

Research of bactericide-inhibitor properties of new compositions based on gossypol resin and chloroprene

Badanie właściwości nowych mieszanin bakteriobójczo-inhibitorowych na bazie żywicy gossypol i chloroprenu

Guseyn R. Gurbanov, Aysel V. Gasimzade, Samira F. Alikishiyeva-Balamiyeva

Azerbaijan State Oil and Industry University

ABSTRACT: Five new compositions with conventional names A-1, A-2, A-3, A-4, and A-5 were prepared using different ratios of chloroprene and gossypol resin reagents, and their corrosion-inhibitory properties were investigated. The sulfate-reducing bacteria *Desulfomicrobium* genus and *Desulfovibrio desulfuricans* species were employed in the study. The effects of the A-series compositions on the bacteria were observed over a 15-day period, during which concentrations of 50, 100, 150, and 200 g/t were tested. Analysis of the results from numerous experiments revealed that the A-3 composition exhibited the highest bactericidal effect among the A-series compositions. Specifically, the bactericidal effect of the A-3 composition at a concentration of 200 g/t was found to be 99%. Under laboratory conditions, the effect of the new A-series compositions on the rate of electrochemical corrosion in formation water containing hydrogen sulfide was investigated. The corrosion rate was determined using the gravimetric method over a six-hour period. Based on the determined corrosion rate, the corrosion protection effect of the new compositions was calculated. The corrosion protection effects of the tested compositions in the order A-1, A-2, A-3, A-4, and A-5 were found to be 98%, 99%, 99%, 92%, and 90%, respectively, at the optimal consumption rate of 200 g/t. Therefore, the results of numerous experiments conducted under laboratory conditions provide evidence suggesting that the A-series compositions possess corrosion-inhibitory properties.

Key words: chloroprene, gossypol resin, composition, corrosion rate, electrochemical corrosion, bactericidal effect.

STRESZCZENIE: Pięć nowych mieszanin o konwencjonalnych nazwach A-1, A-2, A-3, A-4 i A-5 przygotowano przy użyciu różnych proporcji odczynników chloroprenu i żywicy gossypol, a następnie zbadano ich właściwości antykorozyjne. W badaniu wykorzystano bakterie redukujące siarczany z rodzaju *Desulfomicrobium* i gatunku *Desulfovibrio desulfuricans*. Wpływ mieszanin serii A na bakterie obserwowano przez okres 15 dni, podczas których testowano stężenia 50, 100, 150 i 200 g/t. Analiza wyników licznych eksperymentów wykazała, że mieszanina A-3 wykazywała najwyższe działanie bakteriobójcze spośród mieszanin serii A. W szczególności stwierdzono, że działanie bakteriobójcze mieszaniny A-3 w stężeniu 200 g/t wynosi 99%. W warunkach laboratoryjnych zbadano wpływ nowych mieszanin serii A na szybkość korozji elektrochemicznej w wodzie złożowej zawierającej siarkowodór. Szybkość korozji określono metodą grawimetryczną w okresie sześciu godzin. Na podstawie wyznaczonej szybkości korozji obliczono efekt ochrony antykorozyjnej nowych mieszanin. Stwierdzono, że efekty ochrony przed korozją badanych mieszanin w kolejności A-1, A-2, A-3, A-4 i A-5 wynoszą odpowiednio 98%, 99%, 99%, 92% i 90% przy optymalnym zużyciu 200 g/t. Wyniki licznych eksperymentów przeprowadzonych w warunkach laboratoryjnych dostarczają zatem dowodów sugerujących, że mieszaniny serii A posiadają właściwości antykorozyjne.

Słowa kluczowe: chloropren, żywica gossypol, mieszanina, szybkość korozji, korozja elektrochemiczna, działanie bakteriobójcze.

Introduction

In modern civilization, the extraction of formation water exceeds the production capacity of oil, both in Azerbaijan and in other developed oil industry countries, by a factor of five. Additionally, when considering the various sources of formation water injected into the well for formation pressure

maintenance systems, the volume of formation water becomes even greater. Formation water, extracted alongside oil, acts as a strong electrolyte, creating favorable conditions for intensifying the electrochemical corrosion process on the inner surface of industrial equipment (Akramov and Yarkeeva, 2017).

Electrochemical corrosion of metal equipment poses significant economic and environmental risks to oil-producing

Corresponding author: G.G. Gurbanov, e-mail: huseyn.gurbanov@asoiu.edu.az

Article contributed to the Editor: 10.03.2024. Approved for publication: 03.01.2025.

countries. The presence of bacteria in the aggressive corrosion environment created by formation water further exacerbates the environmental and economic damage caused by corrosion (Aliyeva, 2003). Factors such as humidity, composition, solidity of substances in aqueous solutions, osmotic pressure, temperature, and radiation must be considered during the decomposition processes caused by microorganisms (Bao et al., 2012; Xu et al., 2016).

