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Research on Evaluation of Corrosion Inhibitors for Oxygen Reducing Air Drive Gas Wells

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Abstract: Severe CO_2 corrosion and O_2 corrosion occurred during the extraction of a certain gas well. Six commonly used corrosion inhibitors for a certain gas well were evaluated through indoor weight loss tests. It was found that the corrosion inhibition effect of No. 1 corrosion inhibitor in CO_2 and O_2 environments was the best compared to the other five corrosion inhibitors. The corrosion inhibition efficiency can be divided into 96% and 93%, and the dosage is small, which meets the requirements of the target gas well corrosion inhibitor. The corrosion inhibition mechanisms of the six corrosion inhibitors all conform to the adsorption mechanism, and their action mechanisms are all "negative catalytic" effects. Through adsorption, the activation energy of the cathodic and anodic reactions is increased, which hinders the occurrence of corrosion reactions. Among them, corrosion inhibitors 1, 2, 3, and 5 are mixed corrosion inhibitors that mainly inhibit anodic reactions, while corrosion inhibitors 4 and 6 are mixed corrosion inhibitors that mainly inhibit cathodic reactions.

Keywords: Evaluation of Corrosion Inhibitors; Oxygen Corrosion; Carbon Dioxide Corrosion; Corrosion Inhibitor Mechanism.

1. Introduction

In the middle and later stages of a certain gas well exploitation, due to the influence of water injection development, there is an increase in liquid accumulation inside the wellbore, and CO2 is present in the associated gas. When encountering water, it produces extremely strong corrosiveness, causing serious corrosion to metal equipment such as the wellbore and pipe columns. Moreover, due to the influence of oxygen reducing air drive, a large amount of oxygen is generated in the environment after gas lift, which poses a serious corrosion and safety threat to the outer wall of the wellbore [2]. Injecting corrosion inhibitors is a commonly used anti-corrosion measure in oil and gas fields, which has the characteristics of small dosage and significant effects. However, there are various types of corrosion inhibitors, and the effectiveness of corrosion inhibitors varies in different environments. Indoor evaluation of the effectiveness and applicability of corrosion inhibitors is an important factor in the rational application of corrosion inhibitors and the improvement of corrosion control level. Therefore, through indoor weightlessness tests, a study on the performance evaluation of gas well corrosion inhibitors were conducted to select suitable corrosion inhibitors, providing a basis for the application conditions of on-site corrosion inhibitors, ensuring the safe operation and stable production of target gas wells, and providing guidance and suggestions for corrosion protection of similar gas wells.

2. Experiment

2.1. Working Condition Parameters

Before conducting indoor evaluation tests on corrosion inhibitors, conduct research on the actual working conditions and corrosion environment of the target gas well, and the specific working conditions are as follows:

(1) Gas wells generally produce water, with an average mineralization degree ranging from 53000 to 64000 mg/L, but the distribution range of chloride ions is wide (19681 to 73344 mg/L).

(2) The temperature and pressure of the gas well are relatively high, with an average formation temperature of up to 100℃ and a pressure of 30MPa.

(3) The produced gas generally contains CO_2, with an average CO_2 content ranging from 0.16 to 0.78% (corresponding to a partial pressure of 0.03 to 0.39 MPa).

(4) Some gas wells adopt the nitrogen production lift process, and there is a small amount of oxygen content in the gas phase after membrane nitrogen production, ranging from 1% to 5%, corresponding to a partial pressure of 0.1MPa to 0.5MPa.

2.2. Sample

Process N80 and P110 raw steel into a size of 50mm × 10mm × A_3mm corrosion test piece with a 6mm hole on the end face for suspension. The test piece is polished step by step with sandpaper of no less than 600-1200 mesh, and then degreased and dehydrated with acetone and anhydrous ethanol. It is wrapped in filter paper, dried in a drying oven, and weighed for use. The chemical composition table of N80 and P110 steel is shown in Table 1.

