Scaling Inhibitor Impact to Corrosion Resistance of J55 Mild Steel in CO₂ Saturated Brine

Qingbo Zhang¹,a, Xiaowei Xu ², Xueping Hua ², Jianyong Lei ², Yun Ma ³,4,*, Qingsong Yu 5, b

¹ Xinjiang Vocational University, Urumqi, Xinjiang, 830000, China
² No.2 Gas Production Plant, Changqing Oilfield Company, Yulin, Shaanxi, 710200, China
³ College of Petroleum Engineering, Shaanxi Province Key Laboratory of Advanced Stimulation Technology for Oil & Gas Reservoirs, Xi’an Shiyou University, Xi’an, Shaanxi 710065, China
⁴ Engineering Research Center of Development and Management for Low to Ultra-Low Permeability Oil & Gas Reservoirs in West China, Ministry of Education, Xi’an, Shaanxi, 710065, China
⁵ Center for Surface Science and Plasma Technology, Department of Mechanical and Aerospace Engineering, University of Missouri, Columbia, Missouri 65211, USA

a 100020248@qq.com, *Corresponding author e-mail: 23987471@qq.com, b yuq@missouri.edu

Abstract. The corrosion behavior of the J55 mild steel alloy in CO₂ saturated brine have been studied by weight loss technique, potentiodynamic polarization technique and characterization of the corroded surface techniques. The results demonstrate that the corrosion solution is easy to penetrate into the matrix and activate corrosion without scale inhibitor. When the scale inhibitor content was as high as 30 mg/L, the effect of scaling products on corrosion gradually decreased. Adding the corresponding scale inhibitor in the solution was beneficial to slow down the corrosion rate and the possibility of pitting corrosion. The corrosion product film is mainly FeCO₃, and with the increase of scale inhibitor contents, the density of FeCO₃ was stronger and compact, which could greatly prevent the contact between the medium and the matrix.

Keywords: Scale inhibitor, J55 low carbon steel alloy, corrosion.

1. Introduction
In the development of oil and gas industry, corrosion can take place in any production system. Great efforts are being made to relieve the metal corrosion because it is one of the main factors affecting the service of metal equipments and components [1]. It not only causes huge economic loss to the oil field, but also brings some catastrophic consequences [2-3]. Therefore, the safety and reliability of oil and gas well pipes play a decisive role in the development of the oil and gas.

CO₂ corrosion is the most common form of pipeline corrosion failure in oil and gas wells. CO₂ in the oil pipe is mainly derived from the decomposition products of organic biological oxidation in the
formation, and the geological and chemical processes of the earth, and CO₂ is usually found in oil and gas as a component of oil and gas associated gas or natural gas and formation water. In recent years, in order to enhance the efficiency of crude oil recovery, a large body of researchers countered CO₂ capture and storage (CCS) and CO₂ enhanced oil recovery (CO₂-EOR), which will make the content of CO₂ in the oil well pipe increase[2,13] and cause serious corrosion attacks to the pipelines. Many scholars also found that localized corrosion occurred under the scale [4-5]. The reason why is that production and formation water of the oil and gas wells often contain high valence metal ions such as Ca, Mg, and are easy to produce the carbonate scale and deposit along the surface of well pipe and equipment with the corrosion product FeCO₃ in scale. Finally, galvanic corrosion formed after the corrosion products are covered on the surface of the material, which accelerates the local corrosion of carbon steel [6-10]. This paper is to systematically investigating the J55 oil tube steel corrosion behaviors in different CO₂ saturated brine through electrochemical experiments and dynamic corrosion tests and researching the corrosion behavior of scale inhibitor.

The morphology of corrosion layer was studies using a camera, and the microphology of corrosion layer was observed scanning electron microscope (SEM). The corrosion depth was analyzed through optical microscope (OM). The chemical composition was observed by energy dispersive spectrooscope (EDS). Through the above studied and analysis, it could be explained that the relationships between corrosion rate, pitting condition and the characters of corrosion products.

2. Materials and Experiments

2.1. Material and medium
J55 steel alloy, used widely in oil and gas production industries, was machined with 50mm×10mm×3mm and the specimen for electrochemical measurements was sectioned into working electrode (area, 0.785cm²). To make an electrical connection, it was necessary to weld a thread to the sample as the working electrode. The sample was embedded in epoxy coating and left one surface to be exposed to the electrolyte. The model steel was showed in fig.1.

