Evaluation and Optimization of Corrosion Inhibitor System

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Abstract: By combining two methods of weightlessness and electrochemistry, the corrosion inhibitors have been selected and optimized. The orthogonal experiment has been carried out to optimize the inhibitor’s performance. The range analysis results indicated that corrosion inhibition performance of optimized corrosion inhibitor (HZ-1) has been improved remarkably. The corrosion inhibition rate can reach 94.66% with lower corrosion current density. The optimum concentration of HZ-1 is 90 mg/L and working temperature is 80~100℃. Its site application shows that the inhibitor also has remarkable corrosion inhibition effect, the concentration of iron ions is decreases, and the period of pumping wells has been prolonged significantly.

1. Introduction
With the oilfield entering the high water cut development stage, oil well corrosion is becoming seriously. According to statistics, there are more than 30% oil wells having corrosion phenomena in Huabei Oilfield. Among them, the pump inspection cycles of 825 wells are less than one year, accounting for more than 50% of the number of production wells. Because of the synergistic effect of chloride ion, hydrogen sulfide, free carbon dioxide, bacteria and other corrosion factors in the fluid of oil wells, it is very difficult to control the corrosion of oil wells[1]. There are variety of corrosion inhibitors in the market which make the traditional screening experiments have a lot of problem such as large workload, long cycle and lacking pertinence. It is really an urgent problem to effectively improve the study level for the typical problems existing in oil well corrosion. The research of new type corrosion inhibitor has been developed according to the liquid characteristics of oil wells in Huabei Oilfield.

2. Experiment methods

2.1. Experiment materials and instruments
Experiment materials: anhydrous ethanol; petroleum ether; sodium chloride; magnesium chloride; sodium sulphate; calcium chloride; sodium bicarbonate; steels N80(72mm×12mm×2mm);

Experiment instruments:
CT-2 potentiostat (Huazhong university of science and technology);
Electric blast drying oven (Shanghai experimental instrument company);
Multi-parameters water quality tester (Shanghai experimental instrument company).
2.2. Experiment design

2.2.1. Simulated fluid
According to the standard of produced fluid, the fluid has been prepared to simulate characters and environment in oil wells. The salinity of simulated fluid is between 5000~70000 mg/L.

| Component | NaCl | MgCl₂·6H₂O | Na₂SO₄ | CaCl₂ | NaHCO₃ |
|-----------|------|------------|--------|-------|--------|
| ρ, g/L    | 50   | 2          | 6      | 4     | 4      |

2.2.2. Electrochemical evaluation experiment
The electrochemical specimens have been prepared according to the standard GB/13671-92. The N80 steel specimens have been sealed by high temperature resistant resin with a surface area of 1 cm² at the exposed end. The reference electrode, auxiliary electrode and working electrode of CT-2 potentiostat respectively are saturated calomel electrode, platinum electrode and N80 working electrode.

Add chemicals into the simulated fluid, and the ion concentration of the solution is 80mg/L. Then potential scanning has been carried out at 70°C using CT-2 potentiostat. The scanning is ranged from -250 mV to 250 mV relative to the natural corrosion potential, and the scanning rate is 0.5mV/s. The polarization curves of the solution are obtained.

2.2.3. Weightlessness evaluation experiment
According to the standard of SY/T5273-2000, the corrosion rate and inhibiting rate under different corrosion conditions have been evaluated. The corrosion experiments have been carried out in wide-mouth bottles of 500ml. The experiments are during seven days. After the corrosion experiments the loss weights of steel sheets have been measured, and the corrosion rate and corrosion inhibition rate have been calculated according to the following formula.

\[ r_{\text{corr}} = \frac{8.76 \times 10^4 \times (m_0 - m_i)}{s t \rho} \times 100\% \]  \hspace{1cm} (1)

\( r_{\text{corr}} \) — corrosion rate, mm/a;
\( m_0 \) — test specimens quality before experiment, g;
\( m_i \) — test specimens quality after experiment, g;
\( s \) — corrosion surface area of specimens, cm²;
\( t \) — corrosion time, h;
\( \rho \) — density of specimen material, g/cm³;
\( \eta \) — corrosion inhibiting rate, %.

\[ \eta = \frac{\Delta m_0 - \Delta m_i}{\Delta m_0} \times 100\% \]  \hspace{1cm} (2)

\( \eta \) — corrosion inhibiting rate, %;
\( \Delta m_0 \) — loss quality in blank sample, g;
\( \Delta m_i \) — loss quality in adding chemical sample, g;

2.2.4. Ion analysis
The concentration of total iron and ferrous ions has been measured by the field water quality rapid tester.