Table 1. Chemical Composition of Samples

Material	C	Si	Mn	P	S	Cr	Ni	Cu	Fe
N80	0.24	0.22	1.50	0.013	0.002	0.037	0.03	0.09	margin
P110	0.32	0.30	0.50	0.02	0.01	0.15	0.10	0.10	margin

Test instruments: The main instruments used in the experiment are the SA-1 dynamic corrosion and scaling evaluation instrument. Other test instruments include auxiliary devices and tools such as an advection pump, vacuum pump, analytical balance, intermediate container, CO_2 cylinder, N_2 cylinder, etc.; The chemical reagents involved in the experiment (unless otherwise specified) should meet the national chemical purity standards.

Water sample compounding: Based on the ion composition analysis results of the formation water samples in the fluid produced by the reservoir (as shown in Tables 2), water sample compounding was conducted in the laboratory for testing. After compounding, the water sample was used for 45% µ M's membrane filtration treatment is ready for use.

Gas sample: Industrial pure CO_2 gas with a purity of 99.999%; Industrial pure N_2 gas with a purity of 99.9%; Industrial pure O_2 gas with a purity of 99.9%.

Table 2. Analysis results of ion composition of produced water samples

K^++Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	Salinity	water type
8199	14787.5	412.88	39871.2	221.2	63491.3	$CaCl_2$

Reagents: Select 6 commonly used corrosion inhibitors for the target gas well, and their types and main components are shown in Table 3.

Table 3. Types and main components of corrosion inhibitors

Corrosion inhibitor number	types	Main components
1	Pyridine quaternary ammonium salt	benzylpyridine chloride quaternary ammonium salt
2	Imidazoline	Rosin based imidazoline
3	Quinoline quaternary ammonium salt	Benzylquinoline chloride quaternary ammonium salt
4	Ketoaldehyde amine	Ketone aldehyde amine copolymer+ thiourea
5	Imidazoline	Thiourea imidazoline
6	Ketone aldehyde amine	Ketone aldehyde amine copolymer+ phenylpropanetriazole

2.3. Test Process and Principle

The test process refers to the weight loss method in the national recommended standards GB/T 16545-2015 "Corrosion of Metals and Alloys: Removal of Corrosion Products on Corrosion Specimens" and JB/T 6073-92 "Full Immersion Corrosion Test in Metal Coatings Laboratory". The test piece is hung in a dynamic corrosion tester to simulate the corrosion of the test piece under various working conditions. The test process is shown in Figure 1.

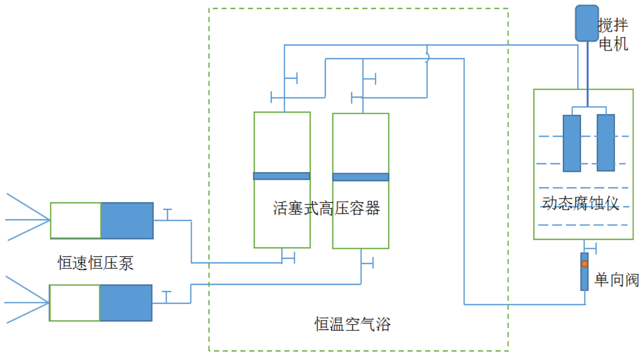

Fig 1. Flow chart of dynamic corrosion evaluation experiment

Before the experiment, the hanging piece should be wiped clean with filter paper, and then placed in a vessel containing petroleum ether with a boiling range of 60-90 ℃. After removing the surface grease of the hanging piece with a degreased cotton ball, it should be soaked in anhydrous ethanol for 5 minutes to further degrease and dehydrate. After removing the grease, place the hanging piece on a filter paper, dry it with cold air, and then wrap the hanging piece with filter paper. Place it in a dryer and weigh the weight before weight loss for one hour, accurate to 1mg. The experiment was conducted in the SA-1 dynamic corrosion and scaling evaluation instrument. The test solution and test specimens were first placed in the reactor, and the reactor was evacuated and treated with a vacuum pump for 30 minutes. Then, CO2 gas was introduced into the reactor according to the test pressure requirements. Finally, nitrogen gas was continued to be introduced to meet the total test pressure requirements and the speed was adjusted.

