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The Corrosion Inhibition of Imidazoline on the Surface of X65 Carbon Steel in Oxygen Environment

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Abstract. The corrosion inhibition of imidazoline on the surface of X65 carbon steel in the oxygen environment was studied by electrochemical measurement and WBE. Also, the microscope was used to observe the corrosion morphology of the specimens. The results show the potential of the electrode increased slightly after the 200 ppm imidazoline was added in the solution in the oxygen-contained environment. Imidazoline can inhibit the corrosion on the surface of carbon steel by constraining the anodic reaction mainly. However, the imidazoline can cause serious localized corrosion on the surface of the X65 carbon steel.

1. Introduction
The existence of corrosive ions often causes severe corrosion in pipelines, which affects the performance and lifetime of pipelines [1, 2]. The perforation due to corrosion will lead to pipe leakage, causing significant economic losses and environmental pollution. Therefore, corrosion inhibitors are widely applied in industry to mitigate the corrosion in pipelines. A corrosion inhibitor is a chemical substance that, when added in small concentrations, can effectively inhibit the corrosion of materials. Imidazoline, an effective organic corrosion inhibitor used in acidic environment, can form an adsorption film on the surface of metal, slowing down the diffusion of ions and inhibiting the occurrence of metal corrosion [3]. In the past decades, many studies have been conducted to figure out the corrosion inhibition of imidazoline in carbonic acid solutions [3-5]. However, few scholars have studied the corrosion inhibition in the oxygen containing environment. Huang et al. [6] studied the corrosion inhibition of imidazoline in the pipe under deposits. It was found that imidazoline at a high concentration could suppress the corrosion on carbon steel. Xu et al. [7-9] also studied the inhibition ability of the organophosphorus corrosion inhibitor on the carbon steel surface in the air. Like imidazoline, a high concentration of organophosphorus inhibitor could inhibit corrosion on the carbon steel surface. In production, oxygen-contained pipelines are widely used such as drainage pipes, cooling water pipes in oil and gas production and so on. Therefore, it is necessary to study the effect of corrosion inhibitors in oxygen containing pipelines.

Wire beam electrode (WBE) sensor, which was applied in this paper to study the corrosion inhibition effect of imidazoline on surface of X65 steel, is used to study the local corrosion effectively by monitoring the galvanic current on the carbon steel surface [5,10,11]. Undoubtedly, electrochemical measurements were essential in this study, including open circuit potential (OCP), linear polarization resistance (LPR) and potential dynamic sweep (PDS). In addition, the morphology of the corrosion specimens was observed by microscope. The effect of imidazoline inhibitor in the oxygen containing solution was preliminarily discussed.
2. Experiment method

2.1. Test specimens
The material used in the tests was API X65 pipeline steel, with a chemical composition (wt.%): C 0.26%, Si 0.40%, Mn 1.45%, P 0.03%, S 0.3%, Ni 0.5%, Cu 0.5%, Cr 0.5%, Mo 0.15%, and the rest being Fe. Two types of specimens were used: one used for electrochemical measurement had the size of $15 \times 10 \times 2 \text{ mm}^3$ (exposed surface being 1.5 cm$^2$ and the rest sealed with epoxy resin), while the other used for fabricating WBE was arranged in 10×10 array, as shown in Fig. 1b. Each electrode had a diameter of 1.5 mm and a center spacing of 2 mm, sealed with epoxy. The specimens and WBE were polished with 400#, 600# and 800# grit wet sand paper sequentially and cleaned with anhydrous ethanol before tests.

2.2. Experiment environment
All corrosion experiments were performed in a solution made by adding 3.5 wt% NaCl to de-ionized water. The corrosion inhibitor used in the experiment was water-soluble imidazoline, and its concentration was 200 ppm. The test solution was exposed directly to the air, and the temperature was kept at 25±1°C.