Numerous research studies have concluded that 80% of electrochemical corrosion occurrences are attributed to biological corrosion. Microorganisms play a dual role in the electrochemical corrosion process: on one hand, they accumulate corrosion-promoting aggressive substances, and on the other, they create conditions for the electrochemical corrosion process to proceed (Xu and Gu, 2014; Dubinskaya et al., 2016).

Sulfate-reducing bacteria (SRB) are considered the main cause of microbiological corrosion, and exhibit a high destructive action, significantly accelerating the electrochemical corrosion of equipment (Espolov et al., 2016). Their presence in the corrosion environment results in the biogenic production of hydrogen sulfide, further exacerbating corrosion. Approximately 80% of electrochemical corrosion observed in metal devices and equipment within oil-collecting systems is directly related to microbiological corrosion caused by SRB (Glushchenko, 2007).

Sulfate-reducing bacteria are anaerobic microorganisms. *Desulfomicrobium* genus and *Desulfovibrio desulfuricans* species bacteria can thrive under atmospheric pressures of up to 1300 atm and temperatures of up to 85°C. The pH level of the aggressive corrosion environment, ranging from 5.5 to 9.5, significantly influences the proliferation of sulfate-reducing bacteria. SRB, as obligate anaerobic bacteria, convert sulfate ions into sulfide ions, synthesizing biogenic hydrogen sulfide (Jennings and Weispfennings, 2005). This process, primarily occurring in the attached form of sulfate-reducing bacteria, is more prevalent on metal equipment, as biogenic hydrogen sulfide acid is formed as a result of equipment or nearby corrosion (Khairov, 1996). The size of SRB cells ranges from 0.1 to 0.3 µm, and the reduction of sulfate ions is markedly increased under optimal conditions (Ivanova et al., 2022). This biogenic product of bacteria contributes to electrochemical biological corrosion forces, transitioning from planktonic forms to adhering onto equipment and installations during oil construction, collection, preparation for storage, and transportation.

Based on the aforementioned factors, it is evident that safeguarding the inner surfaces of oil industry equipment against electrochemical corrosion induced by sulfate-reducing bacteria remains a persistent challenge (Milovzorov et al., 2012). The most effective approach to addressing this issue involves the development of reagents with inhibitory and bactericidal properties, their evaluation under laboratory conditions, and subsequent implementation in industrial settings (Ramazanova et al., 2011).

The objective of this research endeavor is to investigate the corrosion-inhibitory properties of A-series compositions that are formulated from various molar ratios of gossypol resin and chloroprene reagents, under controlled laboratory conditions.

Research methodology

Postgate-"B" nutrient medium was utilized for the cultivation and maturation of sulfate-reducing bacteria (SRB). The morphology of the bacteria was examined using an MBI-6 microscope. The viable cell count was determined using a limited dilution method.

SRB exhibit robust growth in such nutrient-rich environments, as evidenced by the intensive reproduction observed (Table 1) (NACE, 1994). The reagents required for preparing the nutrient medium were calculated per one liter of water, and the pH of the medium should fall within the range of 7 = 7.5; pH verification was conducted using universal indicator paper.

Additionally, the optimization of SRB development in Postgate "B" nutrient medium involved the incorporation of specific additives. Ct 3 brand steel samples were selected for the experiment, and all studies were conducted under static conditions. To ensure optimal SRB growth, corrosion studies were performed under thermostatic conditions (RD., 1982).

To assess the inhibitory properties of the compositions under laboratory conditions, *Desulfomicrobium* genus and *Desulfovibrio desulfuricans* species were employed in the experiment. The sulfate-reducing bacteria used were extracted from the formation waters of well No. 1082 of SOCAR's Bibiheybat OPG.

The equipment utilized included a drying cabinet, microscopes (MBI-1, MBR-1), autoclaves (AQ-1, AV-1), sterilizers, thermostats, medical syringes (1–2 ml), flasks (0.1, 0.5, and

Table 1. Composition of Postgate" B" nutrient medium

Tabela 1. Mieszanina dla pożytki Postgate „B”

Postgate "B" [g/l]	NH ₄ Cl	K ₂ HPO ₄	MgSO ₄ × 7 H ₂ O	CaSO ₄	Lactate-Ca	Na ₂ S	Na ₂ SO ₃	FeSO ₄ (5% solution of in 1% HCl)
	1.0	0.5	2.0	1.0	2.6	0.2	2.0	0.5

1 liter), test bottles, penicillin bottles, rubber stoppers, transmission glasses, and item glasses.

