Inhibitory anticorrosive protection of oilfield equipment

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Abstract. Corrosion is one of the main causes of oilfield equipment failures. The reason is that the metal contacts with process media with high corrosion activity. Due to corrosion failures, the cost of current and unscheduled repairs of oilfield equipment, as well as the reduction of its amortization periods, is rising. A widely used method of corrosion protection of the internal surface of oilfield equipment is inhibitory protection. This paper presents an assessment of the effectiveness of the use of three new corrosion inhibitors for the protection of low carbon and some low alloy steels in the fields medium of one of the oil fields.

1. Introduction
There are three main types of corrosion of equipment and pipelines in oil production field, determined by the influence of gas dissolved in ground water: carbon dioxide, oxygen and hydrogen sulfide corrosion. Carbon dioxide can exist in an aqueous solution in the form of undissociated carbonic acid molecules, bicarbonate ions $\text{HCO}_3^-$, and carbonate ions $\text{CO}_3^{2-}$ [1-4]. In this case, the following reactions occur in the solution:

$$X\text{O}_2 + H_2O \leftrightarrow H_2X\text{O}_3 \leftrightarrow H^+ + HX\text{O}_3^- \leftrightarrow 2H^+ + XO_3^{2-}.$$

Hydrogen depolarization on the cathode sites of the metal occurs by the reaction:

$$2H^+ + 2e^- \rightarrow 2H \rightarrow H_2 \uparrow,$$

and iron is binded on the anode zones in one of three reactions:

$$\text{Fe}^{2+} + \text{CO}_3^{2-} = \text{FeCO}_3; \quad \text{Fe}^{2+} + \text{HCO}_3^- = \text{FeCO}_3 + H^+; \quad \text{Fe}^{2+} + H_2\text{CO}_3 = \text{FeCO}_3 + 2H^+.$$

General, pitting and crevice metal corrosion can be observed in the presence of carbon dioxide [5,6]. In this regard, increased attention is paid to the methods of protecting of oil equipment and facilities from corrosion destruction. The method of inhibitory protection of metals against various types of corrosion is one of the most effective and approved [7-14].

The aim of this research was to evaluate the protective efficiency of three new corrosion inhibitors based on quaternary ammonium compounds under the conditions of corrosion of steels C1020 (rus 20), A 516-55 (rus 09Г2С) and 13CrV (rus 13ХФА) in model solution (MS), simulating the ground water of one of the fields of OJSC "Surgutneftegas".

2. Experimental
Studies were performed on samples of the above mentioned steels in a model solution with the following composition (g/l): NaCl – 17; CaCl$_2$ – 0.14; MgCl$_2$ – 0.9; NaHCO$_3$ – 0.633.
Gravimetric tests were performed during 118 and 138 hours. To determine the mass loss, the surface of the samples after exposure in a corrosive medium was washed with tap water, cleaned of corrosion products with a soft eraser, and then degreased with acetone [15-20]. After an hour of exposure in an oven at 40 ° C, the weighing was carried out on an analytical balance with an accuracy of 0.0001 g. The protective efficiency of each type of inhibitor was determined by the formula

\[ Z = \frac{K_0 - K_1}{K_0} \times 100\%, \]  

where \( K_0, K_1 \) – the corrosion rates of steel samples in the control medium (without inhibitor) and in the medium with inhibitor.

Polarization curves were obtained using an Elins P-30J potentiostat with a potential sweep rate of 2 mV/s in a three-electrode clamping electrochemical cell. A silver chloride electrode was used as a reference electrode, the auxiliary electrode was made of platinum.

The corrosion rate by the method of polarization resistance was determined using the Monicor-2M corrosion meter. The polarization of the main electrode into the cathode and anode region from the corrosion potential was ± 10 mV; the value of the ba and bk coefficients was 120 mV; the duration of polarization in the cathode and anode regions - 30 s.

