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Study of the effect of the composition of high-paraffin oil on their freezing temperature and on the corrosion aggressivity of formation water

Badanie wpływu składu ropy o wysokiej zawartości parafin na ich temperaturę krzepnięcia i agresywność korozyjną wody złożowej

Saida M. Pashayeva

Azerbaijan State Oil and Industry University

ABSTRACT: The effects of gossypol resin and NDP-6 reagents, as well as the Z-1 composition prepared in the ratio of NDP-6 + + gossypol resin = 9:1 on the corrosion aggressiveness of formation water and freezing temperature of high-paraffin model oil were investigated for the first time in laboratory conditions. During the experiments, a model oil sample prepared in a 2:1 ratio of commercial oil from Narimanov and Absheron fields of SOCAR was used as a research object. The electrochemical corrosion medium was a formation water sample taken from well No. 1082 of "Bibiheybatneft" OGPI, SOCAR. It was determined that compared to individual reagents, the new composition has a more effective impact on the corrosion rate in H_2S formation water and the freezing temperature of high-paraffin oil sample. As a result of the conducted research, it was found out that as the concentration of reagents increases, the efficiency of the effect also increases. Thus, the highest protection efficiency for gossypol resin was observed at a concentration of 110 mg/l, resulting in the corrosion rate of 0.09 $g/m^2 \cdot h$ (98% corrosion protection efficiency). The most effective indicator for NDP-6 depressant additive was at 1000 g/t, reducing the freezing temperature of high-paraffin model oil from +16°C to –2°C. However, the strongest effect was observed in Z-1 composition. At a concentration of 700 g/t, it reduced the corrosion rate in the formation water from 4.30 $g/m^2 \cdot h$ to 0.04 $g/m^2 \cdot h$ (99% corrosion protection efficiency) and the freezing temperature of model oil from +16°C to –9°C, respectively (163% of the effect on freezing temperature). Thus, based on the results obtained from the experiments, the efficiency of individual reagents and the composition based on both reagents was calculated. The highest efficiency was observed at a concentration of 700 g/t for the composition "NDP-6 + gossypol resin = 9:1" (conditional name – Z-1).

Key words: composition, corrosion, corrosion efficiency, high-paraffin model oil, formation water, freezing temperature.

STRESZCZENIE: Po raz pierwszy w warunkach laboratoryjnych zbadano wpływ żywicy gossypolowej, odczynników NDP-6 oraz kompozycji Z-1 przygotowanej w proporcji NDP-6 + żywica gossypolowa w stosunku 9:1, na szybkość korozji wody złożowej oraz temperaturę krzepnięcia modelowej ropy o wysokiej zawartości parafin. Jako obiekt badawczy wykorzystano modelową próbkę ropy naftowej przygotowaną w stosunku 2:1 ropy handlowej ze złóż Narimanov i Absheron firmy SOCAR. Jako elektrochemiczne medium korozyjne użyto próbki wody złożowej, pobranej z odwiertu nr 1082 OGPI „Bibiheybatneft", SOCAR. Stwierdzono, że w porównaniu do poszczególnych odczynników zastosowana nowa kompozycja skuteczniej wpływa na szybkość korozji w wodzie złożowej z H_2S oraz na temperaturę krzepnięcia próbki ropy wysokoparafinowej. W wyniku przeprowadzonych badań stwierdzono, że wraz ze wzrostem stężenia odczynników wzrasta także skuteczność działania. Największą skuteczność żywicy gossypolowej zaobserwowano przy stężeniu 110 mg/l, gdy szybkość korozji wynosi 0,09 $g/m^2 \cdot h$ (skuteczność ochrony przed korozją 98%). Najskuteczniejszym wskaźnikiem dla depresatora NDP-6 było stężenie 1000 g/t i w tym czasie zaobserwowano spadek temperatury krzepnięcia modelowej ropy o wysokiej zawartości parafin z +16°C do –2°C. Jednak najsilniejszy efekt zaobserwowano dla kompozycji Z-1. Tym samym kompozycja o stężeniu 700 g/t zmniejsza szybkość korozji w wodzie złożowej z 4,30 $g/m^2 \cdot h$ do 0,04 $g/m^2 \cdot h$ (skuteczność ochrony przed korozją 99%) oraz temperaturę krzepnięcia modelowej ropy odpowiednio od +16°C do –9°C (163% wpływu na temperaturę krzepnięcia). Zatem na podstawie uzyskanych wyników obliczono skuteczność poszczególnych odczynników oraz skład oparty na obu odczynnikach. Największą wydajność zaobserwowano przy stężeniu 700 g/t kompozycji NDP-6 + żywica gossypolowa w stosunku 9:1 (nazwanej Z-1).