During experiments involving sulfate-reducing bacteria, the corrosion medium, dishes, and other objects were sterilized in an autoclave to prevent the growth of foreign bacteria in the experimental environment.

To evaluate the bactericidal properties of the compositions, pre-sterilized test bottles were employed according to the specified methodology.

The bactericidal properties of the compositions were primarily assessed by observing them over a fifteen-day period and subsequently measuring the concentration of hydrogen sulfide formed in the Postgate “B” medium. The formation of hydrogen sulfide was determined using the iodometric titration method. Daily assessments were made of both the concentration of biogenic hydrogen sulfide and the number of microorganism cells.

The Postgate “B” medium was sterilized and oxygen was removed by heating to boiling, followed by rapid cooling to 35°C.

Pre-calculated solutions of the compositions (3.0–10 mg/l) were added to sterilized test bottles along with the Postgate “B” solution and incubated in a thermostat at a temperature of 30–35°C for fifteen days. During the experiment, the development of sulfate-reducing bacteria in the nutrient medium could be visually observed by the formation of a dark-colored precipitate at the bottom of the bottles.

Sulfate-reducing bacteria typically form black colonies due to the biogenic hydrogen sulfide they produce. In cases where the reagent being studied exhibits bactericidal effects, a white precipitate appears at the bottom of the test bottles, indicating the cessation of sulfate-reducing bacteria metabolism.

The number of sulfate-reducing bacteria cells in 1 ml of initial suspension is calculated by the following formula:

$$M = 1000an / hs$$

where:

M – the number of cells in 1 ml suspension,

a – the average number of cells per square cell of the chamber,

h – chamber depth [mm],

S – the area of the square mesh [mm²],

n – the degree of dilution of the suspension.

The growth factor of sulfate-reducing bacterial cells in the presence of an inhibitor is calculated by the following expression:

$$N, \% = \frac{100(n_0 - n_{inh.})}{n_0}$$

n_0 – the number of microorganisms in inhibitor-free medium,

$N_{inh.}$ – the number of microorganisms in the inhibitor medium.

According to the amount of hydrogen sulfide, the bactericidal effect of the inhibitor is calculated by the following formula:

$$S, \% = \frac{C_0 - C_{inh.}}{C_{inh.}} \cdot 100$$

C_0 – the concentration of biogenic hydrogen sulfide in the inhibitor-free environment,

$C_{inh.}$ – the concentration of biogenic hydrogen sulfide in the inhibitory environment.

The coefficient of variation of the concentration of hydrogen sulfide is found by the following mathematical expression:

$$\gamma_c = \frac{C(H_2S)_0}{C(H_2S)_{inh.}}$$

where:

$C(H_2S)_0$ – the concentration of hydrogen sulfide in the medium without inhibitor,

$C(H_2S)_{inh.}$ – the concentration of hydrogen sulfide in the inhibitor medium.

The protective effect of the inhibitor is calculated by the following equation:

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

K_0 – the corrosion rate of the sample in a reagent-free environment [g/m² · h],

K – the corrosion rate of the sample in reagent environment [g/m² · h].

Results and discussion

To conduct experiments, five series of compositions were prepared using chloroprene and gossypol resin reagents in varying molar ratios (Table 2).

Given the potentially higher corrosion aggressiveness of SRB compared to other bacteria, the efficacy of the prepared compositions in destroying SRB was investigated. Additionally, selecting SRB for the study was relevant because their eradi-

Table 2. Composition and brand of compositions made from chloroprene and gossypol resin

Tabela 2. Kompozycja i marka mieszanin wykonanych z żywicy chloroprenowej i gossypolowej

Components of the composition	Mole ratios	Brand
Chloroprene + Gossypol resin	1:1	A-1
Chloroprene + Gossypol resin	2:1	A-2
Chloroprene + Gossypol resin	3:1	A-3
Chloroprene + Gossypol resin	1:2	A-4
Chloroprene + Gossypol resin	1:3	A-5

cation could prevent the proliferation of other physiological groups of microorganisms.

The study of the compositions' effect on the incubation period of sulfate-reducing bacteria over fifteen days was conducted according to the following procedure:

Considering the substantial reproduction of SRB primarily in Postgate "B" nutrient medium, the experiments were conducted using this medium. Reagent-free and reagent-added media were compared. Initially, 1 ml of the medium containing SRB was diluted with distilled water and inoculated into pre-sterilized 10 ml test bottles in a 1:9 ratio with Postgate "B" nutrient medium. The bottles were then placed in a thermostat at 35°C for fifteen days. The bactericidal effect of the test compositions was observed daily, and the results were recorded in a compiled table (Table 3). The presence or development of sulfate-reducing bacteria in the experimental environment was determined based on visual indicators, including:

1. Formation of colored (black or white) sediments at the bottom of the test bottles.
2. Formation of hydrogen sulfide.
3. Presence of living forms of sulfate-reducing bacteria.

