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The inhibitory effect of selected reagents on carbon steel corrosion in formation water containing hydrogen sulfid

Działanie antykorozyjne wybranych odczynników na korozję stali węglowej w wodzie złożowej zawierającej siarkowodór

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ABSTRACT: For the first time, the impact of the composition of gossypol resin and IB-1 reagent, prepared in a 3:1 ratio and conventionally named HS-1, on the corrosion rate in hydrogen sulfide formation water has been investigated under laboratory conditions. Concentrations of 20, 40, 60, 80 mg/l of the new composition were used. During the experiments, a formation water sample taken from well No. 1082 of "Bibiheybatneft" OGPD, SOCAR, served as the electrochemical corrosion medium for the study. To conduct a comparative analysis, gossypol resin, IB-1 inhibitor, and HS-1 composition were used. Concentrations of 50, 100, 150, 200 mg/l of gossypol resin and 10, 15, 20, and 25 mg/l of IB-1 inhibitor were employed in the experiments. Numerous laboratory experiments revealed that the optimal consumption rate for the HS-1 inhibitor is 100 mg/l, for gossypol resin it is 200 mg/l, and for the IB-1 inhibitor it is 25 mg/l. These experiments were conducted under dynamic conditions over six hours. It was determined that the newly developed HS-1 composition offers superior protection in an aggressive medium containing hydrogen sulfide compared to its constituent components, gossypol resin, and IB-1 inhibitor. Specifically, as the concentration of gossypol resin in formation water increases from 50 to 200 mg/l, the corrosion protection effect ranges from 60-82%. When the concentration of IB-1 inhibitor varies between 10-25 mg/l in a hydrogen sulfide medium, the protection effect lies between 65-90%. In the aggressive medium of hydrogen sulfide formation water, increasing the concentration of the new HS-1 composition from 30–80 mg/l results in an enhancement of its electrochemical corrosion protection effect, ranging from 74–98%. Upon analyzing the results of numerous laboratory experiments, it was found that the optimal consumption rate of gossypol resin for corrosion protection in an aggressive medium with hydrogen sulfide is 200 mg/l, the consumption rate of IB-1 inhibitor is 25 mg/l, and for the HS-1 composition is 80 mg/l. The corrosion rates for gossypol resin in the concentrations of 50, 100, 150, 200 mg/l is 1.72, 1.38, 1.12, 0.78 g/m² · h and retardation coefficient is 2.50, 3.10, 3.84, 5.51, respectively. Corrosion rate of IB-1 inhibitor concentration in the amount of 10, 15, 20, and 25 mg/l is 1.5, 1.12, 0.78, 0.43, and retardation coefficient is 2.86, 3.84, 5.51, 10.0, respectively. The corrosion rates for the new HS-1 composition at concentrations of 20, 40, 60, 80 mg/l is 1.12, 0.73, 0.34, 0.08, and the retardation coefficient is 3.84, 5.89, 12.64, 53.75, respectively. Comparing the corrosion rate values obtained for all three reagents with the corrosion rate for hydrogen sulphide formation water shows that new HS-1 composition has a higher effectiveness compared to its constituent components.

Key words: hydrogen sulfide, composition, reagent, corrosion rate, protection, formation water.