Słowa kluczowe: kompozycja, korozja, odporność korozyjna, modelowa ropa o wysokiej zawartości parafin, woda złożowa, temperatura krzepnięcia.

Corresponding author: S. Pashayeva, e-mail: *seide.memmedli@list.ru*

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Introduction

Corrosion protection of units and facilities exploited in the oil industry continues to be a pressing issue, and the damage caused by corrosion to the world economy is measured in billions of dollars per year.

It is known that components exhibiting corrosion aggressiveness, such as sulfur and oxygen compounds, hydrogen sulfide, carbon dioxide, molecular oxygen, as well as mineral salts dissolved in formation waters, contribute to the corrosion of facilities during exploitation. The hydrogen-sulfide contained in formation water is extremely dangerous for the units and facilities. This compound not only exhibits high reactivity, but also induces hydrogen embrittlement in metals (Kuznetsov and Vaganov, 2000, 2001; Kuznetsov, 2002). While the corrosion of metals in a hydrogen sulfide medium has been widely investigated, the solutions to this problem are currently of both practical and economic importance in the oil industry (Kuznetsov and Vaganov, 2001; Vaganov et al., 2002). The presence of hydrogen sulfide in formation waters leads to intensive corrosion of underground facilities in oil wells, oil pipelines, oil storage and settling tanks, as well as the inner surface of oil refinery facilities. Therefore, the selection, testing and widespread application of chemical reagents to reduce the speed of the corrosion process and potentially halt it altogether remains a pertinent and ongoing concern.

On the other hand, during the final stage of oil field development, the formation of asphaltene-resin-paraffin deposits in the well-storage-transportation system is considered as a significant and pressing issue. These deposits are formed in the systems of oil extraction, storage and preparation for transportation. The quantity and characteristics of these deposit undergo changes due to various factors such as pressure, mode, temperature drop, oil degassing and other influences in the well bottom, well body and surface storage-transportation systems. The most important of these factors is temperature drop. Currently, the oils produced in our republic are diverse according to their physical-chemical indicators and rheological properties. This diversity is evident in the indicators such as viscosity, the content of resin, asphaltene and paraffins, among others (Akramov and Yarkeeva, 2017; Gurbanov et al., 2020a, 2020b). Most of the oils produced in Azerbaijan contain varying amounts of asphaltene, resin and paraffin. Consequently, the deposition of these components in the well bottom and pipelines is an inevitable process.

The main rheological parameter of oils is viscosity, which characterizes their fluidity. Paraffinic oils, in particular, are categorized as high-viscosity oils. As viscosity increases, so dees frictional pressure, leading to a degradation in fluidity and subsequent energy loss. Pipeline transportation of paraffinic oils poses several challenges in this context. The main goal in oil extraction is the development of technological processes that will reduce the energy loss while preventing additional losses of hydrocarbon raw materials. Temperature is a critical factor influencing viscosity, where an increase in temperature reduce viscosity, alleviating the challenges associated with transporting high-viscosity oils. Consequently, high-paraffin oil and oil products are often transported using a heating method. However, this approach is economically inconvenient due to its high cost (Ivanova, 2011; Espolov et al., 2016).

A special chemical inhibitor and depressant additive are used to prevent paraffin deposition. When paraffin deposition inhibitors are added to oil at optimal concentrations, they affect the crystallization process of paraffins in such a way that the freezing temperature and viscosity of oil, as well as the amount of deposition of asphaltenes, resins and paraffins (ARPD) are reduced (Markin et al., 2011). It is known that even small additions of surfactants significantly weaken or prevent the formation of dispersed spatial structures formed by paraffin crystals. The presence of resinous components, varying in polarity based on the type and composition of oil, and natural depressants that lower the freezing temperature of oil and its products, can lead to both positive and negative depressant effects due to the participation of resins in the system (Beshagina et al., 2007).

Depressant additives prevent the formation of paraffin by influencing the structure of bulk crystalline lattices. Consequently, the rheological properties of the oil improve, the freezing temperature decreases, and the frictional pressure losses are reduced. Chemical reagents can also be used for hydrotransport of high-viscosity oils (Rakhmankulov et al., 1987; Aldiyarova, 2005).