![Model Steel](image)

**Fig.1** The test model steel of type J55 carbon steel

The material was J55 stainless steel with a composition (wt.%) of 0.19 C, 0.31 Si, 1.39 Mn, 0.014 P, 0.004 S, 0.2 Cr, 0.017 Ni, 0.017 Cu, and Fe balance. The corrosion coupon was cleaned with petroleum ether and ethanol, stove-dried, weighted and stored in a vacuum desiccator before carrying out any surface analysis experiments. The test solution used high total-dissolved-solid (TDS) in this study and the composition was reflected in Table1.
Table.1 The composition of the aqueous solution used for scaling test [g]

| TDS(mg/L) | NaCl | CaCl₂ | MgCl₂ | Na₂SO₄ | NaHCO₃ |
|-----------|------|-------|-------|--------|--------|
| 33000     | 18.5028 | 13.7338 | 0.5897 | 0.2440 | 0.0631 |

2.2. Dynamic corrosion tests

The corrosion evaluation system (CONSYAT TEMPERATURE BRITEDING SHAKER) was made by Shanghai TENSUC Company (CHINA). Before corrosion test, the solution was deoxygenated with N₂ for 0.5h, and then bubbled CO₂ gas (>99.99%) at 1 bar for 1.5 h to saturated solution. Corrosion scale was removed using acid cleaning liquid n (500 ml of HCl and 3.5 g of hexamethylenamine brought to volume with water to 1000 ml) for 10 min, and then the specimens were rinsed by distilled water, finally the weight of the samples were measured to within an accuracy of 0.1 mg to calculate the average corrosion rate, as presented in following Eq.1 [11].

\[ r_{corr} = \frac{8.76 \times 10^4 \times (m - m_i)}{S \times t \times \rho} \]  

Where: \( m-m_i \) is the weight loss, g ; \( S \) is the exposed surface area, cm²; \( \rho \) is the density of the steel, g/cm²; \( t \) is the immersion time, h.

2.3. Maximum pitting depth

One of the most serious pitting was selected to observe the pitting using Olympus high power optical microscope dsx-500. In the experiment, the positive and negative surfaces of each hanging piece are divided into eight areas, as shown in Figure 1 (a). The nine visual threshold mosaic is carried out with 10% coincidence degree, and the rainbow 10 with the highest recognition degree is selected for evaluation, with ten colors (table 2) [12-15, 26].

Table.2 List of RGB numbers of ten color scales

| Deep/μm | 0-10 | 10-20 | 20-30 | 30-40 | 40-50 | 50-60 | 60-70 | 70-80 | 80-90 | 90-100 |
|---------|------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| R       | 254  | 255   | 254   | 255   | 138   | 0     | 0     | 0     | 0     | 128    |
| G       | 0    | 127   | 177   | 255   | 255   | 255   | 182   | 66    | 0     | 0      |
| B       | 0    | 0     | 0     | 0     | 0     | 29    | 255   | 245   | 192   | 128    |

2.4. Corrosion layer analysis

The morphology of corrosion layer was studied using a camera (D810, NiKon, Japan), and the microphology of corrosion layer was observed SEM (Quantu 600FEG, USA). The 3D morphology of the corroded samples was surveyed with OM (Opto-digital DSX-500, Olympus, Japan). The chemical composition was observed by EDS (OXFORD INCA x-act, UK).

2.5. Electrochemical experiments

The specimen was carried out to analyze by electrochemical measurement (ParStat-2273, USA). Linear polarization resistance and electrochemical impedance spectroscopy measurements were carried out in a typical three-electrode system, Specimens were cleaned by washing with degreased and dehydration by Petroleum ether and anhydrous ethanol. The glass electrolys pool has a capacity of 500 ml. Before the measurements, the test solution was deoxygenated for 2h using purified N₂ (>99.99%). And then bubbled CO₂ gas (>99.99%) at 0.1 bar to saturated solution. The corrosion rate was calculated as following Eq. 2[16-19].

\[ r(\text{mm} / \text{y}) = \frac{0.00327 \times i_{corr} \times \text{eq.wt}}{d} \]
Where $i_{corr}$ is the current density in $\mu$A/cm$^2$; $d$ is the density of the steel, g/cm$^2$; eq.wt is the specimen equivalent weight, g.