SRB reproduce intensively and produce biogenic hydrogen sulfide as a byproduct of their metabolism, resulting in black-colored colonies. However, when a chemical reagent with bactericidal properties is added to the medium, a white sediment forms at the bottom of the test bottles, indicating the cessation of bacterial metabolism.

During daily observations, black sediment was denoted with a "+" sign, and white sediment with a "-" sign (Table 3). Analysis of these signs revealed that a positive sign indicated the inability of the composition to effectively inhibit SRB growth, as evidenced by the darkening of the test bottle bottom. Conversely, a negative sign indicated complete cessation of SRB development due to the high bactericidal effect of the composition. If partial blackening and white sediment coexist, it suggests a biostatic effect of the composition, as indicated in the table.

Table 3 demonstrates that composition A-1, at a concentration of 200 g/t, exhibited a pronounced effect on inhibiting SRB development over fifteen days, as indicated by the "-" sign, signifying complete cessation of SRB growth from the outset. However, at concentrations of 50 g/t, 100 g/t, and 150 g/t of

Table 3. Effects of the compositions on the vital activity of sulfate-reducing bacteria for 15 days

Tabela 3. Wpływ kompozycji na aktywność życiową bakterii redukujących siarczyn przez 15 dni

Compositions	Rigidity [g/t]	Incubation period with SRB [days]															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
A-1	50	-	-	-	-	-	-	-	-	-	⊥	⊥	⊥	+	+	+	+
	100	-	-	-	-	-	-	-	-	-	-	-	-	⊥	+	+	+
	150	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+	+
	200	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
A-2	50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+	+
	100	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	150	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	200	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
A-3	50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+
	100	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	150	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	200	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
A-4	50	-	-	-	-	-	-	-	-	+	+	+	+	+	+	+	+
	100	-	-	-	-	-	-	-	-	-	+	+	+	+	+	+	+
	150	-	-	-	-	-	-	-	-	-	-	-	-	+	+	+	+
	200	-	-	-	-	-	-	-	-	-	-	-	-	-	+	+	+
A-5	50	-	-	-	-	-	-	-	+	+	+	+	+	+	+	+	+
	100	-	-	-	-	-	-	-	-	-	+	+	+	+	+	+	+
	150	-	-	-	-	-	-	-	-	-	-	-	+	+	+	+	+
	200	-	-	-	-	-	-	-	-	-	-	-	-	+	+	+	+
Environment without SRB		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Environment with SRB		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

A-1, darkening of the test bottle bottoms and SRB development were observed on day 9, 12, and 14, respectively, denoted by the “+” sign in the table.

Similarly, the growth of bacteria was only observed on the 15th day at a concentration of 50 g/t for composition A-2, which displayed a strong bactericidal effect, inhibiting bacteria growth from the outset. In contrast, composition A-3 completely halted bacterial growth at all four concentrations over the fifteen-day period.

However, the results varied slightly for compositions A-4 and A-5, where gossypol resin was predominant. For composition A-4, darkening of the test bottle bottoms and SRB development were observed on the days 8, 10, 13 and 14 at concentrations of 50 g/t, 100 g/t, 150 g/t, and 200 mg/l, respectively. Similarly, blackening was observed in the test bottles for composition A-5 on the days 7, 9, 12 and 13 at concentrations of 50 g/t, 100 g/t, 150 g/t, and 200 g/t, indicating SRB development on those days.

At the conclusion of the fifteen-day experiment, the number of sulfate-reducing bacteria (cell count/ml) was determined in both reagent-free and reagent-added environments under a microscope (Table 4).

As shown in Table 4, millions of sulfate-reducing bacteria (SRBs) grew in reagent-free Postgate “B” medium, which served as the control. In environments where additional compositions were introduced, the bacterial population varied as follows:

- $n = 10^6$ at 50 g/t of composition A-1,
- $n = 10^4$ at 100 mg/l,
- $n = 10^2$ at 150 g/t and $n = 0$ at 200 g/t.

In the media with compositions A-2 and A-3, except for the concentration of 50 g/t ($n = 10^2$ and $n = 10^1$, respectively) in the remaining concentrations $n = 0$. Composition A-4 had $n = 10^6$ at 50 g/t, $n = 10^5$ at 100 g/t, $n = 10^4$ at 150 g/t and $n = 10^3$ at 200 g/t. For the concentrations of 50, 100, 150 and 200 g/t of composition A-5, the value of n was 10^6 , 10^5 , 10^4 and 10^3 , respectively.

