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Comparative study of the effect of gossypol resin and HS-1 inhibitors on the corrosion rate in aggressive corrosion environments

Badanie porównawcze wpływu żywicy gossypolowej i inhibitorów HS-1 na szybkość korozji w agresywnych środowiskach korozyjnych

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ABSTRACT: For the first time, the effect of the gossypol resin and the HS-1 inhibitor on the corrosion rate in aggressive environments was studied on a sample of St3 steel in various environments in laboratory conditions. During the experiments, 20%, 40%, 60%, and 80% solutions ($H_2S + CO_2$) and oil from well No. 412 of the May 28 field were used as research objects. Laboratory experiments were carried out over six hours under dynamic conditions. Concentrations of both inhibitors of 40, 60, 80, and 100 mg/l were used. As a result of numerous laboratory tests, it was found that an increase in the effect of corrosion protection is observed as the concentration of both inhibitors increases. Thus, the highest value for both samples was exactly 100 mg/l. Currently, the corrosion protection effect of gossypol resin in pure oil, pure oil + 20% $H_2S + CO_2$ solution, pure oil + 40% $H_2S + CO_2$ solution, pure oil + 60% $H_2S + CO_2$ solution, pure oil + 80% solution content $H_2S + CO_2$ was 88%, 90%, 93%, 98% and 97% for reagent HS-1 and 89%, 93%, 95%, 97% and 99%, respectively. From numerous experiments, it was found that gossypol resin showed the highest performance in pure oil + 60% $H_2S + CO_2$ solution environment, and the rate of corrosion at this time was 0.11 $g/m^2 \cdot h$, while the HS-1 reagent showed the highest performance in pure oil + 80% $H_2S + CO_2$ in the solution medium, and at this time, the rate of corrosion was the smallest, i.e. 0.05 $g/m^2 \cdot h$. The highest effect was observed in a more acidic environment, i.e. in pure oil + 80% $H_2S + CO_2$ solution environment at a concentration of 100 mg/l of HS-1 inhibitor.

Key words: inhibitor, reagent, corrosion rate, protection efficiency, pure oil, $H_2S + CO_2$ solution.

STRESZCZENIE: Po raz pierwszy zbadano wpływ żywicy gossypolowej i inhibitora HS-1 na szybkość korozji w tych środowiskach na próbce stali St3 w różnych środowiskach agresywnych w warunkach laboratoryjnych. Podczas eksperymentów jako obiekty badawcze wykorzystano 20%, 40%, 60% i 80% roztwory ($H_2S + CO_2$) oraz ropę naftową z odwiertu nr 412 ze złoża May 28. Eksperymenty laboratoryjne przeprowadzono w ciągu sześciu godzin w warunkach dynamicznych. Zastosowano stężenia obu inhibitorów wynoszące 40, 60, 80 i 100 mg/l. W wyniku licznych badań laboratoryjnych stwierdzono, że wraz ze wzrostem stężenia obu inhibitorów obserwuje się wzrost efektu ochrony antykorozyjnej. Tym samym najwyższa wartość dla obu próbek wyniosła dokładnie 100 mg/l. Obecnie efekt ochrony antykorozyjnej żywicy gossypolowej w czystym oleju, czystym oleju + 20% roztworze $H_2S + CO_2$, czystym oleju + 40% roztworze $H_2S + CO_2$, czystym oleju + 60% roztworze $H_2S + CO_2$, czystym oleju + 80% zawartości roztworu $H_2S + CO_2$ wynosił odpowiednio 88%, 90%, 93%, 98% i 97% dla odczynnika HS-1 oraz 89%, 93%, 95%, 97% i 99%. Na podstawie licznych eksperymentów stwierdzono, że żywica gossypolowa wykazała najwyższą wydajność w czystym oleju + 60% $H_2S + CO_2$ w środowisku roztworu, a szybkość korozji w tym czasie wynosiła 0,11 $g/m^2 \cdot h$, podczas gdy odczynnik HS-1 wykazał najwyższą wydajność w czystym oleju + 80% $H_2S + CO_2$ w środowisku roztworu, a w tym czasie szybkość korozji była najmniejsza, tj. 0,05 $g/m^2 \cdot h$. Najwyższy efekt zaobserwowano w bardziej kwaśnym środowisku, tj. w środowisku czystego oleju + 80% $H_2S + CO_2$ w roztworze przy stężeniu 100 mg/l inhibitora HS-1.

Słowa kluczowe: inhibitor, odczynnik, szybkość korozji, skuteczność ochrony, czysta ropa, roztwór $H_2S + CO_2$.

