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STUDY OF THE CORROSION PROTECTION EFFECT OF THE NEW COMPOSITION BASED ON GOSSYPOL RESIN IN THE HYDROGEN SULFIDE FORMATION WATER

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We investigated the impact of a new composition (HS-1) composed of gossypol resin and IB-1 reagent taken in the ratio of 3:1 on the corrosion rate in the hydrogen sulfide formation water under laboratory conditions. Concentrations of 20, 40, 60 and 80 mg/l of the new composition were used. The formation water sample taken from well No. 1082 of «Bibiheybatneft» OGPD, SOCAR was used as an corrosion medium. The corrosion effects were also investigated at the concentrations of 50, 100, 150 and 200 mg/l of gossypol resin and 10, 15, 20 and 25 mg/l of IB-1 inhibitor. When the concentration of gossypol resin in the formation water increased by 50–200 mg/l, the corrosion protection effect took a value in the range of 60–82%. When the concentration of IB-1 inhibitor varied between 10–25 mg/l in a hydrogen sulfide medium, the protection effect was between 65–90%. Increasing the concentration of new HS-1 composition in the range of 30–80 mg/l resulted in an increase in its corrosion protection effect between 74–98%. It was found that the optimal consumption rate of gossypol resin, IB-1 inhibitor and HS-1 composition for corrosion protection in an aggressive medium with hydrogen sulfide was 200 mg/l, 25 mg/l and 80 mg/l, respectively.

Keywords: hydrogen sulfide, reagent, inhibitor, corrosion rate, formation water, optimal consumption rate.

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Introduction

Protection of units and facilities used in the oil industry from corrosion remains an urgent issue, and the damage caused by corrosion to the world economy is measured in billions of dollars per year. It is known that the presence of components with corrosion aggressiveness, including sulfur and oxygen compounds, hydrogen sulfide, carbon dioxide, molecular oxygen, as well as mineral salts dissolved in formation water, causes corrosion of facilities during exploitation. Hydrogen sulfide in formation water is extremely dangerous for the units and facilities. This compound is highly reactive and causes hydrogen brittleness in metals [1,2]. Despite the extensive research of the corrosion process of metals in the hydrogen sulfide medium, the solution to this problem in the oil industry is still very important [3,4].

It should be noted that the main factor affecting the corrosion rate of the internal surface of oil industry facilities is the hydrogen sulfide factor. Hydrogen sulfide is the most aggressive corrosion agent. Being well soluble in formation waters and fluid hydrocarbons, it promotes further activation of cathode and anode processes in electrochemical corrosion. It was discovered that hydrogen sulfide dissociates into ions as a weak acid, and HS^- ion is adsorbed on the surface of iron, changing its electrode potential to the negative side. This reduces the overvoltage in hydrogen separation and intensifies the cathodic process [5]. For the iron family metals, hydrogen sulfide stimulates hydrogen brittleness by accelerating cathode and anode processes. During the process, the reduced hydrogen atoms diffuse to the surface of the metal, creating hydrogen fatigue or hydrogen brittleness, as a result of which the metal loses its property of plasticity. In addition, the corrosion product formed during the process has an effect on the intensification of the corrosion rate in the presence of H_2S. Thus, during the research of the effect mechanism of iron (II) sulfide coating formed in the hydrogen sulfide medium on the corrosion process, it was determined that in the course of corrosion, iron (II) sulfide acts as the cathode, and the iron atom acts as the anode, forming a Fe–FeS microgalvanic pair.

The presence of hydrogen sulfide in formation waters leads to intensive corrosion of the internal surface of underground facilities in oil wells, oil pipelines, oil storage and sedimentation tanks, as well as facilities exploited in an oil refinery. For this reason, the issue of selection, checking and wide application of chemical reagents for reducing the rate of the corrosion process and even completely stopping it remains relevant.

Corrosion inhibitors are divided into non-volatile and volatile inhibitors according to the application conditions in various industries. In addition, the protection effect of inhibitors depends on the pH of the aggressive medium. In this regard, corrosion inhibitors are divided into inhibitors used for neutral, alkaline and acidic media. During protection, inhibitors either reduce the rate of electrochemical corrosion or completely reduces it to zero by reacting with the metal to form a passive coating on the surface of the metal, forming several molecular coating layers on the surface of the metal, eliminating the effect of corrosive ions, or removing those ions from the corrosion medium and forming a deposit on the metal surface, covering the surface.