The bactericidal effect of the compositions was studied mainly by observing the effect for fifteen days and finally calculating the density of hydrogen sulfide formed in Postgate “B” environment. Both the concentration of biogenic hydrogen sulfide and the number of microorganism cells were determined on a daily basis. Reagents were titrated by the iodometric method and the amount of biogenic hydrogen-sulfide formed in the Postgate “B” environment was calculated.

The results of the bactericidal effects of the compositions based on the amount of biogenic hydrogen sulfide formed in the environment are given in Table 5.

Analysis of the results presented in Table 5 reveals that the bactericidal effect of the compositions increased with subsequent concentrations of the tested compositions A-1 to A-4.

Table 4. Effect of compositions on the number of sulfate-reducing bacteria during 15 day incubation

Tabela 4. Wpływ mieszanin na liczbę bakterii redukujących siarczynany podczas 15-dniowej inkubacji

Composition	Concentration of compositions [g/t]			
	50	100	150	200
	Bacterial count (n cell count/ml)			
Without reagent	10^7	10^7	10^7	10^7
A-1	10^6	10^4	10^2	–
A-2	10^2	–	–	–
A-3	10^1	–	–	–
A-4	10^6	10^5	10^3	10^2
A-5	10^6	10^5	10^4	10^3

Table 5. The bactericidal effect of the compositions

Tabela 5. Bakteriobójcze działanie mieszanin

Composition	Concentration of compositions [g/t]	C_{H_2S} [g/t]	Bactericidal effect, S [%]
A-1	50	110	59
	100	70	74
	150	50	81
	200	40	85
A-2	50	42	84
	100	30	88
	150	20	92
	200	15	94
A-3	50	18	93
	100	10	96
	150	6	97
	200	3	99
A-4	50	120	56
	100	80	70
	150	60	78
	200	50	81
A-5	50	135	50
	100	95	65
	150	75	72
	200	65	76
C_{H_2S} (Environment without SRB)	34 mg/l		
C_{H_2S} (in an environment with SRB)	270 mg/l		

However, there is a relative decrease in the bactericidal effect of compositions A-4 and A-5. The highest effect was observed at a concentration of 200 g/t of the A-3 composition (99%), while the weakest effect was observed at a concentration of 50 g/t of the A-5 composition (50%).

One of the primary reasons for the corrosion of steel pipes used in the oil industry is the presence of various factors in formation waters, including dissolved gases, mineral and organic salts, mechanical mixtures, and notably, hydrogen sulfide. Formation water, acting as a natural electrolyte solution, accelerates the electrochemical corrosion process by creating an aggressive environment on the inner surface of pipes.

It is well-established that hydrogen sulfide, dissolved in formation waters and present in the form of free gas, is a key factor in accelerating electrochemical corrosion. Additionally, hydrogen sulfide in the environment of formation waters, combined with salts of various origins, further exacerbates corrosion.

Considering the factors outlined above, the inhibitory properties of the compositions prepared under laboratory conditions were studied in formation water containing hydrogen sulfide, and their corrosion protection effect was evaluated.

Formation water samples from well No. 1082 of SOCAR's Bibiheybat OPG were used as an electrochemical corrosion medium. The composition of formation water from well No. 1082 is provided in Table 6.

Table 6. The ionic composition of formation water extracted from well No. 1802

Tabela 6. Mieszanka wody złożowej wydobytej z odwiertu 1802

Ions	Concentration of ions [g/l]	Equivalent concentration of ions [mg/l]	Equivalent quantity [%]
Na ⁺ + K ⁺	31298.9	1304.1	46.6
Ca ²⁺	1122.2	56.0	2.0
Mg ²⁺	486.4	40.0	1.3
Fe ³⁺	2561.6	853.9	–
Cl ⁻	49010.5	1382.5	49.4
SO ₄ ²⁻	28.8	0.6	0.1
CO ₃ ²⁻	0.0	0.0	0.0
HCO ₃ ⁻	1037.0	17.0	0.6

To investigate the inhibitory properties of compositions derived from different mole ratios of chloroprene and gossypol resin in hydrogen sulfide formation water obtained from well No. 1082 of the Bibiheybat OPG, laboratory experiments were conducted following the sequence outlined below.