After the experiment is completed, the test solution is discharged from the reactor, and the test piece is taken out from the reactor. It is further decontaminated and dehydrated with petroleum ether and anhydrous ethanol, and the surface corrosion products are removed with hydrochloric acid cleaning solution. The test piece is rinsed with water and immediately washed and dehydrated in anhydrous ethanol. After drying with cold air, it is weighed. Record the weight loss of the test pieces before and after the test. Take three test pieces from each group for parallel testing, and calculate the uniform corrosion rate of the test pieces using Equation 1-1. Take the average value of the three test pieces for each group of data, and calculate the corrosion inhibition efficiency using Equation 1-2.

$$v = \frac{87600 \times (m_1 - m_2)}{S \cdot t \cdot \rho} \tag{1}$$

In the formula: v - corrosion rate, mm/a; m_1- Mass of test piece before test, g; m_2- mass of test piece after cleaning, g; S - Exposed area of the test piece, $cm_{2;}$ T - experimental time, h; ρ - Relative density, g/cm_3

$$\eta_1 = \frac{\Delta m_0 - \Delta m_1}{\Delta m_0} \tag{2}$$

In the equation, η_1 is the uniform corrosion inhibition rate, %; Δm_0 is the mass loss of the test piece in the blank test, g; Δm_1 is the mass loss of the test piece in the dosing test, g.

2.4. Test Conditions

Based on the analysis of the temperature and pressure characteristics of the target gas well reservoir and the output fluid characteristics, the experimental conditions for this indoor evaluation test are determined, as shown in Table 4.

Three parallel samples are taken from each group of tests, and the control group has a dosing concentration of 0.

Table 4. Test Conditions

Norrosion type	Steels	Pressure MPa	temperature ℃	CO_2 partial pressure MPa	Cl - concentration mg/L	Experimental time h	Dosing concentration mg/L
CO_2	N80, P110	30	100	0.4	50000	72	200
O_2		10	100	0.5	50000	72	200

3. Testing Results and Analysis

The corrosion rate and inhibition rate results of six corrosion inhibitors under CO_2 partial pressure of 0.4MPa are shown in Figures 2 and 3. Analysis shows that the anti-corrosion performance of N80 steel is better than that of P110 steel in CO_2 environment. The order of the six corrosion inhibitors' CO_2 corrosion resistance from strong to weak is: 1>6>3>2>4>5. The addition of corrosion inhibitor No. 5 actually promoted the CO_2 corrosion of the test piece, with inhibitor No. 1 having the best effect. The corrosion rate of N80 steel was 0.038mm/a, and that of P110 steel was 0.044mm/a, All are within the required range of the oil and gas industry standard SY/T5329-94 "Recommended indicators and analysis methods for water injection quality in clastic rock reservoirs" (<0.076mm/a, the corrosion inhibition rates for N80 steel and P110 steel are 96.13% and 96.38% respectively; the corrosion inhibition effect of No. 2-4 corrosion inhibitor after injection is average, both below 90% and not meeting the corrosion inhibition requirements; No. 5 corrosion inhibitor after injection does not have a corrosion inhibition effect but promotes corrosion reaction; No. 6 corrosion inhibitor after injection, the corrosion inhibition rate can reach over 90%, but the corrosion rate of P110 steel does not meet the standard requirement of 0.076mm/a.).

The corrosion rate and inhibition rate results of six corrosion inhibitors under 0.5 MPa O_2 partial pressure are shown in Figures 4 and 5. Analysis shows that in the O_2 environment, No. 1 corrosion inhibitor has the best effect, with a corrosion rate of 0.48 mm/a for N80 steel and 0.433 mm/a for P110 steel. The corrosion inhibition rates for N80 steel and P110 steel are 93.47% and 94.01%, respectively; The effectiveness of corrosion inhibitors 2-5 has a small difference, all around 80%; The corrosion inhibitor No. 6 has a poor effect, with a corrosion rate of 2.586mm/a for N80 steel and 3.078mm/a for P110 steel. The corrosion inhibition rates for N80 steel and P110 steel are 64.79% and 57.47%, respectively.