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Introduction

Salt deposits occur on the walls of elevator pipes, pumping equipment, as well as on the internal surface of the oil field regardless of the method of development and operation of oil fields, at all stages of oil production, transportation and refining. As a result of the salt deposition process, well repair time is reduced, the operational process is complicated, equipment corrosion is observed, and oil production is reduced. Mixing of formation waters of incompatible chemical composition, changes in thermobaric conditions, water degassing, evaporation at oil production facilities, dissolution of minerals in reservoirs, injection of chemical waters of various compositions used for the extraction of residual oil (watering process), etc. is one of the main causes of corrosion.

Thus, based on the above, we can say that one of the biggest problems in the oil industry is the failure of oilfield equipment as a result of corrosion processes. Therefore, to reduce the cost of oil production and increase the service life of oilfield equipment, the study of chemical inhibitors in laboratory conditions and their use in the industry remains an urgent task (Kunakova et al., 2011; Omelyanyuk, 2012; Shangaraeva and Petukhov, 2013; Shangaraeva and Sulianova, 2015; Sibiryakov et al., 2016).

Nitrogenous organic compounds, amines, imidazolinamines, amine and imidazoline complexes, and other organic compounds with added halogens, and double and triple bonds are used as corrosion inhibitors (Gurbanov et al., 2020). It is noted that at high pH values inhibitors are mainly anodic inhibitors, at pH values close to neutral, they practically do not slow down cathodic reactions, and sometimes accelerate these processes (Azizbeyli et al., 2012). It can also be noted that cationic inhibitors slow down the corrosion process in pure acid. But in the presence of hydrogen sulfide in the medium the protection effect of these compounds increases significantly (Vigdorovich et al., 2004; Lusk et al., 2008; Alieva, 2014; Abbasov et al., 2018).

In general, it should be noted that with an increase in the percentage of the $H_2S + CO_2$ mixture in the oil, the corrosion process accelerates. The reason for this is that the pH level increases as a result of the increased acidity on the internal surface of oilfield equipment and pipelines, which creates an aggressive corrosive environment (Vigdorovich et al., 2002; Azimov et al., 2015; Guliev et al., 2015; Murzalov et al., 2015).

Performance of work

In order to conduct laboratory tests, steel samples of Ct3 prepared according to the rules are placed in a corrosion medium without an inhibitor and with the addition of an inhibitor, and the time is recorded.

A special device is used to check the protective effect of the inhibitor using the gravimetric method. To determine the optimum protective concentration of the inhibitor, a large number of experiments are carried out in the laboratory, starting from low concentration to high concentration. After the laboratory tests are completed, the steel plates are removed from the medium and cleaned of the corrosion products on the surface. For this purpose, the plates are cleaned with cotton wool in a solution of 10% hydrochloric acid and 40% formalin, washed with running water and dried with acetone. The plates are kept in the desiccator for 10–12 hours to bring them to a constant weight both before and after the experiment. Then the plates are weighed again (Pashaeva, 2020).

In gravimetric tests, the mass index of corrosion rate in both reagent-free and reagent media is characterized by K_m and is calculated using the following mathematical equation:

$$K_m = \frac{m_0 - m_1}{S} \, [\mathrm{g} / (\mathrm{m}^2 \cdot \mathrm{hour})]$$

where:

m_0 – is the mass of the sample before testing [g],
m_1 – is the mass of the sample after testing [g],
S – is the average surface area calculated for three samples [m^2],
τ – is the duration of the test [hour].

The equation used to calculate the deceleration coefficient is as follows:

$$\gamma = \frac{K_0}{K_{inh}}$$

where:

K_0 – is reagent free corrosion rate [g/m$^2 \cdot$ hour],
K_{inh} – is the corrosion rate with reagent [g/m$^2 \cdot$ hour].

The protection effect of the reagent is calculated using the following equation:

$$Z = \frac{K_0 - K}{K_0} 100\%$$

where:

K_0 – is the corrosion rate of the sample in a reagent-free medium [g/m$^2 \cdot$ hour],
K_{inh} – is the corrosion rate of the sample in the reagent medium [g/m$^2 \cdot$ h].

Experimental part

The purpose of the research work is to study the effect of the gossypol resin and the HS-1 inhibitor on the corrosion rate of St3 steel sample in various environments in laboratory conditions.

The studies used oil from well No. 412 of the May 28 field (Table 1), 20%, 40%, 60%, and 80% solutions ($H_2S + CO_2$), and a Ct3 steel sample (Table 2).