2.3. Experiment measurement
The three-electrode electrochemical system was used for electrochemical measurement. The system, as shown in Fig. 1a, consisted of the X65 steel specimen as working electrode (WE), platinum plate as counter electrode (CE) and saturated calomel electrode (SCE) as reference electrode (RE), which were alternately connected to the electrochemical station CS 350 (CorroTest, China). The LPR was applied after the WE was immersed in the solution for 2 h, with intervals of 6 h. PDS was conducted when the experiment time reached 144 h. Detailed information is shown in Table 1. Three groups of parallel experiments were carried out in each solution. After the experiment, the rust layer on the surface of the specimens was removed, and the corrosion morphology of the surface was observed with microscope.

| Scan range      | Scan rate |
|-----------------|-----------|
| LPR ±0.01 V vs. OCP | 0.2 mV/s |
| PDS -0.2 ~ 0.3 V vs. OCP | 2 mV/s |

The WBE could effectively monitor the local corrosion on the surface of carbon steel. The schematic diagram is shown in Fig. 1c, and the scanning measurement on the WBE was conducted with CST520 (CorroTest, China) with SCE as reference electrode. CST520 can measure the OCP of each individual electrode and the galvanic current between the measured electrode and the other 99 electrodes. In other cases, all electrodes were coupled together as the equivalent of a one-piece electrode.
3. Result and discussion

3.1. Result of Electrochemical measurement

The corrosion rate of X65 steel was monitored by LPR. Fig. 2a shows the variation of uniform corrosion rate with time for the two solutions. The corrosion rate shown in the chart is the average value of that in 3 groups of parallel experiments. The corrosion rate of X65 carbon steel increased slightly with time, and the corrosion rate tended to be stable at about 0.28 mm/a. In the solution with 200 ppm imidazoline inhibitor, the uniform corrosion rate dropped quickly at the early stage. Fig. 2b shows the corrosion inhibition efficiency of imidazoline inhibitor. There was a jump in corrosion efficiency within 24 h, before gradually stabilizing at 35%.

As shown in Fig. 3, the potential of the WE was initially high, reaching -617 mV. Then it dropped rapidly and gradually stabilized at -725 mV. In the solution with imidazoline inhibitor, the potential of WE was lower than that in the NaCl solution initially. But it dropped more slowly, stabilizing at -680 mV, slightly higher than that in NaCl solution. The end of the experiment involved PDS measurement. The results are shown in Fig. 3b. The results of Tafel fitted from PDS are shown in Table 2. It is seen that the anodic Tafel slope and the cathodic Tafel slope both increased when adding imidazoline into the solution. Generally, the inhibitor is an anodic inhibitor when the potential shift is higher than 85 mV [12]. In this test, the maximum move of the potential was 45 mV, indicating imidazoline acted as a mixed type inhibitor in oxygen-containing solution. Imidazoline could form an absorption film on the steel surface so that the solution phase was isolated from the carbon steel surface and the anodic
reaction was inhibited predominantly [13]. However, it took time for imidazoline inhibitor to form the adsorption film. In addition, the mechanism of the inhibitor needs to be further studied.

Figure 3. The OCP (a) and the PDS (b) of the carbon steel.

| Table 2. The Tafel fitting results of the PDS. |
|------------------------------------------------|
| E0(V vs. SCE) | B_a(mV) | B_c(mV) |
|----------------|---------|---------|
| In NaCl Solution | -0.744  | 93.7    | -130.5  |
| In imidazoline Solution | -0.715  | 102.8   | -187.2  |

3.2. WBE result
The distribution of the galvanic current was mapped by WBE measurement, shown in Fig. 4. In NaCl solution, localized corrosion initially appeared and then rapidly transformed into uniform corrosion. After 144 h, the anode area accounted for 80% of all the electrodes, and the current distribution was uniform. The maximum anode current density was $2.55 \times 10^{-7}$ A/cm². When the imidazoline was added, the anode area decreased rapidly, accounting for 30% to 40%. However, the maximum anode current density increased to $1.13 \times 10^{-6}$ A/cm². It indicated that serious localized corrosion occurred on the surface of the WBE. The pictures of the WBE were also taken by digital camera and are shown in Fig. 6. It can be seen that the rust layer of WBE was thinner and smaller in the solution with imidazoline. The uniform corrosion was inhibited while the localized corrosion was aggravated. Fig. 5 shows the distribution of the potential mapped by the WBE measurement. The potential increased when the inhibitor was added, which was in conformity with the electrochemical measurement. Meanwhile, there were several electrodes at lower potential that are consistent with the case in NaCl solution. This might be explained as the nonuniform adsorption of imidazoline on the surface of carbon steel. The galvanic current between the high potential area and the low potential area would increase the corrosion of the anode, the low potential area. Therefore, severe localized corrosion occurred on the carbon steel surface.
Figure 4. The current distribution of WBE, (a) 2 h, (b) 12 h, (c) 144 h, and the current distribution of WBE after adding imidazoline, (d) 2 h, (e) 12 h, (f) 144 h.