3. Experiment results and discussions

3.1. Primary selection of different inhibitors
Imidazoline corrosion inhibitors, as a new and broad-spectrum corrosion inhibitor, have good corrosion inhibition effect on carbon steel in fluid containing CO₂[2]. They also have the
characteristics of good thermal stability and low toxicity[3]. They are widely used in oil field at home and abroad.

Firstly, four different types of imidazoline corrosion inhibitors have been screened according to the properties of the produced fluid in Huabei oil field. As the evaluation result shows in Figure 1, HS-2 cationic corrosion inhibitor has the best performance in four inhibitors. The corrosion potential has the maximal negative displacement in the polarization curves. But HS-2 also needs more optimization to attend satisfied performance in field application.

![Figure 1. The electrochemical evaluation results of inhibitors](image)

3.2. Formulation system optimization

According to the field requirements, the selected HS-2 needs to be optimized. Therefore, FJ-1, FJ-2 and FJ-3 additives have been added together which have been selected according to the corrosion characteristics of oil wells and polarization curves. The experiment design has been carried out according to L₉(3⁴) orthogonal table as shown in Table 2. The inhibition efficiency has been evaluated by static weightlessness method, the concentrations of the corrosion inhibitors are 80mg/L, and the temperature is 70 ℃.

The range analysis has been carried out on the weightlessness experiment results. The analysis indicates that the order of chemicals impacting the inhibitor’s performance is HS-2, FJ-1, FJ-3, FJ-2 from high to low. Nine groups of experiments have been carried out. The optimal level is group 1 named HZ-1, and the ratio of HS-2, FJ-1, FJ-2 and FJ-3 is 20:20:2:2. The performance of the initial corrosion inhibitor has been significantly improved, and the corrosion inhibiting rate reaches 94.66% with no pitting corrosion.
Table 2. The result of orthogonal experiment

|   | HS-2 | FJ-1 | FJ-2 | FJ-3 | ηi, % |
|---|------|------|------|------|-------|
| 1 | 20   | 20   | 2    | 2    | 94.66 |
| 2 | 20   | 10   | 1    | 1    | 90.25 |
| 3 | 20   | 5    | 0.5  | 0.5  | 89.03 |
| 4 | 10   | 20   | 1    | 0.5  | 87.43 |
| 5 | 10   | 10   | 0.5  | 2    | 85.50 |
| 6 | 10   | 5    | 2    | 1    | 85.00 |
| 7 | 5    | 20   | 0.5  | 1    | 84.21 |
| 8 | 5    | 10   | 2    | 0.5  | 82.11 |
| 9 | 5    | 5    | 1    | 2    | 83.23 |
| K₁ | 273.94 | 266.3 | 262.89 | 263.39 |
| K₂ | 257.93 | 257.86 | 260.91 | 259.46 |
| K₃ | 248.55 | 257.26 | 258.74 | 258.57 |
| k₁ | 91.31  | 88.77  | 87.63  | 87.80  |
| k₂ | 85.98  | 85.95  | 86.97  | 86.49  |
| k₃ | 82.85  | 85.75  | 86.25  | 86.19  |
| R  | 8.46   | 3.02   | 1.37   | 1.61   |

3.3. Performance evaluation of optimization formulation system

3.3.1. Evaluation of electrochemical performance

![Figure 2. The polarization curves before and after mixing](image)

By comparing two polarization curves before and after optimization, the current density decreases obviously after optimization, which indicates that additives have good synergistic effect. It forms a continuous and compact protective film on the metal surface. The FJ-1 shows weak alkaline and therefore it plays the role of dissolving free carbon dioxide in water and adjusting pH value[4]. At the same time, it also contains a lone pair of electrons, which is profit the molecular structure of imidazole rings to fill into the empty d orbit of iron, thus forming a stable multicentre adsorption structure[5]. This structure is favourable to form an adsorption film on the metal surface by directional alignment of corrosion inhibitor molecules, which are closely wrapped around the metal surface like a network[6]. The additive FJ-2 effectively controls the growth of bacteria and algae in production fluid, so the corrosion inhibition efficiency is grown better after using. The FJ-3 forms stable complex compounds with various metal ions, and dissolves some oxides on the metal surface, which help the main agent to form protective film on the metal surface.

