------|----------------------------|----------------------------------|----------------------------|
|       | BX245-1Cr 20#                    |                            | BX245-1Cr 20#                    |                            |
| I     | 0.0270 0.0294                    | 8.16                       | 0.3224 0.5659                    | 43.03                      |
| II    | 0.0091 0.0105                    | 13.33                      | 0.1024 0.1217                    | 15.86                      |
| III   | 0.0617 0.0633                    | 2.53                       | 0.2585 0.4032                    | 35.89                      |
| Average | 0.0235 0.025                     | 8.01                       | 0.2463 0.3717                    | 31.59                      |

It can be obtained from Table 18 that the uniform corrosion rate and pitting rate of BX245-1Cr steel are smaller than those of 20# steel, and the pitting corrosion resistance of BX245-1Cr steel is more obvious. The corrosion rates of the two materials in Phase II are lower than that of Phase I, because of the dissolution of Cr in the BX245-1Cr material, the corrosion product film, which is mainly the amorphous substance Cr(OH)$_3$, is formed on the metal surface. The corrosion product film has a specific anion selectivity, which can effectively prevent the anion from penetrating the corrosion product film to the metal surface, reducing the anion concentration at the interface between the film and the metal,
thereby reducing the corrosion rate of the metal. However, before Phase III, the corrosion product film, which is mainly composed of Cr(OH)$_3$ on the surface of the coupon, is removed, resulting in partial damage of the corrosion product film on the metal surface, then put in the corrosion medium again, and the corrosion rate is accelerated.

5. Conclusions

Aiming at the corrosion problem of pipelines in Tahe Oilfield, this paper conducted an in-depth study on the corrosion laws of pipelines. In this paper, indoor tests were carried out from the aspects of the corrosive environment and operating conditions, the main factors of corrosion were studied, and the corrosion law of metal pipeline in different corrosive media was clarified. On this basis, a new material was proposed. The main conclusions are as follows:

1. In the H$_2$S–CO$_2$–Cl$^-$ corrosion environment, H$_2$O is the carrier of corrosion, Cl$^-$ is the corrosion catalyst, H$_2$S is a strong hydrogen permeation medium, CO$_2$ dissolves in water to cause electrochemical corrosion, and O$_2$ is a kind of depolarization agent.

2. The content of CO$_2$ has a significant influence on the corrosion form of 20# steel; the content of H$_2$S has a certain influence on the corrosion morphology and corrosion tendency of 20# steel, and the concentration of Cl$^-$ has a great influence on the local corrosion rate but little effect on the surface film and the uniform corrosion rate.

3. Under the simulated experimental conditions, the uniform corrosion resistance and the pitting corrosion resistance of BX245-1Cr steel was 30.25% and 29.66% higher than that of 20# steel, which means BX245-1Cr steel has better resistance to pitting corrosion.

The problem of pitting corrosion was analyzed in this paper. However, combined with engineering practice, in the future work, more in-depth research will be carried out from two aspects: (1) the corrosion mechanism of wet H$_2$S, and (2) the fracture mechanism of new materials in a corrosive environment. In addition, under the background of artificial intelligence, some new materials can be developed by machine learning [19].

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Appendix A

Table A1. Average corrosion rate in the case of CO$_2$ partial pressure of 0.1 MPa.

| Material | Surface Area of Coupon (m$^2$) | Weighing before the Experiment (g) | Weighing after the Experiment (g) | Weight Loss (g) | Corrosion Rate (mm/year) | Average Corrosion Rate (mm/year) |
|----------|-------------------------------|-----------------------------------|----------------------------------|----------------|-------------------------|----------------------------------|
| 20#      | 0.002884                      | 27.9962                           | 27.8860                          | 0.1102         | 0.089                   | 0.085                            |
|          | 0.002884                      | 27.4859                           | 27.3854                          | 0.1005         | 0.081                   |                                   |
| 20J      | 0.002884                      | 27.4367                           | 27.3523                          | 0.0844         | 0.068                   | 0.074                            |
|          | 0.002884                      | 26.3870                           | 26.2875                          | 0.0995         | 0.080                   |                                   |
| XA       | 0.002884                      | 27.8179                           | 27.7474                          | 0.0705         | 0.057                   | 0.059                            |
|          | 0.002884                      | 27.8340                           | 27.7589                          | 0.0751         | 0.060                   |                                   |
### Table A1. Cont.