3. Results and discussion

3.1. Dynamic corrosion tests

Fig. 2 showed the corrosion rates of J55 steel as a function of scaling inhibitor content (0, 10, 30, 100 mg/L) under CO$_2$ saturated brine condition.

The average corrosion rate decreased with the increase of the scale inhibitor content, which indicated that the scale products had a significant influence on the corrosion rate. Without scale inhibitor, the distribution of pitting pits is dense, and the maximum pitting depth is about 90μM. When the scale inhibitor content was as high as 30 mg/L, the effect of scaling products on corrosion gradually decreased and the surface of the substrate is basically free of pitting corrosion, but the corrosion rate was over 0.2 mm/a, which was far higher than the standard of oil and gas field pipeline corrosion rate. This may be mainly because Ca$^{2+}$, Mg$^{2+}$ in solution were difficult to scale and replaced Fe$^{2+}$ in the corrosion product film of FeCO$_3$. The corrosion product film was mainly FeCO$_3$, and the density of FeCO$_3$ was strong, which could greatly prevent the contact between the medium and the matrix[20]. And the maximum pitting depth decreased with the increase of the scale inhibitor content, which indicated that adding the corresponding scale inhibitor in the solution was beneficial to slow down the corrosion rate and the possibility of pitting corrosion.

![Fig.2 Average corrosion rate and maximum corrosion depth at different scaling inhibitor content](image-url)
Fig. 3 3D photo of optical microscope after pickling of corrosion coupon with different content of scale inhibitor

### 4. Corrosion layer analysis

Fig. 3 showed the macroscopic morphology of corrosion product film at different scale inhibitor content.

When the scale inhibitor contents were 0 mg/L and 10 mg/L, there was a lot of brown and yellow corrosion product on the surface of the hanging piece after corrosion. When the scale inhibitor content were 30 mg/L and 100 mg/L, there was a small amount of black corrosion product on the surface of the hanging piece after corrosion. According to the analysis of average corrosion rate, adding appropriate scale inhibitor in solution was beneficial to slow down the corrosion rate.

Fig. 5 showed the SEM images of the surface of J55 at the magnification of ×1000. With the increase of scale inhibitor content, the corrosion product film gradually thinned. When the scale inhibitor was greater than 30 mg/L, a small amount of corrosion product film covered the substrate surface. Table 3 showed the EDS Element analysis of external surface of J55. The results of EDS indicated that the composition of corrosion scales was FeCO₃.
5. Electrochemical experiments
The open-circuit potential (OCP) curve was shown in Fig. 6. The stable potential of scale inhibitor content of 100 mg/L was obviously higher than that of the scale inhibitor content of 0, 10, 30 mg/L, indicating that the surface activity ratio of steel in this solution was inhibited. It could also be concluded that with the increase of scale inhibitor content, Ca$^{2+}$ in solution was difficult to replace Fe$^{2+}$ in the corrosion product film of FeCO$_3$, which resulted in strong density of FeCO$_3$ and prevented the contact between the medium and the matrix [21-26].

![Fig.6 The OCP curve of different scale inhibitor content](image)

![Fig.7 The EIS plot of different scale inhibitor content](image)
From the Fig. 7, the impedance spectra showed single capacitive arc resistance characteristics, which indicated that there was corrosion product film on the metal surface. With the increase of scale inhibitor content, the radius of impedance spectrogram first decreased and then increased. When the scale inhibitor content was less, the electrode activity was faster, which made the metal dissolve easily and accelerated corrosion. When the scale inhibitor content was higher than 30 mg/L, the impedance spectrum capacitance resistance radius increased obviously.

The EIS results were fitted by ZsimpWin in Fig. 8 and Table 4.