The mechanism of effect of depressant additives has not been fully elucidated to date. It is believed that the additive adsorbs onto the surface of the formed crystals, resulting in their growth occurring only externally. During this process, the crystals take on a needle-shaped and branched structure, with thickness comparable to their length and width. The solution contains surface crystals with various modifications, reducing the likelihood of their convergence (Taranova et al., 2008).

The difference in the effectiveness of additives can be attributed to the diversity of their composition and technology of their introduction into oil. Their application in the general technological stage consists of heating, preparation of liquid solutions and dosing of oil through dispensers. At this time, it is important to take into account the individual compatibility of oils with additives from a technological point of view. In other words, the additive with the most efficient additive for each oil should be experimentally determined. When establishing the optimal properties of the depressant, it is also economically essential to choose the minimum concentration that ensures its maximum depressant effect (Vasilyanova, 2006).

As mentioned, during corrosion, the smoothness of the inner surface of the pipeline is compromised, and the surface becomes rough. In such a case, the adhesion of oil depositions to the surface and the increase in its quantity become more intense. Therefore, it is more appropriate to address the issues of paraffin deposition and corrosion simultaneously to enhance the efficiency of high-paraffin oils in the storage-transportation system. Specifically, there is a need to develop a reagent or composition that exhibits a high efficacy against both corrosion and paraffin deposition.

The goal of this study is to investigate the properties of individual reagents and new compositions in laboratory conditions.

Performance of work

Gravimetric tests in laboratory conditions were carried out in accordance with the requirements of SS 9.502-82 and SS 9.506-87, and Ct3 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 mixer. Then, the calculated volume of formation water and the required amount of gossypol resin and composition were separately introduced into the flask. It should be noted that the amount of gossypol resin and composition was calculated according to the known rule for one liter of corrosion medium. The test process was carried out at a temperature of 20 ±3°C for six hours with constant mixing (rotation speed 800 rpm). After six hours, the system was allowed to rest for a while, following which the steel samples were washed, cleaned, wiped with alcohol, dried and weighed again on an analytical balance. As a result of the research conducted at the end, the corrosion protection efficiency of gossypol resin and Z-1 reagents was calculated.

Determination of the freezing temperature of oil in laboratory conditions was carried out according to the methodology of SS 20287-91.

A specified volume of oil sample was poured into test bottles with a diameter of 20 mm and a height of 160 mm, heated to a temperature of 55–60°C, and depressant additives of different concentrations were added. The mixture was gradually cooled to a temperature of 30–40°C (for comparison, no additive was added to a test bottle). Subsequently, the test bottles were placed in the thermostat and the cooling process was continued. During the temperature drop, the test bottles were kept at an angle of 45° every three degrees. In such successive examinations, the temperature at which the level of oil in the test bottles was immobile was noted, and the test bottles were kept in a horizontal position for 5 seconds. The complete solidification of the liquid was determined by the immobility of the upper liquid layer.

Experimental part

In the experiment, gossypol resin, NDP-6 depressant additive, and a composition with the conventional name Z-1 prepared based on them in a ratio of NDP-6 + gossypol resin = = 9:1 were used as individual reagents.

First of all, a model oil sample was prepared in a 2:1 ratio of commercial oils from Narimanov and Absheron fields and its physical and chemical parameters were determined (Table 1).

As seen in Table 1, the prepared oil sample exhibits a high paraffin content and a high freezing point. Table 2 shows the ionic composition of the formation water sample taken from well No. 1082 of the "Bibiheybatneft" oil refinery used during the experiment.

Table 1. Physical and chemical properties of model oil
Tabela 1. Właściwości fizyko-chemiczne modelowej ropy

Parameters	Quantity	Method of determination
Water content in the sample [%]	0.2	SS 2477-65
Density, ρ_4^{20} [kg/m^3]	894.3	SS 3900-85
Paraffin content [%]	11.6	SS 11851-85
Resin content [%]	10.2	SS 11851-85
Asphaltene content [%]	5.2	SS 11851-85
Freezing temperature [°C]	+16	SS 20287-91
Melting point of paraffin [°C]	57	SS 11858-83
Sulfur content [%]	0.22	SS 1437-75
A/P	0.509	–