| Material | Surface Area of Coupon (m²) | Weighing before the Experiment (g) | Weighing after the Experiment (g) | Weight Loss (g) | Corrosion Rate (mm/year) | Average Corrosion Rate (mm/year) |
|----------|----------------------------|----------------------------------|----------------------------------|----------------|--------------------------|---------------------------------|
| XB       | 0.002884                   | 28.0804                          | 28.0291                          | 0.0513         | 0.041                    | 0.055                           |
|          | 0.002884                   | 28.2411                          | 28.1554                          | 0.0857         | 0.069                    |                                  |
| XC       | 0.002884                   | 27.8875                          | 27.7990                          | 0.0885         | 0.071                    | 0.062                           |
|          | 0.002884                   | 27.6426                          | 27.5780                          | 0.0646         | 0.052                    |                                  |
| XD       | 0.002884                   | 27.8113                          | 27.7386                          | 0.0727         | 0.059                    | 0.061                           |
|          | 0.002884                   | 27.8542                          | 27.7748                          | 0.0794         | 0.064                    |                                  |
|XE        | 0.002884                   | 27.6187                          | 27.5488                          | 0.0699         | 0.056                    | 0.056                           |
|          | 0.002884                   | 27.3169                          | 27.2465                          | 0.0704         | 0.057                    |                                  |
|XF        | 0.002884                   | 27.8958                          | 27.8469                          | 0.0489         | 0.039                    | 0.055                           |
|          | 0.002884                   | 28.0224                          | 27.9359                          | 0.0865         | 0.070                    |                                  |
|XG        | 0.002884                   | 27.6899                          | 27.6075                          | 0.0824         | 0.066                    | 0.063                           |
|          | 0.002884                   | 27.8840                          | 27.8088                          | 0.0752         | 0.061                    |                                  |
|XH        | 0.002884                   | 27.3599                          | 27.2879                          | 0.072          | 0.058                    | 0.062                           |
|          | 0.002884                   | 27.6775                          | 27.5943                          | 0.0832         | 0.067                    |                                  |

### Table A2. Corrosion rate in the case of pH value of 2.5.

| Material | Surface Area of Coupon (m²) | Weighing before the Experiment (g) | Weighing after the Experiment (g) | Weight Loss (g) | Corrosion Rate (mm/year) |
|----------|----------------------------|----------------------------------|----------------------------------|----------------|--------------------------|
| 20#      | 0.002884                   | 28.6523                          | 28.1380                          | 0.5143         | 0.32                     |
| 20J      | 0.002884                   | 27.5736                          | 27.0887                          | 0.4849         | 0.30                     |
| XA       | 0.002884                   | 28.2801                          | 27.9700                          | 0.3101         | 0.20                     |
| XB       | 0.002884                   | 28.4495                          | 28.0112                          | 0.4383         | 0.27                     |
| XC       | 0.002884                   | 28.2940                          | 27.8512                          | 0.4428         | 0.27                     |
| XD       | 0.002884                   | 28.4589                          | 27.9913                          | 0.4646         | 0.28                     |
|XE        | 0.002884                   | 28.1906                          | 27.9080                          | 0.2826         | 0.17                     |
|XF        | 0.002884                   | 28.2113                          | 27.9654                          | 0.2459         | 0.15                     |
|XG        | 0.002884                   | 28.2166                          | 27.2803                          | 0.9313         | 0.57                     |
|XH        | 0.002884                   | 28.1653                          | 27.3393                          | 0.826          | 0.51                     |

### Table A3. Corrosion rate in the case of CO₂ partial pressure of 1 MPa and 80 °C.

| Material | Surface Area of Coupon (m²) | Weighing before the Experiment (g) | Weighing after the Experiment (g) | Weight Loss (g) | Corrosion Rate (mm/year) |
|----------|----------------------------|----------------------------------|----------------------------------|----------------|--------------------------|
| 20#      | 0.002884                   | 28.2034                          | 22.1055                          | 6.0979         | 4.91                     |
| 20J      | 0.002884                   | 26.8695                          | 22.7886                          | 4.0809         | 3.29                     |
| XA       | 0.002884                   | 27.9966                          | 24.8759                          | 3.1207         | 2.51                     |
| XB       | 0.002884                   | 28.2109                          | 25.3080                          | 2.9029         | 2.34                     |
| XC       | 0.002884                   | 27.7977                          | 25.9100                          | 1.8877         | 1.52                     |
| XD       | 0.002884                   | 28.0624                          | 26.1737                          | 1.8887         | 1.52                     |
|XE        | 0.002884                   | 27.8477                          | 26.1219                          | 1.7258         | 1.39                     |
|XF        | 0.002884                   | 27.9163                          | 26.2380                          | 1.6783         | 1.35                     |
|XG        | 0.002884                   | 27.9493                          | 26.3295                          | 1.6198         | 1.30                     |
|XH        | 0.002884                   | 27.7710                          | 27.5841                          | 0.1869         | 0.15                     |

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