![Equivalent circuit of J55 steel at different scaling inhibitor content](image)

**Fig.8** Equivalent circuit of J55 steel at different scaling inhibitor content

| Scale inhibitor content [mg/L] | R_s/ohm | CPE/μF | R_t/ohm |
|-------------------------------|---------|--------|---------|
| 0                             | 0.991   | 168.2  | 135.8   |
| 10                            | 0.225   | 325.4  | 95.9    |
| 30                            | 2.144   | 159.8  | 343.7   |
| 100                           | 1.073   | 148.8  | 420.5   |

With the increase of scale inhibitor content, the change of solution resistance $R_s$ was relatively small, ranging from 1 to 2 ohm, while the change of passive film resistance $R_t$ was more obvious. It could be considered that the addition of scale inhibitor had little effect on the system, but mainly on the dissolution and formation of corrosion product film on the substrate surface. When the scale inhibitor content was 10 mg/L, the passive film resistance $R_t$ reached the minimum value, while CPE is the largest, and the corrosion resistance of the material was the worst. When the scale inhibitor content was increased to 100 mg/L, the maximum value of $R_t$ was 420.5 ohm.

![Polarization curves of J55 steel at different scaling inhibitor content](image)

**Fig.9** Polarization curves of J55 steel at different scaling inhibitor content
Table 5: Fitting results of the potentiodynamic polarization curve

| Scale inhibitor content mg/L | $b_0$/mV | $b_c$/mV | $J_{corr}$/($\mu$A.cm$^2$) | $E_{corr}$/mV | $E_{pp}$/mV |
|------------------------------|----------|----------|-----------------------------|--------------|------------|
| 0                            | 66.5     | 476.3    | 102.4                       | -681.1       | -287.9     |
| 10                           | 81.1     | 387.4    | 94.6                        | -684.4       | -339.7     |
| 30                           | 86.5     | 374.2    | 189.3                       | -625.8       | 126.8      |
| 100                          | 98.7     | 372.26   | 165.9                       | -623.3       | 273.2      |

Fig. 9 and Table 5 showed the relationship between the polarization curve and pitting potential of J55 steel sample under different of scale inhibitor contents. With the increase of scale inhibitor contents, the corrosion potential moved forward and the corrosion tendency begins to decrease gradually. When potential scanning enters the anode region, the stainless steel metal surface entered the passivation state, but a small passivation transition zone appeared, which indicated that the passivation film was easy to break down and passivation film was in this state. The dissolution was greater than the formation process. This was mainly due to the fact that the corrosion product film was easily broken down at higher potential, which made the corrosion product film more vulnerable to damage. Table 4 showed that with the increase of scale inhibitor dosage, $E_{pp}$ also increased. It could be prove again that adding appropriate scale inhibitor in solution was beneficial to slow down corrosion rate.

6. Conclusions

1) The scale products had a significant influence on the corrosion rate;
2) Without scale inhibitor, the corrosion solution is easy to penetrate into the matrix and activate corrosion. When the scale inhibitor content was as high as 30 mg/L, the effect of scaling products on corrosion gradually decreased;
3) Adding the corresponding scale inhibitor in the solution was beneficial to slow down the corrosion rate and the possibility of pitting corrosion.
4) The corrosion product film is mainly FeCO$_3$, and with the increase of scale inhibitor contents, the density of FeCO$_3$ was stronger and compact.

References

[1] Crolet J, Dugstad A, Thevenot N. Role of Free Acetic Acid on the CO2 Corrosion of Steels. Corrosion Houston Tx, 1999, 99.
[2] Heuer J K, Stubbins J F. An XPS characterization of FeCO$_3$ films from CO2 corrosion. Corrosion science, 1999, 41(7):1231-1243.
[3] Zhang X, Wang F, He Y, et al. Study of the inhibition mechanism of imidazoline amide on CO2 corrosion of Armco iron. Corrosion Science, 2001, 43(8):1417-1431.
[4] Damián A. López, Simison S N, S.R.de Sánchez. The influence of steel microstructure on CO2 corrosion. EIS studies on the inhibition efficiency of benzimidazole. Electrochimica Acta, 2003, 48(7):845-854.
[5] K.Videm, A.Dugstad. Film Covered corrosion film break down and pitting attack of Carbon steel in aqueous CO2 environments. Corrosion /88, paper number 186, (Houston, TX; NACE, 1998).
[6] K.Abd E H S M, Abd E W S, Bahgat A. Environmental factors affecting the corrosion behaviour of reinforcing steel. V. Role of chloride and sulphate ions in the corrosion of reinforcing steel in saturated Ca(OH)$_2$ solutions. Corrosion Science, 2013, 75(12): 1-15.
[7] Cho K W, Rao V S, Kwon H S. Microstructure and electrochemical characterization of trivalent chromium based conversion coating on zinc. Electrochimica Acta, 2007, 52(13):4449-4456.
[8] Chen C F, Lu M X, Zhao G X, et al. Effects of temperature, Cl- concentration and Cr on electrode reactions of CO2 corrosion of N80 steel. Acta Metallurgica Sinica Chinese Edition, 2003, 39(8):848-854.
corrosion. EIS studies on the inhibition efficiency of benzimidazole. Electrochimica Acta, 2003, 48(7):845-854.