Corrosion inhibitors are also divided into two groups, inorganic and organic inhibitors according to their chemical composition. In recent years, in various fields of industry, especially in the oil industry, inhibitors of organic origin have been applied, most of which weaken the rate of electrochemical corrosion in acidic media. Thus, based on the effect mechanism of these inhibitors the adsorption process stops. They are adsorbed in the anode and cathode areas, preventing metal ionization and hydrogen ion release. For this reason, when adding inhibitors to acidic medium, although the corrosion rate is reduced enough, the numerical value of the stationary potential is almost unchanged. The protection effect of organic inhibitors depends on their nature, temperature and concentration of hydrogen ions. When protecting the internal surface of industrial facilities from electrochemical corrosion in an acidic medium, inhibitors of organic origin are mostly used. It is in such a medium that organic inhibitors have a stronger effect than inorganic complexes, while showing a high protection effect [6–9].

As corrosion inhibitors, individual compounds and compositions are used that lead to a sharp reduction or complete stoppage of electrochemical corrosion loss of metals in harsh operating media. Therefore, the synthesis of new types of reagents with inhibitory properties, the research of their properties and effect mechanism in terms of corrosion protection have become the area of interest of the modern era [10,11].

The research objective was to conduct comparative study of the effect of reagents in an aggressive medium under laboratory conditions.

Experimental

Table 1 shows the ionic composition of the formation water sample taken from the well No. 1082 of «Bibiheybatneft» OGPD used for the experiments.

Table 1

Ionic composition of formation water taken from well No. 1082

Ions	Concentration of ions, mg/l	Equivalent concentration of ions, mg-eq/l	Equivalent amount, %
Na^{+}+K^{+}	31298.987	1304.12	46.57
Ca^{2+}	1122.24	56	1.9998
Mg^{2+}	486.4	40	1.4284
Fe^{3+}	2561.58	853.86	–
Cl^{-}	49010.49	1382.52	49.37
SO_4^{2-}	28.81	0.60	0.0214
HCO_3^{-}	1037.00	17.00	0.6071
H_2S	15	–	–

During the laboratory experiments, gossypol resin, IB-1 inhibitor and a composition containing gossypol resin and IB-1 inhibitor at the ratio of 3:1 and a new composition with conventional name HS-1 were used as reagents. It should be noted that gossypol resin is an intermediate-level waste product obtained during the production of cottonseed oil, and IB-1 inhibitor is an unsaturated organic compound the molecular composition of which contains carbon, hydrogen, oxygen and halogen atoms.

Under laboratory conditions, gravimetric experiments were carried out in accordance with the requirements of the state standards SS 9.502-82 and SS 9.506-87, and Ст3 steel samples were used during the experiment. For this, pre-prepared and cleaned steel plates were weighed on an analytical balance and placed in a rectangular flask equipped with a mechanical stirrer. Then, the calculated volume of formation water and the required amount of reagent were added into the flask. It should be noted that the amount of the reagent was calculated according to the known rule for one liter of corrosion medium. The test process was carried out at a temperature of $20\pm3^{0}C$ for six hours with constant stirring at a rotation speed of 800 rpm. After six hours, the system was kept at rest for a while, and then the steel samples were washed, cleaned, wiped with alcohol, dried and reweighed on an analytical balance. Then, the corrosion protection efficiency of the researched reagents was calculated.

Results and discussion

First of all, the effect of gossypol resin on the corrosion rate of formation water was researched and the corrosion protection efficiency was calculated. The results obtained from the experiments are given in Table 2.

Table 2

Protection effect of gossypol resin in the formation water with H_2S

C_{inh}, mg/l	Corrosion rate, K, g/m^2·hour	Inhibition factor, γ	Protection effect, Z, %
50	1.72	2.50	60
100	1.38	3.10	68
150	1.12	3.84	74
200	0.78	5.51	82

As is seen from Table 2, an increase in the concentration gossypol resin in the hydrogen sulfide formation water results in an increase in the corrosion protection effect. Thus, the protection effect is 60, 68, 74 and 82% in the aggressive medium with the gossypol resin concentrations of 50, 100, 150 and 200 mg/l, respectively. At the given concentrations, the inhibition coefficient is 2.50, 3.10, 3.84 and 5.51, respectively.

Figure 1 shows the effect of gossypol resin concentration on the corrosion rate.