The following corrosion inhibitors developed in [21] were analyzed:

1. The product obtained by condensation of polyethylene polyamine with 1,2-dichloroethane with formation of high-molecular compounds of a cyclic structure (Corazil-1 inhibitor).
2. Based on triethanolamine (0.1 % aqueous solution), 85 % orthophosphoric acid and water in a molar ratio of 1: 0.5: 10, respectively (Corazil-2 inhibitor).
3. Based on triethylamine and 1,3-dichloropropene (Corazil-3 inhibitor).

3. Results and discussion

A film of corrosion products was formed on the surface of the samples after gravimetric tests. It was established that an increase of inhibitors concentration in the model medium led to decrease in the thickness of the deposit layer on the steel surface (figures 1, 2).

![Figure 1. Appearance of steel A 516-55 samples after gravimetric tests in the control medium and the medium with different contents of the inhibitor Corazil-1.](image)

![Figure 2. Appearance of steel A 516-55 samples after gravimetric tests in the control medium and the medium with different contents of the inhibitor Corazil-2.](image)

During the processing of data obtained by the gravimetric method, it was found that when inhibitors are added to the model medium, corrosion rates of 13CrV and A 516-55 steels decrease significantly. Corazil-3 with a content of 60 and 80 g/t (for steel A 516-55) showed efficiency above 80 %. In the case of 13CrV steel, the maximum efficiency was 64 % at an inhibitor dosage rate of 80 g/t.

Results of gravimetric tests are presented in figure 3.
Results of polarization studies for the most effective dosage rates of the reagents according to gravimetric analysis are presented in figure 4 and in table 1.

| Table 1. Results of polarization studies. |
|------------------------------------------|
| \( a_a \) | \( b_a \) | \( a_k \) | \( b_k \) | \( i, \text{A/m}^2 \) | \( K_{mp}, \text{g/m}^2\text{•h} \) | \( P, \text{mm/year} \) |
|-----|-----|-----|-----|-----|-----|-----|
| A 516-55 |
| MS | 61.023 | 26.763 | -47.245 | -30.543 | 0.02574 | 0.0268 | 0.0298 |
| MS + Corazil-1, 80 g/t | 179.113 | 94.654 | 166.852 | -104.102 | 0.00005 | 0.00005 | 0.00006 |
| MS + Corazil-2, 80 g/t | 103.409 | 35.102 | -50.587 | -25.868 | 0.0128 | 0.0133 | 0.01485 |
| MS + Corazil-3, 60 g/t | 53.407 | 22.752 | -55.189 | -34.883 | 0.02259 | 0.023513 | 0.02621 |
| 13CrV |
| MS | 79.551 | 21.230 | -51.887 | -22.507 | 0.05076 | 0.05284 | 0.0588 |
| MS + Corazil-1, 40 g/t | 81.363 | 21.697 | -43.205 | 0.00876 | 0.009118 | 0.01016 |
| MS + Corazil-2, 80 g/t | 70.294 | 20.355 | 109.264 | -26.81 | 0.01535 | 0.015979 | 0.0178 |
| MS + Corazil-3, 80 g/t | 68.559 | 21.522 | -53.387 | -26.81 | 0.0197 | 0.020586 | 0.0229 |

The mass and corrosion depth rates, as well as protective efficiency of inhibitors were determined using the construction and analysis of polarization diagrams. The values of the tafel coefficients of the anodic \((a_a, b_a)\) and cathodic \((a_k, b_k)\) branches of the polarization diagram were calculated by the method of their approximation.