The 1st and 3rd corrosion inhibitors belong to the pyridine quaternary ammonium salt corrosion inhibitors and quinoline quaternary ammonium salt corrosion inhibitors, both of which are mainly composed of quaternary ammonium salt compounds and have benzyl chloride groups. Quaternary ammonium salt compounds are a widely used adsorbent corrosion inhibitor and are commonly used as the main inhibitor. [4] In aqueous solution, these compounds can completely dissociate into positively charged quaternary ammonium cations and halogen anions. Quaternary ammonium cations can undergo physical adsorption in the cathode area of the metal surface, i.e., electrostatic adsorption occurs between quaternary ammonium cations and negatively charged metal surfaces in the acid solution, which has a significant impact on hydrogen ion discharge and can effectively prevent H+from approaching the metal surface, thereby inhibiting the reduction reaction of H+and inhibiting the cathodic reaction. The Cl^- in quaternary ammonium salts has a certain synergistic effect on the corrosion inhibition of iron, promoting the adsorption of organic cations on the metal surface to form a stable protective film. Its hydrophobic non-polar groups are oriented away from the metal surface, effectively preventing the diffusion of corrosion products such as iron ions into the solution and the migration of hydrogen ions into the metal during the corrosion reaction process. From an electrochemical perspective, the corrosion inhibition effect of this type of corrosion inhibitor belongs to the "negative catalytic" effect of interfacial corrosion inhibitors. After the corrosion inhibitor or its reaction product is adsorbed on the metal surface, it affects one or both of the anodic and cathodic reactions of the corrosion process like a catalyst, or simultaneously affects both reactions, causing their reaction activation energy barrier to increase or decrease. If the corrosion inhibitor increases the activation energy barrier of the reaction, the reaction rate decreases, and the corrosion inhibitor plays a "negative catalytic" role in the reaction [5-8]. The No.1 and No.3 corrosion inhibitors increase the "activation energy" required for corrosion reactions due to adsorption, thereby slowing down the progress of corrosion reactions. They suppress both anodic and cathodic electrode reactions through chemical adsorption on the anode and physical adsorption on the cathode, but have a stronger inhibitory effect on the anodic reaction. Therefore, corrosion inhibitors 1 and 3 are also mixed corrosion inhibitors that mainly suppress anodic reactions.

The 2nd and 5th corrosion inhibitors are imidazoline type corrosion inhibitors, and their corrosion inhibition mechanism can also be explained by adsorption theory. Multiple adsorption centers (such as N, O and other elements) in the main product molecules of corrosion inhibitors provide lone pair electrons to the metal surface, forming coordination bond compounds that adsorb on the bare metal surface without an oxide film; Then, the non-polar groups (thiourea and rosin groups) in the molecule are laid flat on the metal surface, forming a relatively complete hydrophobic protective layer, forming a barrier between the metal and preventing the diffusion of corrosion products such as iron ions into the solution and the migration of H^+into the metal during the corrosion reaction process, slowing down the corrosion reaction speed and achieving the goal of metal corrosion inhibition. The corrosion inhibition mechanism of such inhibitors is also a "negative catalytic" effect [9-11]. After the addition of corrosion inhibitor No. 5, the corrosion became more severe. It is speculated that the reason is that the environmental temperature is high, and the amount of corrosion inhibitor added results in incomplete film formation after the addition of No. 5 corrosion inhibitor. The high content of chloride ions in the water sample exacerbates local corrosion of the sample.