3.3.2. The influence of concentration

Through the weightlessness method find the optimum concentration of optimization inhibitor in different blocks. The experiment time is 7 days, the temperature is 70 ℃, and the concentration
respectively are 60 mg/L, 70 mg/L, 80 mg/L, 90 mg/L and 100 mg/L.

Because imidazoline corrosion inhibitors belong to adsorption type, the adsorption capacity on the metal surface increases with the concentration of inhibitor. The inhibitor molecules are aligned on the metal surface to form a more complete protective film. It shows the inhibition rate reaches 97.8% when the inhibitor concentration is 90 mg/L, and a complete protective film formed on the metal surface with strong anti-corrosion ability.

3.3.3. The influence of temperature

Because Huabei Oilfield belongs to a complexity fault reservoirs with different reservoir temperatures in each block, it is necessary to study the influence of temperature on corrosion inhibition. The static corrosion evaluation experiment has been carried out at five different temperatures from 80℃ to 120℃ using producing liquid from C19-109 oil well, the concentration of HZ-1 is 90 mg/L, and the experiment lasted 7 days.

The corrosion rate decreases slowly when the temperature is range from 80℃ to 100℃. But when the temperature is above 100℃ the corrosion inhibition rate decreases rapidly. The corrosion inhibition rate decreases to only 51.9% when the temperature is 120℃. The surfaces of steel sheets are darkness and lots of the corrosion productions have been accumulated at the bottom of bottle. The result shows that the HZ-1 performance is relatively stable when the temperature at range of 80℃ to 100℃. But it is easy to break the molecular bond at high temperature which leads to lack integrity of the adsorption films on the metal surface. Therefore, the formulation HZ-1 is suitable for oil wells below 100℃.

4. Field Application

Well c19-22 has been selected to evaluate the application effect. The production fluid is 31m³/d, and the water cut is 97%. It has been found a serious corrosion in April 2010. The 144th rod has been
severely corroded and broken. The average pump inspecting period was only 193 days.

Through the analysis of the production liquid from well c19-22, the free CO$_2$ concentration is 26.7 mg/L, the bacterial content of SRB is 12/ml, the salinity is 18641 mg/L, and the chloride ion concentration is 10599 mg/L. According to the corrosion characteristics of rods and pipes in site, the optimized HZ-1 formula has been selected to use. Through indoor evaluation the corrosion inhibition rate of HZ-1 has reached 86.7%. Thus it has been selected for corrosion treatment in well c19-22, and the adding chemical period is 7 days. In order to investigate the long-term corrosion treatment effect, a half-year monitoring is carried out as shown in Figure 7.

The field monitoring indicates that the ion indexes have a significant downward trend after using 3 days. The total iron concentration has decreased from 18.80 mg/L to 0.70 mg/L and remained at about 1 mg/L for a long term. The ferrous ion has also decreased from 18.50 mg/L to 0.63 mg/L. The period of pump inspection has been prolonged from 193 days to 966 days after application. The corrosion situation is grown better and the corrosion trend has been restrained significantly.

Figure 7. The long term ion monitoring results

5. Conclusion
According to the characteristics of oil wells produced fluid in Huabei oil field, different types of corrosion inhibitors have been selected, optimized and evaluated by electrochemical method and weightlessness method. The range analysis shows that the formulation HZ-1 has good corrosion inhibition performance and its inhibition rate is above 90%. The well c19-22 application indicates that optimized HZ-1 has satisfied corrosion inhibition effect. After application the concentration of iron ions decrease significantly, the period of pump inspection has been prolonged significantly, and the corrosion situation on site has been inhibited.

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