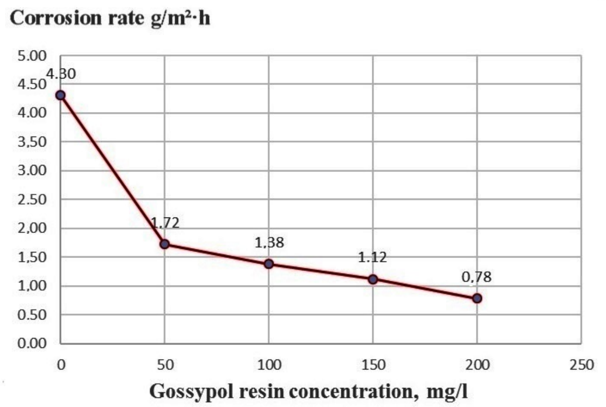

Fig. 1. Dependence of the corrosion rate on the gossypol resin concentration

As is seen from the dependence presented in Fig. 1, after six hours from adding 50, 100, 150 and 200 mg/l of gossypol resin to the medium with a net corrosion rate of 4.30 g/m^2·h, the corrosion rate gets the value of 1.72, 1.38, 1.12 and 0.78 g/m^2·h, respectively.

In order to establish the effect of organic IB-1 inhibitor on the corrosion rate in the medium with the hydrogen sulfide formation water, its concentrations was varied in the range of 10 to 25 mg/l and the results obtained are given in Table 3.

Table 3

Protection effect of IB-1 inhibitor in the H_2S formation water

C_{inh}, mg/l	Corrosion rate, K, g/m^2·hour	Inhibition factor, γ	Protection effect, Z, %
10	1.5	2.86	65
15	1.12	3.84	74
20	0.78	5.51	82
25	0.43	10.0	90

As is seen from Table 3, the corrosion protection effect increases as the concentration of IB-1 inhibitor increases in the hydrogen sulfide formation water. Thus, the protection effect is 65, 74, 82, 90%, respectively, in an aggressive medium where concentrations of 10, 15, 20, 25 mg/l of the reagent are added. At the given concentrations, the inhibition factor is 2.86, 3.84, 5.51 and 10.0, respectively.

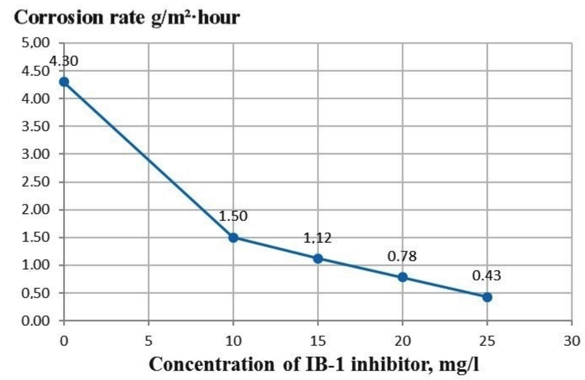

Fig. 2. Dependence of the corrosion rate on the IB-1 inhibitor concentration

Figure 2 shows the effect of the IB-1 inhibitor concentration on the corrosion rate.

As it seen from Fig. 2, when adding 10, 15, 20 and 25 mg/l of IB-1 inhibitor to the hydrogen sulfide formation water, the corrosion rate in the is equal to 1.5, 1.12, 0.78 and 0.43 g/m^2·h for six hours, respectively.

The effect of new HS-1 composition on the rate of electrochemical corrosion in the hydrogen sulfide formation water was also studied (Table 4).

As is seen from the results given in Table 4, HS-1 composition has a higher impact in an aggressive corrosion medium compared to its individual constituents. Thus, the corrosion rate decreases sharply and takes a very small value at a concentration of 20–80 mg/l. The protection effect of HS-1 composition varies between in the range of 74 to 98%.

Figure 3 shows the dependence of the corrosion rate on the concentration of new composition HS-1.

As is seen from Fig. 3, when adding 20, 40, 60 and 80 mg/l IB-1 of HS-1 inhibitor to the hydrogen sulfide formation water, the corrosion rate in the medium takes a value of 1.12, 0.73, 0.34 and 0.08 g/m^2·h for six hours, respectively.