The tangent to the cathode curve at a point of overvoltage \(-20\text{ mV}\) from the corrosion potential is described by the equation (if the model medium contains 80 g/t of Corazil-1 inhibitor):

\[
\lg I = -166.8E -104.1.
\]

The tangent to the anode curve at the point of over voltage of \(+20\text{ mV}\) from the corrosion potential:
The point of intersection of the tangents corresponds to the potential and corrosion current density of the two electrode system:

\[-166.8E - 104.1 = 179.1E + 94.6;\]

\[\lg I_{\text{corr}} = -8.246 \quad \text{and} \quad I_{\text{corr}} = 0.00000001 \ \text{A} / \text{m}^2.\]

Mass rate of corrosion

\[K_m = \frac{I_{\text{corr}} \cdot A \cdot 3600}{96487 \cdot S \cdot n} = \frac{i_{\text{corr}} \cdot A}{268 \cdot n},\]

(2)

where: \(I_{\text{corr}}\) – corrosion current, A; \(A\) – atomic mass of metal, g/mol; 3600 – the number of seconds in an hour; 96487 – Faraday number, C/mole (A·s/mol); \(S\) – contact surface of the metal, m\(^2\); \(n\) – the valence of the metal.

After substitutions, we obtain \(K_m = 0.000052 \ \text{g/m}^2\cdot\text{h}\).

Depth rate of corrosion

\[P = \frac{K_m \cdot 8760 \cdot 10^{-3}}{\rho},\]

(3)

where: \(\rho\) – metal density, g/cm\(^3\); 8760 – number of hours per year; \(10^{-3}\) – conversion factor.

Thus, \(P = 0.000058 \ \text{mm/year}\).

Corazil-1 inhibitor, therefore, proved to be very effective, because corrosion rate and corrosion current density have rather small values.

It can be seen from the diagram presented in Figure 4 that in a model solution of ground water the corrosion potential for A 516-55 steel sample is 0.53 V. Introduction of 80 g/t of Corazil-1 (figure 5) not only reduces corrosion rate, but also shifts the potential to negative values of –0.58 V. This indicates that this reagent is the cathode type inhibitor. The protective efficiency of this inhibitor dosage rate was 99.8 %.

\[\text{Figure 4. Polarization diagrams of the steel A 516-55 in a MS.}\]
Figure 5. Polarization diagram of the steel A 516-55 in a MS + Corazil-1 (80 g/t).

Polarization diagrams analysis for 13CrV steel indicates that the introduction of 40 g/t Corazil-1 or 80 g/t Corazil-2 leads to a shift of the corrosion potential to the negative values from - 0.33 V to - 0.34 and - 0.38 V, respectively. This phenomenon is associated with the activation of the anodic corrosion process. However, this reduces the corrosion loss of the metal, since the corrosion products formed as a result of the anodic reaction prevent the interaction of the corrosive medium with the steel surface. It is worth noting that Corazil-2 is also an inhibitor of cathodic type. For 13CrV steel protective efficiency of Corazil-1 at a dosage rate of 40 g / t was 82.7 % and Corazil-2 with a dosage rate of 80 g/t - 69.7 %.

Table 2 presents the main results of research.

Table 2. The maximum efficiency of tested inhibitors for different steels.

| Inhibitor   | Maximum efficiency, % |
|-------------|-----------------------|
|             | C1020       | A 516-55      | 13CrV       |
| Corazil-1   | 47 (m)      | 99.8 (p)      | 82.7 (p)    |
| Corazil-2   | 68 (m)      | 58.7 (g)      | 69.7 (p)    |
| Corazil-3   | 40 (m)      | 84.3 (g)      | 63.5 (g)    |

m - polarization resistance method, g - gravimetric analysis, p - potentiodynamic method.

4. Conclusions

It has been established that an increase of the inhibitors Corazil-1, Corazil-2 and Corazil-3 dosage rate in a model medium that simulates the ground water of the oil field OJSC «Surgutneftegaz» leads to significant decrease of corrosion rate of common pipe steels.

Studied inhibitors have shifted the corrosion potential of steels to negative values, that is, they are cathode type inhibitors.

Inhibitors Corazil-1 and Corazil-3 showed the greatest protective efficiency (99.8 and 84.3 %, respectively) for steel A 516-55. It is recommended to use the inhibitor Corazil-1 for corrosion protection of steel 13CrV. At the same time, all the tested inhibitors were ineffective in the case of C1020.

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