Initially, pre-cleaned steel samples were weighed on an analytical balance and placed into a rectangular flask equipped with a mechanical stirrer. Subsequently, a calculated volume

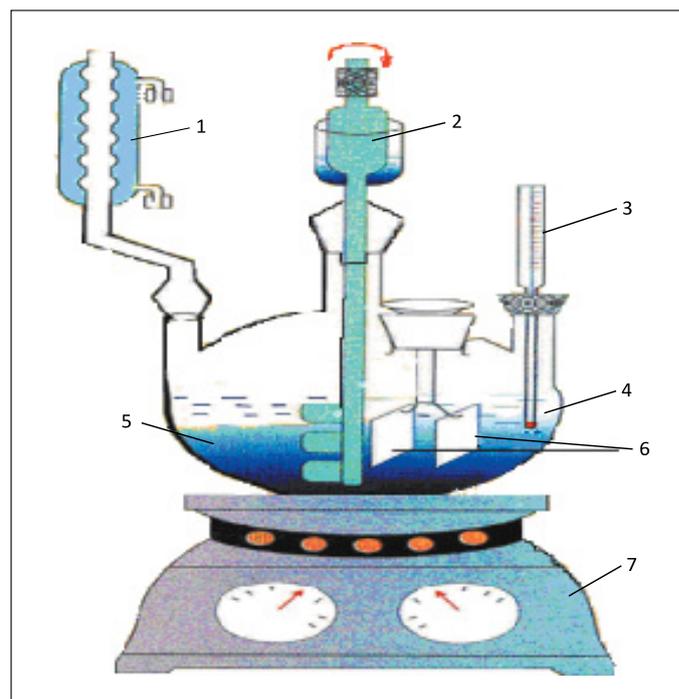


Figure 1. A laboratory device for determining the corrosion of Ct3 grade steel samples; 1 – cooler, 2 – mechanical stirrer, 3 – thermometer, 4 – flask, 5 – corrosion medium or inhibitor, 6 – steel samples, 7 – heating device

Rysunek 1. Urządzenie laboratoryjne do oznaczania korozji próbek stali klasy Ct3; 1 – chłodnica, 2 – mieszadło mechaniczne, 3 – termometr, 4 – kolba, 5 – czynnik lub inhibitor korozji, 6 – próbki stali, 7 – urządzenie grzewcze

of formation water extracted from well No. 1082 and the appropriate quantity of composition were added to the flask (Figure 1). It is noteworthy that the number of compositions was determined in accordance with established guidelines for one liter of corrosion medium.

The experimental process was conducted at a controlled temperature of 20 ±3°C for six hours, with continuous stirring at a rotation speed of 800 revolutions per minute. Following the six-hour period, the system was allowed to rest briefly before the steel samples were subjected to a series of post-treatment steps. These steps included washing, cleaning, wiping with alcohol, drying, and subsequent re-weighing using an analytical balance.

In addition to experiments conducted with the addition of compositions, parallel experiments were also conducted in the environment without the inclusion of compositions. The rate of electrochemical corrosion and the protective efficacy of the compositions were determined using the gravimetric method. The results obtained from these experiments are presented in Table 7.

Based on the analysis of the results presented in Table 7, it is evident that the protective effect of all compositions increased along with their concentration in the formation water. Specifically, the increase ranged from 85% to 98% for A-1,

Table 7. The results of the study of the inhibitory properties of the compositions in formation water containing hydrogen-sulfide ($C_{H_2S} = 15 \text{ mg/l}$)

Tabela 7. Wyniki badań właściwości inhibitorowych mieszanin w wodzie złożowej zawierającej siarkowodór ($C_{H_2S} = 15 \text{ mg/l}$)

Composition	C_{inh} [mg/l]	K [g/m ² ·hour]		Retardation factor, γ	Penetration coefficient, P_K [mm/year]	Protective effect, Z [%]
		without inhibitors	with an inhibitor			
A-1	0.00	1.3260	1.32600	–	–	–
	50	1.3260	0.19890	6.67	0.222768	85
	100	1.3260	0.13260	10.00	0.148512	90
	150	1.3260	0.03978	33.26	0.044554	97
	200	1.3260	0.02652	50.00	0,029702	98
A-2	0.00	1.3260	1.32600	–	–	–
	50	1.3260	0.10608	12.50	0.118809	92
	100	1.3260	0.05304	25.00	0.059405	96
	150	1.3260	0.02652	50.00	0.029702	98
	200	1.3260	0.01326	100.00	0.014851	99
A-3	0.00	1.3260	1.32600	–	–	–
	50	1.3260	0.06630	20.00	0.074256	95
	100	1.3260	0.03978	33.26	0.044554	97
	150	1.3260	0.01326	100.00	0.014851	99
	200	1.3260	0.01326	100.00	0.014851	99
A-4	0.00	1.3260	1.32600	–	–	–
	50	1.3260	0.33150	4.00	0.371280	75
	100	1.3260	0.18564	7.14	0.207917	86
	150	1.3260	0.13260	10.00	0.148512	90
	200	1.3260	0.10608	12,50	0.118809	92
A-5	0.00	1.3260	1.32600	–	–	–
	50	1.3260	0.37128	3.57	0.415834	72
	100	1.3260	0.21216	6.25	0.237619	84
	150	1.3260	0.15912	8.33	0.178214	88
	200	1.3260	0.13260	10.00	0.148512	90

92% to 99% for A-2, 95% to 99% for A-3, 75% to 92% for A-4, and 72% to 90% for A-5. Upon closer examination, it becomes apparent that while the corrosion protection effect generally escalated from A-1 to A-4, a decrease was observed in A-4 and A-5.