[10] Ren G Q, Shen Y, Wang R, et al. Effect of Temperature on Electrochemical Corrosion Behavior of CT80 Coiled Tubing Steel. Corrosion and Protection, 2015, 036(003):245-249.

[11] Wang F P, li X G. Influence of NaCl on Corrosion Behavior of API P105 Steel in CO2 Saturated Solution. Journal of university of science and technology Beijing, 2002, 24(2):197-199.

[12] Fan Z H, Lu X H, Zhao G X, Lu M X, et al. Electrochemical characteristics of CO2 induced corrosion of N80 steel. Corrosion science and protection technology, 2005, 017(002):75-78.

[13] Zhang X, Wang F, He Y, et al. Study of the inhibition mechanism of imidazoline amide on CO2 corrosion of Armco iron. Corrosion Science, 2001, 43(8):1417-1431.

[14] Guo M L. Inhibition of CO2 corrosion of carbon steel by rosin amide. Anticorrosion Methods & Materials, 2003, 50(6):410-413.

[15] Yin Z F, Feng Y R, Zhao W Z, et al. Effect of temperature on CO2 corrosion of carbon steel. Surface & Interface Analysis, 2009, 41(6):517-523.

[16] Nafday O A, Nesic S. Iron Carbonate Scale Formation and CO2 Corrosion in the Presence of Acetic Acid. Corrosion Houston Tx, 2005, 51(10):3.

[17] Guoan, Zhang, Minxu, et al. Effect of HCO3- concentration on CO2 corrosion in oil and gas fields. Journal of Beijing University of science and technology, 2006(1):44-49.

[18] Zhong B, Chen Y Q, Meng F L, et al. Perforation Failure Analysis of N80 Pipe. Corrosion and Protection, 2018, 039(008):647-650[21]

[19] Wan L P, Meng Y F, Liang F S. Carbon Dioxide Corrosion and Its Influence Factors in Oil/Gas Field Exploitation. Total corrosion control, 2003(02):17-20.

[20] Chen G H. Study on the mechanism and synergistic effect of carbon dioxide corrosion inhibitor. Beijing University of Chemical Technology, 2012.

[21] Palacios C A, Shadley J R. Characteristics of corrosion scales on steels in CO2-saturated NaCl brine. Corrosion, 1991, 47(2): 122-127.

[22] C.A.Palacios, J.R.Shadley. CO2 corrosion of N80 Steel at 71°C in a Two-Phase flow system. Corrosion engineering, 1993, 866-892.

[23] Cui Z.D, Wu S L, Li C F, et al. Corrosion behavior of oil tube steels under conditions of multiphase flow saturated with super-critical carbon dioxide. Materials Letters, 2004, 58(6): 1035-1040.

[24] Nyborg R, Dugstad A. Mesa Corrosion attack in Carbon Steel and 0.5% Chromium Steel. Corrosion Paper, NACE, 1998, NO.29.

[25] Liang Wei, Xiaolu Pang, Chao Liu, et al. Formation mechanism and protective property of corrosion product scale on X70 steel under supercritical CO2 environment. Corrosion Science, 2015, (100): 404–420.

[26] Bai H T, Wang Y Q, Ma Y. Effect of CO2 Partial Pressure on the Corrosion Behavior of J55 Carbon Steel in 30% Crude Oil/Brine Mixture. Materials, 2018, 11, 1765.