In laboratory conditions, the effect of a steel sample on the corrosion rate was studied by conducting experiments in various environments both without inhibitors and in the presence of gossypol resin and HS-1 inhibitor. The results obtained are reflected in Tables 3, 4 and 5. As can be seen from Table 3, with an increase in the percentage of $H_2S + CO_2$ solution in the oil content, an increase in the corrosion rate was observed, and the fastest corrosion process occurred in the environment of pure oil + 80% $H_2S + CO_2$ solution. At this time, the corrosion rate was 5.40 $g/m^2 \cdot h$. As can be seen from Tables 4 and 5, with an increase in the

Table 1. Physico-chemical characteristics of oil from well No. 412 of May 28 field

Tabela 1. Charakterystyka fizykochemiczna ropy naftowej z odwiertu nr 412 ze złoża 28 May

Composition	Amount of paraffin [%]	Method of determination
Paraffin	14.2	SS 11851-85
Asphaltene	3.4	SS 11851-85
Tar	8.2	SS 11851-85
Freezing temperature [°C]	+15	SS 20287-91
Amount of water	60	SS 24477-65

Table 2. Chemical composition of Ct3 steel sample

Tabela 2. Skład chemiczny próbki stali Ct3

C	Mn	Si	P	S	Cr	N	Ni
0.14–0.22	0.4–0.65	0.15–0.3	up to 0.04	up to 0.05	up to 0.30	up to 0.008	up to 0.30

Table 3. Corrosion of Ct3 grade steel specimen without inhibitor

Tabela 3. Korozja próbki stali gatunku Ct3 bez inhibitora

Environment	K [$g/m^2 \cdot h$]
Pure oil	3.30
Pure oil + 20% $H_2S + CO_2$ solution	3.90
Pure oil + 40% $H_2S + CO_2$ solution	4.50
Pure oil + 60% $H_2S + CO_2$ solution	5.10
Pure oil + 80% $H_2S + CO_2$ solution	5.40

Table 4. Effect of gossypol resin on corrosion rate

Tabela 4. Wpływ żywicy gossypolowej na szybkość korozji

C_{ing} [mg/l]	K [$g/m^2 \cdot h$]	Retardation factor, γ	Protection effect, Z [%]
Pure oil			
40	0.53	6.23	84
60	0.50	6.60	85
80	0.43	7.67	87
100	0.40	8.25	88
Pure oil + 20% H_2S+CO_2 solution			
40	0.55	7.09	86
60	0.51	7.65	87
80	0.43	9.07	89
100	0.39	10.00	90
Pure oil + 40% H_2S+CO_2 solution			
40	0.49	9.18	89
60	0.45	10.00	90
80	0.36	12.50	92
100	0.32	14.06	93
Pure oil + 60% H_2S+CO_2 solution			
40	0.36	14.17	93
60	0.26	19.62	95
80	0.20	25.50	96
100	0.10	51.00	98
Pure oil + 80% H_2S+CO_2 solution			
40	0.38	14.21	93
60	0.32	16.88	94
80	0.22	24.55	96
100	0.16	33.75	97

Table 5. Effect of HS-1 reagent on corrosion rate

Tabela 5. Wpływ odczynnika HS-1 na szybkość korozji

C_{ing} [mg/l]	K [g/m^2 · h]	Retardation factor, γ	Protection effect, Z [%]
Pure oil			
40	0.52	6.35	84
60	0.49	6.73	85
80	0.39	8.46	88
100	0.36	9.17	89
Pure oil + 20% H_2S+CO_2 solution			
40	0.55	7.09	86
60	0.43	9.07	89
80	0.39	10.00	90
100	0.27	14.44	93
Pure oil + 40% H_2S+CO_2 solution			
40	0.49	9.18	89
60	0.36	12.50	92
80	0.32	14.06	93
100	0.23	19.57	95
Pure oil + 60% H_2S+CO_2 solution			
40	0.46	11.09	91
60	0.36	14.17	93
80	0.26	19.62	95
100	0.15	34.00	97
Pure oil + 80% H_2S+CO_2 solution			
40	0.32	16.88	94
60	0.27	20.00	95
80	0.16	33.75	97
100	0.05	108.00	99