STRESZCZENIE: Po raz pierwszy w warunkach laboratoryjnych zbadano wpływ składu żywicy gossypolowej i odczynnika IB-1, przygotowanej w stosunku 3:1 i umownie nazwanej HS-1, na szybkość korozji w wodzie złożowej zawierającej siarkowodór. Zastosowano stężenia 20, 40, 60, 80 mg/l nowego składu. Podczas eksperymentów jako elektrochemiczne medium korozyjne do badań posłużyła próbka wody złożowej pobrana z odwiertu nr 1082 "Bibiheybatneft" OGPD, SOCAR. W celu przeprowadzenia analizy porównawczej w doświadczeniach wykorzystano żywicę gossypolową, inhibitor IB-1 oraz komponent HS-1. Pobrano 50, 100, 150, 200 mg/l żywicy oraz 10, 15, 20 i 25 mg/l inhibitora IB-1. Liczne badania laboratoryjne wykazały, że optymalne zużycie inhibitora HS-1 wynosi 100 mg/l, żywicy gossypolowej 200 mg/l, a inhibitora IB-1 25 mg/l. Doświadczenia te prowadzono w warunkach dynamicznych przez sześć godzin. Stwierdzono, że nowo opracowana kompozycja HS-1 zapewnia lepszą ochronę w agresywnym środowisku zawierającym siarkowodór w porównaniu z jej składnikami, żywicą gossypolową i inhibitorem IB-1. Zatem gdy stężenie żywicy gossypolowej w wodzie złożowej wzrośnie o 50–200 mg/l, efekt ochrony przed korozją przyjmuje wartość w przedziale 60–82%. Gdy stężenie inhibitora IB-1 waha się w granicach 10–25 mg/l w środowisku siarkowodorowym, efekt ochronny wynosi 65–90%. W agresywnym środowisku wód złożowych zawierających siarkowodór zwiększenie stężenia nowej mieszaniny HS-1 w zakresie 30–80 mg/l powoduje wzrost jej elektrochemicznego efektu antykorozyjnego w granicach 74–98%. Analizując wyniki licznych eksperymentów laboratoryjnych stwierdzono, że optymalne zużycie żywicy gossypolowej do ochrony przed korozją w agresywnym środowisku z siarkowodorem

wynosi 200 mg/l, zużycie inhibitora IB-1 25 mg/l, a stopień zużycia kompozycji HS-1 80 mg/l. Szybkość korozji żywicy gossypolowej w stężeniach 50, 100, 150, 200 mg/l wynosi 1,72; 1,38; 1,12; 0,78 g/m²·h, a współczynnik opóźnienia wynosi odpowiednio 2,50; 3,10; 3,84; 5,51. Szybkość korozji przy stężeniu inhibitora IB-1 w ilościach 10, 15, 20 i 25 mg/l wynosi 1,5; 1,12; 0,78; 0,43, a współczynnik opóźnienia wynosi odpowiednio 2,86, 3,84, 5,51, 10,0. Szybkość korozji nowego składu HS-1 w stężeniach 20, 40, 60, 80 mg/l wynosi 1,12; 0,73; 0,34; 0,08, a współczynnik opóźnienia wynosi odpowiednio 3,84; 5,89; 12,64; 53,75. Porównanie wartości szybkości korozji uzyskanych dla wszystkich trzech odczynników z szybkością korozji w wodzie złożowej zawierającej siarkowodór wskazuje, że nowa kompozycja HS-1 ma wyższą skuteczność w porównaniu do jej poszczególnych składników.

Słowa kluczowe: siarkowodór, skład, odczynnik, szybkość korozji, działanie ochronne, woda złożowa.

Introduction

Protection of units and facilities used in the oil industry against corrosion remains a pressing issue, with the associated economic damage amounting to billions of dollars annually. The presence of elements with corrosive properties, such as sulfur and oxygen compounds, hydrogen sulfide, carbon dioxide, molecular oxygen, as well as mineral salts dissolved in formation water, cause corrosion of facilities during exploitation. Hydrogen sulphide in formation water is particularly hazardous, as it is highly reactive and induces hydrogen embrittlement in metals (Kuznetsov and Vaganov, 2000, 2021; Kuznetsov, 2002). Despite the extensive research into the corrosion process of metals in hydrogen sulphide medium, finding solutions that are both practical and economically viable remains a critical challenge in the oil industry (Kuznetsov and Vagannov, 2001; Vaganov et al, 2002).