Figure 5. The potential distribution of WBE, (a) 2 h, (b) 12 h, (c) 144 h, and the potential distribution of WBE after adding imidazoline, (d) 2 h, (e) 12 h, (f) 144 h.
Figure 6. The picture of WBE after corrosion, (a) without inhibitor and (b) with 200 ppm imidazoline.

3.3. Morphology analysis
The layer of rust was removed after test and the surface morphology of specimens was analyzed using microscope, and the localized corrosion was investigated. The morphology image of steel surface after corrosion is shown in Fig. 7. In NaCl solution, the uniform corrosion occurred dominantly on the steel surface (Fig. 7a). When adding 200 ppm imidazoline into the solution, certain areas on steel surface (Fig. 7d) were protected from corrosion, as shown in Fig. 6b, thus the grinding marks on the surface are clear. Pits can be found at corrosion areas and non-corrosion areas, especially at the border area around the corrosion areas. It is indicated that the imidazoline inhibitor had inhibitory effect on the uniform corrosion, however, it aggravated the localized corrosion, which verified the conclusion drawn from the WBE measurement.

Figure 7. The morphology of the carbon steel after corrosion, NaCl solution (a) and imidazoline solution, (b) the area with serious corrosion, (c) the border area around the corrosion and (d) the area without corrosion.

4. Conclusions
The main results obtained from this work can be summarized as follows:
1) The imidazoline inhibitor could not only be used in acidic environment, but also be efficient in oxygen containing environment.
2) The imidazoline inhibitor acted as a mixed type, predominantly inhibiting the anodic reaction in the oxygen-containing environment.
3) Imidazoline can constrain the corrosion on the surface of carbon steel in oxygen-contained environment, however, it could aggravate the localized corrosion due to the damage of absorption film.

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References
[1] X. W. Zhou, Y. F. Shen, 2013, Acta Metall. Sin. 49(9), 1121-1130.
[2] C. F. Lu, M. X. Lu, G. X. Zhao, et al. 2003, Acta Metall. Sin. 39(8), 848-854.
[3] J. Zhang, 2008, Theoretical Investigation on Corrosion Inhibition Mechanism of Imidazoline Inhibitors, Ph.D. thesis, China University of Petroleum.
[4] V. Pandarinathan, K. Lepková, S. I. Bailey and R. Gubner, 2004, Corros. Sci. 72, 108-117.
[5] Y. Tan, Y. Fwu, K. Bhardwaj, 2011, Corros. Sci. 53(4), 1254-1261.
[6] Y. Huang, Y. Z. Xu, B. Li, et al, 2016, Corros. Eng. Sci. Techn. 51(3), 211-222.
[7] Y. Z. Xu, Y. Huang, L. Ying, et al, 2016, Journal of Materials Engineering, 44(10), 100-108.
[8] Y. Z. Xu, Y. Huang, L. M. He, et al, 2017, Anti-Corros. Method M. 64(2), 148-161.
[9] Y. Z. Xu, L. J. Yang, L. M. He, et al, 2016, Corros. Eng. Sci. Techn. 51(8), 606-620.
[10] L. J. Yang, Y. Z. Xu, Y. S. Zhu, et al, 2016, Int. J. Electrochem. Sci. 11, 6943-6958.
[11] G. A. Zhang, N. Yu, L. Y. Yang, et al, 2014, Corros. Sci. 86, 202-212.
[12] Y. Zhu, M. L. Free, R. Woollam, W. Durnie, 2017, Prog. Mater. Sci. 90, 159–223.
[13] P. Han, C. F. Chen, W. H. Li, H. B. Yu, Y. Z. Xu, L. Ma, Y. J. Zheng, 2018, J. Colloid Interf. Sci. 516, 398-406