amount of both reagents from 40 mg/l to 100 mg/l in each medium, a decrease in the corrosion rate was observed, and the highest rate was precisely at 100 mg/l. Thus, the corrosion rate at a gossypol resin concentration of 100 mg/l is 0.40 g/m^2 · h in pure oil, 0.39 g/m^2 · h in pure oil + 20% H_2S + CO_2 solution and 0.32 g/m^2 · h in pure oil + 40% H_2S + CO_2solution, 0.10 g/m^2 · h in pure oil + 60% H_2S + CO_2 solution and 0.16 g/m^2 · h in pure oil + 80% H_2S + CO_2 solution, at the concentration of HS-1 reagent 100 mg/l the corrosion rate is 0.36 g/m^2 · h in pure oil, 0.27 g/m^2 · h in pure oil + 20% H_2S + CO_2 solution and 0.23 g/m^2 · h in pure oil + 40% H_2S + CO_2 solution per hour,

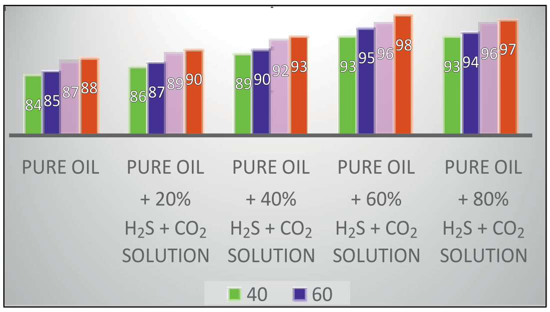

Figure 1. Effect of gossypol resin on corrosion protection efficiency in different environments

Rysunek 1. Wpływ żywicy gossypolowej na skuteczność ochrony antykorozyjnej w różnych środowiskach

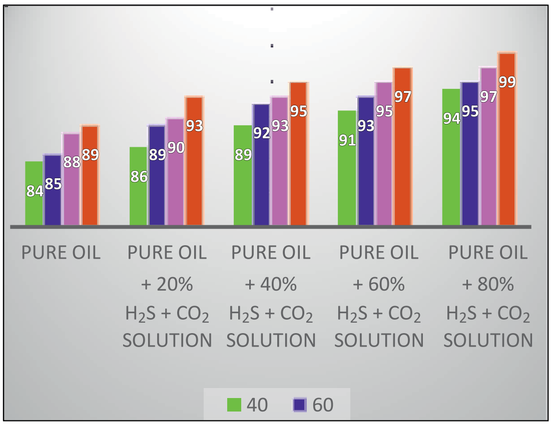

Figure 2. Effect of HS-1 reagent on corrosion protection efficiency in different environments

Rysunek 2. Wpływ odczynnika HS-1 na skuteczność ochrony antykorozyjnej w różnych środowiskach it was 0.15 g/m^2 · h in pure oil + 60% H_2S + CO_2 solution and 0.05 g/m^2 · h in pure oil + 80% H_2S + CO_2 solution.

As can be seen from Figures 1 and 2, the highest value of the effectiveness of corrosion protection with gossypol resin at a concentration of 100 mg/l was obtained in an environment of pure oil + 60% H_2S + CO_2 solution, and at that time was 98%. At a concentration of HS-1 inhibitor of 100 mg/l, the highest value was obtained in the medium of pure oil + 80% H_2S + CO_2 solution and this figure was 99%.

Conclusion

1. For the first time in laboratory conditions, the optimal consumption rate of the gossypol resin and the HS-1 inhibitor in solutions prepared from different percentages of the H_2S + CO_2 mixture of oil from well No. 412 of the May 28 field was determined.
2. First, the density of gossypol resin in pure oil, pure oil + 20% H_2S + CO_2 solution, pure oil + 40% H_2S + CO_2 solution, pure oil + 60% H_2S + CO_2 solution, pure oil + 80% H_2S + CO_2solution environments. Its effect on the rate of corrosion was studied when it changed between 40–100 mg/l. The highest effect was pure oil + 60% H_2S + CO_2 solution and the corrosion protection efficiency was 98% (the rate of corrosion was 0.10 g/m^2 · h).
3. As the concentration of the HS-1 inhibitor increases from 40 mg/l to 100 mg/l in each environment mentioned, its effectiveness on corrosion rate increases. The greatest efficiency was observed at 100 mg/l and in an environment of pure oil + 80% H_2S + CO_2 solution. The rate of this corrosion was 0.05 g/m^2 · h, the effectiveness of corrosion protection was 99%.
4. On the basis of the conducted experiments, it was determined that the highest effect in each of the mentioned environments was observed in a more acidic environment, i.e. in pure oil + 80% H_2S + CO_2 solution environment at a concentration of 100 mg/l of HS-1 inhibitor.

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