Table 4

Protection effect of HS-1 composition in the formation water with H_2S

C_{inh}, mg/l	Corrosion rate, K, g/m^2·hour	Inhibition factor, γ	Protection effect, Z, %
20	1.12	3.84	74
40	0.73	5.89	83
60	0.34	12.64	92
80	0.08	53.75	98

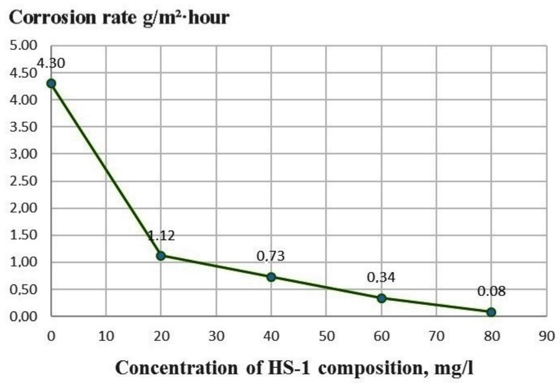

Fig. 3. Dependence of the corrosion rate on the HS-1 inhibitor concentration

Figure 4 compares the corrosion protection effects of gossypol resin, IB-1 inhibitor and HS-1 composition in the hydrogen sulfide formation water at the optimal consumption rate, based on the results of laboratory experiments.

Thus, the results presented in Fig. 4 reveals that the HS-1 composition has the highest protection effect compared to its individual constituents.

Conclusions

1. The effect of new HS-1 composition and its constituent components, gossypol resin and IB-1 inhibitor, on the rate of electrochemical corrosion in the hydrogen sulfide formation water was investigated under laboratory conditions for the first time, and their corrosion protection effects and optimal consumption rate were determined.

2. It was revealed that new HS-1 composition

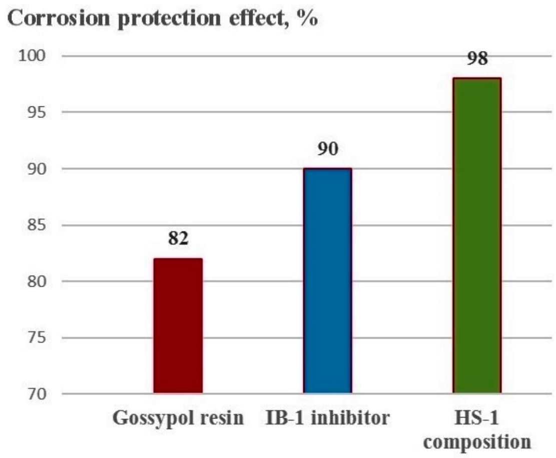

Fig. 4. Protection effects of reagents at their optimal consumption rates

has a high protection effect, having a more impact on the corrosion rate in the hydrogen sulfide formation water compared to its individual constituents.

3. It was determined that optimal consumption rate of gossypol resin, IB-1 inhibitor, and HS-1 composition during corrosion protection is 200, 25, and 80 mg/l, and protection effects is 82, 90, and 98%, respectively.

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ДОСЛІДЖЕННЯ ЗАХИСНОГО КОРОЗІЙНОГО ЕФЕКТУ НОВОЇ КОМПОЗИЦІЇ НА ОСНОВІ ГОСИПОЛУ В СІРКОВОДНЕВІЙ ПЛАСТОВІЙ ВОДІ

Г.Р. Гурбанов, С.М. Пашаєва

Досліджено вплив нової композиції (HS-1), що складається зі смоли госиполу та реагенту IB-1, взятих у співвідношенні 3:1, на швидкість корозії у сірководневій пластовій воді за лабораторних умов. Для цього використовувалися концентрації 20, 40, 60 та 80 мг/л нової композиції. Як корозійне середовище використовувалася проба пластової води, взята з свердловини № 1082 ОГПД «Бібі-Гейбатнефт», АО «СОКАР». Також досліджено вплив корозії при концентраціях 50, 100, 150, 200 мг/л госиполу та 10, 15, 20 та 25 мг/л інгібітора IB-1. При збільшенні концентрації госиполу у пластовій воді до 50–200 мг/л, величина захисної здатності від корозії знаходилася у діапазоні 60–82%. При зміні концентрації інгібітору IB-1 від 10 до 25 мг/л у сірководневому середовищі захисний ефект становив від 65 до 90%. Збільшення концентрації нового складу HS-1 в діапазоні від 30 до 80 мг/л призвело до зростання ефективності його захисту від корозії від 74 до 98%. Було виявлено, що оптимальна швидкість споживання госиполу, інгібітора IB-1 та складу HS-1 для захисту від корозії в агресивному сірководневому середовищі становила 200 мг/л, 25 мг/л та 80 мг/л, відповідно.

Ключові слова: сірководень, реагент, інгібітор, швидкість корозії, пластова вода, оптимальна швидкість споживання.

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