It should be noted that hydrogen sulfide is the main factor affecting the corrosion rate of the internal surface of oil industry facilities. Hydrogen sulfide is the most aggressive corrosive agent. Being highly soluble in formation waters and fluid hydrocarbons, it promotes further activation of cathodic and anodic processes in electrochemical corrosion. It was discovered that hydrogen sulfide, acting as a weak acid, dissociates into ions. The HS-1 ion is adsorbed onto the surface of iron, changing its electrode potential towards the negative side (Ioffe and Kam, 1974). For ferrous metals, hydrogen sulfide stimulates hydrogen embrittlement by accelerating cathodic and anodic processes. During the process, the reduced hydrogen atoms diffuse to the metal's surface, creating hydrogen-induced fatigue or hydrogen embrittlement, as a result of which the metal loses plasticity. Additionally, the corrosion product formed during the process intensifies the corrosion rate in the presence of H₂S. In research exploring the effect mechanism of iron (II) sulfide coating formed in a hydrogen sulfide medium on the corrosion process, it was determined that iron (II) sulfide acts as the cathode, and the iron atom acts as the anode, forming a Fe-FeS microgalvanic pair (Abbasov et al., 2018).

The presence of hydrogen sulphide 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 operated in an oil refinery. Given these issues, the selection, verification and wide application of chemical reagents for reducing the rate of the corrosion process and even completely stopping it remains a relevant issue. Corrosion inhibitors are divided into non-volatile and volatile inhibitors according to the application conditions in various industries. Additionally, the protection effectiveness of inhibitors depends on the pH of the aggressive medium. Consequently, corrosion inhibitors are divided into inhibitors used for neutral, alkaline and acidic media. In terms of protection mechanisms, inhibitors either reduce the rate of electrochemical corrosion or completely stop it by reacting with the metal forming a passive coating on its surface, forming several molecular coating layers on the surface of the metal, eliminating the effect of corrosive ions, or removing those ions from the corrosive medium and forming a deposit on the metal surface (Gutman et al., 1988; Vigdorovich and Tsygankova, 2011).

Corrosion inhibitors are classified into two main groups based on their chemical composition: inorganic and organic. In recent years, organic inhibitors, most of which mitigate the rate of electrochemical corrosion in acidic media, have seen an increase in frequency of application in various industries, particularly in the oil industry. The mechanism of action of these inhibitors primarily involves the halting of the adsorption process. They are adsorbed in the anode and cathode areas, preventing metal ionization and hydrogen ion release. As a result, when adding inhibitors to acidic medium, although the corrosion rate is reduced enough, the numerical value of the stationary potential remains almost unchanged. The protection effectiveness 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, organic inhibitors are used most commonly. It is in such a medium that organic inhibitors have a stronger effect than inorganic ones, exhibiting a high protection (Blustein et al., 2006; Salasi et al., 2007; Radojčić et al., 2008; Lecante et al., 2011).

Corrosion inhibitors, comprising individual compounds and compositions, are utilized to significantly reduce or completely halt the electrochemical corrosion loss of metals in harsh operating environments. Consequently, the synthesis of new types of reagents with inhibitory properties, and the investigation of their properties and mechanisms of action in terms of corrosion protection have become the area of interest contemporary research (Aghazade, 2016; Flat, 2016; Efendiyeva, 2017; Mammadov et al., 2012, 2013; Mamedov, 2013; Plennevaux et al., 2013; Kuliev et al., 2015; Zuev, 2015; Salmanli and Mammadov, 2017; Pashaeva, 2020).

The goal of the paper is to conduct comparative study of the effect of reagents in an aggressive medium in laboratory conditions.

Research methodology

In laboratory conditions, gravimetric experiments were carried out in accordance with the requirements of SS 9.502-82 and SS 9.506-87, and Ct3 steel. The procedure involved prepreparing and cleaning steel plates, which 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 established principle for one liter of corrosive medium. The test process was maintained at a temperature of 20 ± 3 °C for six hours with constant stirring at a rotational 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. The corrosion protection efficiency of the investigated reagents was calculated based on the results of this test.

Experimental part

During the laboratory experiments, gossypol resin, IB-1 inhibitor and a composition containing gossypol resin and IB-1 inhibitor an a 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.