Table 2. Ionic composition of formation water taken from well No. 1082
Tabela 2. Skład jonowy wody złożowej pobranej z odwiertu 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	56.00	1.9998
Mg^{2+}	486.4	40.00	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_2S	15	–	–

Table 3. Protection effect of gossypol resin in H_2S-containing formation water

Tablica 3. Efekt ochronny żywicy gossypolowej w wodzie złożowej zawierającej H_2S

Cinh [mg/l]	*K* [g/m² · hour]		Retardation factor, *γ*	Protection effect, *Z* [%]
	inhibitor-free	with an inhibitor		
0.0	4.30	–	–	–
50.0	4.30	0.43	10.00	91
70.0	4.30	0.26	16.54	94
90.0	4.30	0.13	33.08	97
110.0	4.30	0.09	47.78	98

The impact of gossypol resin on the corrosion rate of formation water was investigated, and the corrosion protection efficiency was calculated. The experimental results are given in Table 3 and Figure 1.

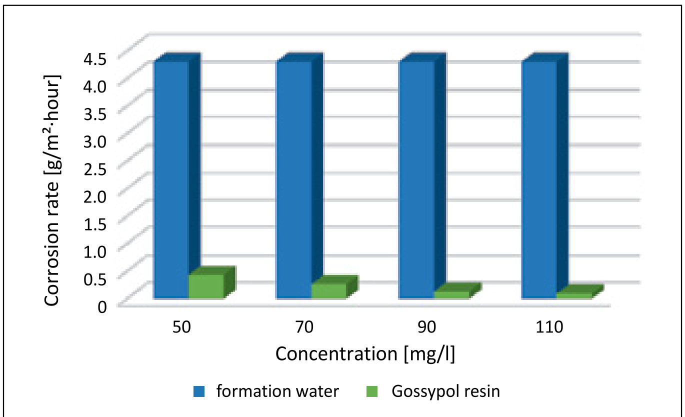

Figure 1. The effect of gossypol resin on corrosion rate in H_2S-containing formation water

Rysunek 1. Wpływ żywicy gossypolowej na szybkość korozji w wodzie złożowej zawierającej H_2S

As evident from Table 3 and Figure 1, an increase in the concentration of gossypol resin leads to a corresponding enhancement in its impact effect. Based on the results obtained from the laboratory experiments, it can be noted that the highest effect of gossypol resin on the corrosion process was observed at a concentration of 110 mg/l, resulting in a corrosion protection efficiency of 98%.

The impact of NDP-6 depressant additive on the freezing temperature of high-paraffin oil was investigated, and the efficiency of this impact on the freezing temperature was calculated. The results from the experiments are presented in Table 4 and Figure 2.

As seen in Table 4 and Figure 2, an increase in the impact effect is observed with the rising concentration of the depressant additive. Based on the results obtained from the laboratory experiments, it can be noted that the freezing temperature of model oil at concentration of 1000 g/t of the depressant additive decreases from +16°C to –2°C, and the effect on the freezing temperature is 113%. Also, the impact of Z-1 composition on the corrosion process in formation water and the freezing temperature of model oil was studied and the obtained results are presented in Table 5 and Figure 3.

Table 4. The impact of NDP-6 depressant additive on freezing temperature of model oil

Tabela 4. Wpływ depresatora NDP-6 na temperaturę krzepnięcia modelowej ropy

The concentration of the depressor additive	Freezing temperature	The impact effect on freezing temperature
[g/t]	[°C]	[%]
0	+16	0
300	+10	38
500	+5	69
700	0	100
1000	–2	113

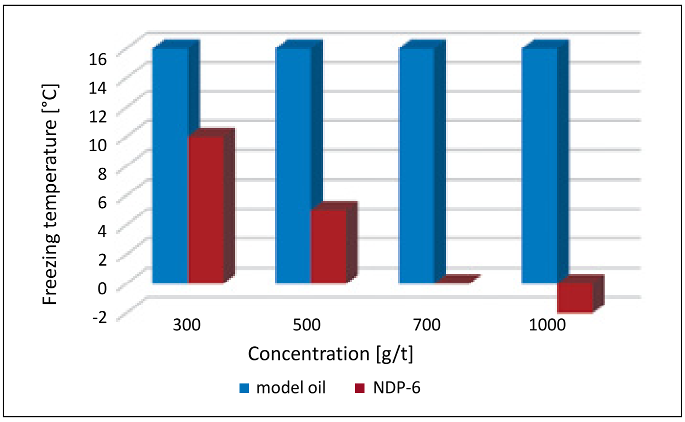

Figure 2. Impact of NDP-6 depressant additive on freezing temperature of model oil