Compositions A-2 and A-3 achieve complete cessation of corrosion in the formation water at a concentration of 200 g/t. Composition A-1 reduced the corrosion rate by 50 times, A-4 by 12.5 times, and A-5 by 10 times. In summary, the results indicate that all prepared compositions exhibit highly effective inhibitory properties at laboratory conditions. Table 8 provides a comparative analysis of the corrosion-inhibitory properties of the compositions.

From the comparative analysis of the bactericidal and corrosion protection effects of A-series compositions in Table 8, it can be seen that the increase in the concentration of reagents

in the medium from 50 g/t to 200 g/t leads to an increase in their effectiveness.

As can be seen in the table 8, the corrosion protection effect is higher than the bactericidal effect in the same layer of A-series compositions.

Conclusions

This study marks the first examination of the A-1, A-2, A-3, A-4, and A-5 compositions, formulated from varying mole ratios of chloroprene and gossypol resin, in laboratory settings over a fifteen-day period using the Postgate “B” nutrient medium to determine the activity of sulfate-reducing bacteria. Additionally, their impact on the activity and electrochemical corrosion rate in hydrogen-sulfide formation water

Table 8. Comparative analysis of corrosion-inhibitory (in acidic environment) properties of A-series compositions**Tabela 8.** Analiza porównawcza właściwości antykorozyjnych (w środowisku kwaśnym) mieszanin serii A

Brand of reagents	The hardness that provides protection against corrosion [g/t]	Corrosion protection effect [%]	Bactericidal effect of reagents [%]
A-1	3	85	59
	5	90	74
	7	97	81
	10	98	85
A-2	3	92	84
	5	96	88
	7	98	92
	10	99	94
A-3	3	95	93
	5	97	96
	7	99	97
	10	99	99
A-4	3	75	56
	5	86	70
	7	90	78
	10	92	81
A-5	3	72	50
	5	84	65
	7	88	72
	10	90	76

was evaluated over a six-hour duration. For experimentation, sulfate-reducing bacteria of the and *Desulfomicrobium* genus and *Desulfovibrio desulfuricans* species, along with formation water, were sourced from well No. 1082 of Bibiheybat OPG.

The findings of the experiments conducted in both environments underscore the notable corrosion-inhibitory properties exhibited by the A-series compositions. Notably, an increase in the concentration of reagents in the medium correlated with heightened effectiveness. The highest observed bactericidal effect in the Postgate “B” nutrient medium was attained at a concentration of 200 g/t of composition A-3 (99%). Additionally, compositions A-2 and A-3 demonstrated a substantial protective effect against electrochemical corrosion (99%).

References

- Akramov T.F., Yarkееva N.R., 2017. Treatment of paraffin deposits, asphaltene-resin components of oil. *Oil and Gas Business*, 4: 67–72.
- Aliyeva A.I., 2003. Investigations of the rheological properties of highly paraffinic oils. *News of the Academy of Sciences of Azerbaijan*, 3: 88–93.
- Bao Q., Zhang D., Lv D., Wang P., 2012. Effects of two main metabolites of sulphate-reducing bacteria on the corrosion of Q235 steels in 3.5 wt.% NaCl media. *Corrosion Science*, 65: 405–413. DOI: 10.1016/j.corsci.2012.08.044.
- Dubinskaya E.V., Vigdorovich V.I., Tsygankova L.E., 2013. Inhibitor protection of steel in hydrogen sulfide environments. *Bulletin of TSU*, 5: 2814–2822.
- Espolov I.T., Ayapbergenov E.O., Serkebaeva B.S., 2016. Features of rheological properties of high-viscosity oil during pipeline transportation. *Journal of Transport and Storage of Oil Products and Hydrocarbon Raw Materials*, 3: 35–39.
- Glushchenko V.N., 2007. Evaluation of the effectiveness of inhibitors of asphaltene resin paraffin deposits. *Oil Economy*, 5: 84–87.
- Ivanova V.L., Makarov I.A., Primerova O.V., 2022. Comparative study of the effectiveness of action of depressor-dispersing additives in diesel fuel, news of higher educational institutions. *Chemistry and Chemical Technology*, 3: 60–66.
- Jennings D.W., Weispfenning K., 2005. Effect of shear and Temperature on WOX Deposition Cold finger investigation with a Gulf of Mexico Crude Oil. *Energy Fuels*, 19: 376–1386.
- Khairov G.I., 1996. Study of the influence of magnetic treatment of aqueous solutions of PAV on their oil-displacing ability. *Construction of on-Shore and Offshore Oil and Gas Wells*, 18–19.
- Milovzorov G.V., Makletsov V.G., Trefilova T.V., 2012. On the use of inhibitors - bactericides in conditions of hydrogen sulfide corrosion of steel. *Bulletin of the Udmurt University*, 3: 44–47.
- Ramazanova E.E., Nasibov S.M., Guliev F.A., 2011. New highly effective reagents for use in transportation and production of high-viscosity paraffinic oils. *Azerbaijan Oil Industry*, 11: 55–61.
- Xu D., Gu T., 2014. Carbon source starvation triggered more aggressive corrosion against carbon steel by the *Desulfovibrio vulgaris* biofilm. *International Biodeterioration & Biodegradation*, 91: 74–81. DOI: 10.1016/j.ibiod.2014.03.014.