Table 1 shows the ionic composition of the formation water sample taken from well No. 1082 of "Bibiheybatneft" OGPD used during the experiment. The content of hydrogen sulfide in formation water was determined using the iodometric method (GOST 39-234-89 Water for flooding oil reservoirs).

Table 1. Ionic composition of formation water taken from well No. 1082

Tabela 1. Skład jonowy wody złożowej pobranej z otworu wiertniczego nr 1082

Ions	Concentration of ions	Equivalent concentration of ions	Equivalent amount	
	[mg/l]	[mgekv/l]	[%]	
Na++K+	31298.987	1304.12	46.57	
Ca ²⁺	1122.24	56	1.9998	
$\mathrm{Mg}^{2^{+}}$	486.40	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	
CO ₃ ²⁻	0.00	0.00	0.0000	
HCO ₃ -	1037.00	17.00	0.6071	
H ₂ S	15	_	_	

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

Table 2. Protection effectiveness of gossypol resin in formation water with H₂S

Tabela 2. Skuteczność ochronna żywicy gossypolowej w wodzie złożowej z H₂S

C _{inh} [mg/l]	K [g/m² · hour]		Detaudation	Protection
	inhibitor free	with an inhibitor	Retardation coefficient, γ	effectiveness, Z [%]
0	4.30	_	-	-
50	4.30	1.72	2.50	60
100	4.30	1.38	3.10	68
150	4.30	1.12	3.84	74
200	4.30	0.78	5.51	82

As can be seen from Table 2, since the amount of gossypol resin in hydrogen sulphide formation water increases, the corrosion protection effectiveness also increases. Thus, in the aggressive medium the protection effectiveness of the reagent with concentrations of 50, 100, 150, 200 mg/l is 60, 68, 74, 82%, respectively. In the given concentrations, the retardation coefficient is 2.50, 3.10, 3.84, 5.51, respectively.

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

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

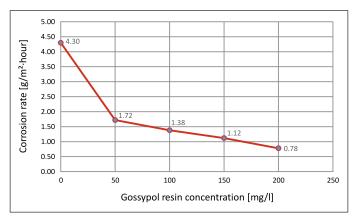


Figure 1. The dependence of the corrosion rate on gossypol resin concentration

Rysunek 1. Zależność tempa korozji od stężenia żywicy gossypolowej

In order to study the effect of IB-1 organic inhibitor on the corrosion rate in the medium with hydrogen sulphide formation water, its amounts of 10, 15, 20 and 25 mg/l were used and the results obtained from numerous experiments are presented in Table 3.

Table 3. Protection effectiveness of IB-1 inhibitor in formation water with H_2S

Tabela 3. Skuteczność ochronna inhibitora IB-1 w wodzie złożowej z H₂S

C _{inh} [mg/l]	K [g/m² · hour]		D. A. J. C.	Protection
	inhibitor free	with an inhibitor	Retardation coefficient, γ	effectiveness, Z [%]
0	4.30	_	_	_
10	4.30	1.5	2.86	65
15	4.30	1.12	3.84	74
20	4.30	0.78	5.51	82
25	4.30	0.43	10.0	90

As can be seen from Table 3, the corrosion protection effectiveness increases as the concentration of IB-1 inhibitor increases in hydrogen sulphide formation water. Thus, the protection effect is 65, 74, 82, 90%, respectively, in an aggressive medium where concentrations of the reagent of 10, 15, 20, 25 mg/l were added. In the given concentrations, the retardation coefficient is 2.86, 3.84, 5.51, 10.0 respectively.

Figure 2 shows the dependence of IB-1 inhibitor concentration on the corrosion rate. As can be seen from Figure 2, when adding 10, 15, 20 and 25 mg/l of IB-1 inhibitor to hydrogen sulphide formation water, the corrosion rate in the medium is 1.5, 1.12, 0.78, 0.43 g/m² · h for six hours, respectively.