Rysunek 2. Wpływ depresatora NDP-6 na temperaturę krzepnięcia modelowej ropy

As evident from Table 5 and Figure 3, the impact of the composition at concentrations of 300, 500, 700 and 1000 g/t is apparent, leading to a decrease in the corrosion rate of formation water from 4.30 g/m² · hour to 0.04 g/m² · hour, and a reduction

Table 5. The impact of Z-1 composition on freezing temperature and corrosion process
Tabela 5. Wpływ kompozycji Z-1 na temperaturę krzepnięcia i proces korozji

The concentration of depressant additive	*K*	Corrosion protection effect	Freezing temperature	Effect on freezing temperature
[g/t]	[g/m^2 · hour]	[%]	[°C]	[%]
0	4.30	0	+16	0
300	0.26	94	+7	56
500	0.13	97	0	100
700	0.04	99	–9	163
1000	0.09	98	–8	156

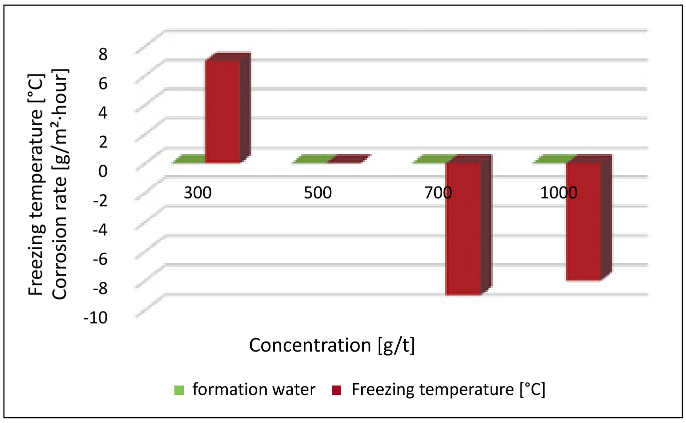

Figure 3. The impact of composition on corrosion rate and freezing temperature

Rysunek 3. Wpływ kompozycji na temperaturę krzepnięcia i proces korozji

in the freezing temperature of the model from +16°C to –9°C. Based on the results obtained from the experiment, it can be noted that the optimal concentration for the impact effect of Z-1 composition was 700 g/t for both processes, and at this concentration, the corrosion protection effect was 99% and the efficiency of the effect on the freezing temperature was 163%. Therefore, it can be concluded that Z-1 composition demonstrated an effective impact on both the corrosion process and the freezing temperature simultaneously.

Conclusions

1. The impact of the depressant additive NDP-6 and Z-1 composition on the freezing temperature of a model oil sample prepared by mixing commercial oils from the Narimanovskoye and Apsheronskoye fields of SOCAR in a 2:1 ratio was studied for the first time. The optimal consumption rate has been studied and determined.
2. The impact of gossypol resin and composition Z-1 on the corrosion process of a sample of formation water taken from well No. 1082 of SOCAR "Bibiheybatneft" NKITs as an electrochemical corrosive medium was studied for the first time in laboratory conditions, and the optimal consumption rate was determined.
3. It was determined that the freezing temperature of oil in the concentration range of 300–1000 g/t of NDP-6 additive varies between +10°C – (–2°C), with an impact ranging from 38–113%. At gossypol resin amounts of 50–110 mg/l, the corrosion rate during laboratory experiments in formation water ranged from 0.43 to 0.09 g/m^2 · h, and the corrosion protection efficiency varied between 91–98%.
4. The change in the concentration of Z-1 composition in the range of 300–700 g/t leads to a decrease in the freezing temperature of oil from +7°C to –9°C, and a decrease in the rate of corrosion from 0.26 g/m^2 · h to 0.04 g/m^2 · h. At this time, the efficiency of the composition varies between 56–163%, and the protection effect varies between 94–99%.

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Saida Meydan PASHAYEVA, Ph.D.
Teacher at the Department of Oil and Gas Transportation and Storage
Azerbaijan State Oil and Industry University
16/21 Azadliq Ave., Baku AZ1010, Azerbaijan
E-mail: *seide.memmedli@list.ru*