Xu D., Li Y, Gu T., 2016. Mechanistic modeling of biocorrosion caused by biofilms of sulfate reducing bacteria and acid producing bacteria. *Bioelectrochemistry*, 110: 52–58. DOI: 10.1016/j.bioelechem.2016.03.003.

Legislative acts and normative documents

NACE Standard TM0194-94 Item-21224 1994. Standard Test Method Field Monitoring of Bacterial Growth in Oilfield Systems.18.
RD 39-3-812-82 1982. Methodology for determining the solidification temperature of paraffin oils Rheological properties, 9.



Prof. Guseyn Ramazan GURBANOV, Ph.D.
Head of the Department of Oil and Gas Transportation and Storage
Azerbaijan State Oil and Industry University
16/21 Azadliq Ave., AZ1010 Baku, Azerbaijan
E-mail: huseyn.gurbanov@asoiu.edu.az



Aysel Valiyaddin GASIMZADE, Ph.D.
Associate Professor at the Department of Oil and Gas Transportation and Storage
Azerbaijan State Oil and Industry University
31 Khagani Street, AZ1010 Baku, Azerbaijan
E-mail: qasimzade92@inbox.ru



Samira F. ALIKISHIYEVA-BALAMIYEVA, M.Sc.
Laboratory technician and teacher at the Department of Oil and Gas Transportation and Storage
Azerbaijan State Oil and Industry University
16/21 Azadliq Ave., AZ1010 Baku, Azerbaijan
E-mail: samira.alikishiyeva@gmail.com

OFERTA BADAWCZA ZAKŁADU TECHNOLOGII EKSPLOATACJI PŁYNÓW ZŁOŻOWYCH

Zakład oferuje:

- opracowanie kompleksowej technologii bioremediacji in-situ gruntu zanieczyszczonego substancjami ropopochodnymi;
- rekultywację terenów skażonych substancjami ropopochodnymi;
- opracowanie technologii oczyszczania i utylizacji wód złożowych i odpadów po zabiegach stymulacyjnych z zastosowaniem nowoczesnych rozwiązań technicznych i technologicznych oraz metod biologicznych;
- optymalizacja procesów wydobycia i przygotowania do transportu ropy i gazu;
- monitorowanie zmian zawartości związków siarki w podziemnych magazynach gazu;
- badania i dobór inhibitorów parafinowo-hydratowych oraz deemulgatorów stosowanych w procesach eksploatacji złóż węglowodorów.

Badania i analizy laboratoryjne:

- analizy chromatograficzne:
 - » składu gazu ziemnego ($C_1 - C_8$, N_2 , CO_2 , He, H_2),
 - » związków siarki w gazie ziemnym,
 - » węglowodorów ciężkich ($C_3 - C_{36}$, BTEX),
- analizy toksykologiczne z wykorzystaniem nowoczesnych testów: Microtox, zestawów testów typu „toxkit” i testu MARA;
- analizy zawartości wielopierścieniowych węglowodorów aromatycznych (WWA) w próbkach środowiskowych z wykorzystaniem HPLC;
- analiza płynów złożowych, zanieczyszczeń gleby i ścieków, odpadów eksploatacyjnych i wiertniczych z wykorzystaniem chromatografii jonowej;
- nieniszczące badania grubości materiałów konstrukcyjnych (certyfikat UT2).



Kierownik: dr hab. inż. Teresa Steliga, prof. INiG – PIB Adres: ul. Armii Krajowej 3, 38-400 Krosno
Telefon: 13 436 60 29, 13 436 89 41 w. 5222 Faks: 13 436 79 71 E-mail: teresa.steliga@inig.pl



INSTYTUT NAFTY I GAZU
– Państwowy Instytut Badawczy