During laboratory tests, the effect of the new HS-1 composition on the rate of electrochemical corrosion in hydrogen sulphide formation water was studied (Table 4).

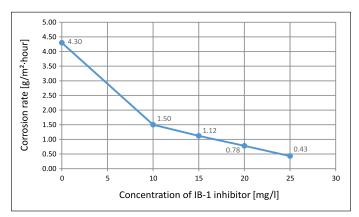


Figure 2. Dependence of the corrosion rate on IB-1 inhibitor concentration

Rysunek 2. Zależność tempa korozji od stężenia inhibitora IB-1

As can be seen from the results presented in the Table 4, HS-1 composition has higher effectiveness in an aggressive corrosion medium compared to its constituent components. Thus, the corrosion rate decreases sharply and takes a very low value at a concentration of 20–80 mg/l. At this time, the protection effect of HS-1 composition varies between 74–98%.

Table 4. Protection effectiveness of HS-1 composition in formation water with H₂S

Tabela 4. Skuteczność ochronna związku HS-1 w wodzie złożowej z H₂S

C _{inh} [mg/l]	K [g/m² · hour]		Detaudation	Protection
	inhibitor free	with an inhibitor	Retardation coefficient, γ	effectiveness, Z [%]
0	4.30	_	_	_
20	4.30	1.12	3.84	74
40	4.30	0.73	5.89	83
60	4.30	0.34	12.64	92
80	4.30	0.08	53.75	98

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

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

Figure 4 shows the corrosion protection effectiveness of gossypol resin, IB-1 inhibitor and HS-1 composition in the hydrogen sulphide formation water at the optimal consumption at the same on the results of numerous laboratory experiments. Thus, the results presented in Figure 4 show HS-1 composition to have higher effectiveness compared to its constituent components. Thus, protection effectiveness of gossypol resin, IB-1 inhibitor, and HS-1 composition at the optimal consumption rate are 82, 90, and 98%, respectively.

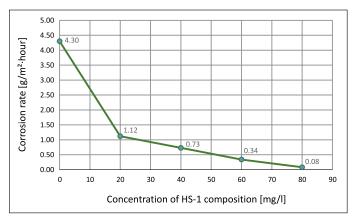


Figure 3. Dependence of the corrosion rate on HS-1 inhibitor concentration

Rysunek 3. Zależność tempa korozji od stężenia inhibitora HS-1

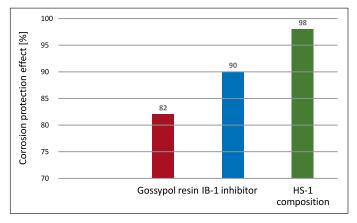


Figure 4. Protection effectiveness of reagents at optimal consumption rates

Rysunek 4. Skuteczność ochronna odczynników przy optymalnym zużyciu

Conclusions

- The effectiveness of the new HS-1 composition and its constituent components, gossypol resin and IB-1 inhibitor, on the rate of electrochemical corrosion in hydrogen sulphide formation water was investigated in laboratory conditions for the first time, and their corrosion protection effectiveness and optimal consumption rate were determined.
- 2. It was revealed that the new HS-1 composition has high protection effectiveness by impacting corrosion rate in hydrogen sulphide formation water much more compared to its constituent components.
- 3. From the analysis of the results of numerous laboratory experiments, 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 effectiveness are 82, 90, and 98%, respectively.

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 - » zaawansowanych technologicznie specyfików dla wojska,
 - » preparatów myjących,
 - » inhibitorów korozji i rdzewienia,
 - » dodatków i pakietów dodatków uszlachetniających (dobieranie do paliw indywidualnie):
 - do przerobu ropy naftowej (procesowe),
 - do benzyn silnikowych,
 - do paliw lotniczych,
 - do olejów napędowych,
 - do olejów opałowych,
 - do paliw alternatywnych (biopaliw),
 - biocydów do paliw naftowych i biopaliw,
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