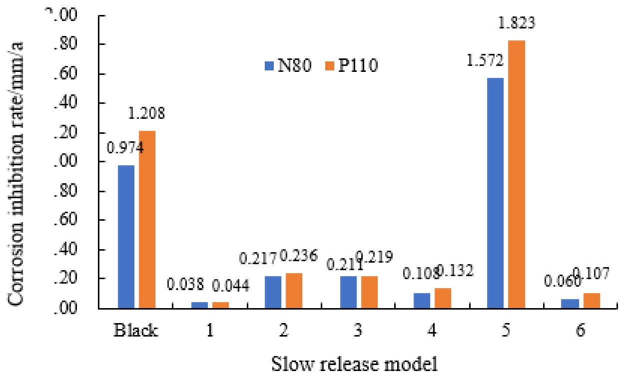

Fig 2. CO_2 corrosion rate result chart

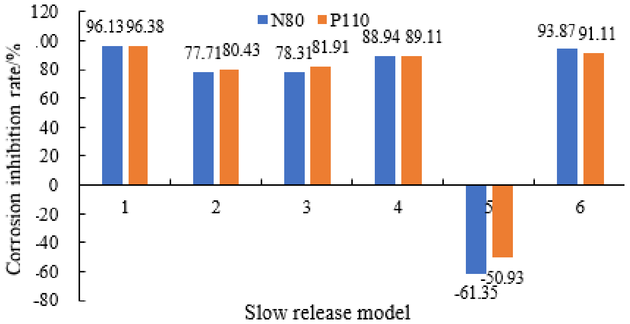

Fig 3. CO_2 Corrosion inhibition rate result chart

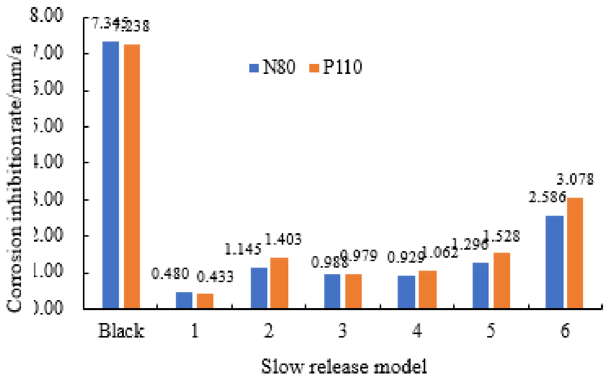

Fig 4. O_2 Corrosion Rate Result Chart

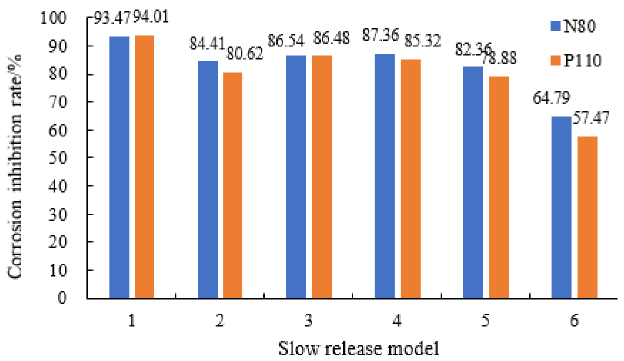

Fig 5. O_2 corrosion inhibition rate result chart

The main inhibitors of No. 4 and No. 6 are ketone aldehyde amine copolymers, also known as Mannich bases. Their corrosion inhibition mechanism is also adsorption. Mannich bases are chelating ligands, and the lone pair electrons of their coordination atoms enter the hybrid empty orbitals of $Fe^{3+}$to form coordination bonds, which undergo complexation reactions and form stable cyclic chelates that adsorb on the metal surface, forming a stable hydrophobic protective film, thereby preventing the diffusion of Fe^{3+}generated by corrosion into the solution, At the same time, it hinders the cathodic reaction process of H^+moving towards the metal direction, in order to achieve the goal of metal corrosion inhibition. The corrosion inhibition mechanism can also be summarized as a mixed type corrosion inhibitor that mainly suppresses cathodic processes, and the corrosion inhibition mechanism is a "negative catalytic effect". That is, aldehyde ketone amine corrosion inhibitor forms a protective film by adsorbing on steel sheets, increasing the activation energy of anodic and cathodic reactions to reduce the reaction rate, thereby reducing the corrosion rate and achieving the effect of corrosion inhibition [12-14].

4. Conclusion

(1) Indoor weight loss evaluation tests were conducted on six commonly used corrosion inhibitors in oil and gas fields. Among them, the corrosion inhibition effect of No. 1 corrosion inhibitor in CO2 and O2 environments was the best compared to the other five corrosion inhibitors, with corrosion inhibition efficiency reaching 96% and 93% respectively, and the dosage was small, meeting the requirements of the target gas well corrosion inhibitor.

(2) The corrosion inhibition mechanisms of the six corrosion inhibitors all conform to the adsorption mechanism, and the action mechanism is a "negative catalytic" effect. Through adsorption, the activation energy of the cathodic and anodic reactions is increased, which hinders the occurrence of corrosion reactions. Among them, corrosion inhibitors 1, 2, 3, and 5 are mixed corrosion inhibitors that mainly inhibit anodic reactions, while corrosion inhibitors 4 and 6 are mixed corrosion inhibitors that mainly inhibit cathodic reactions.

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