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EFFECT OF VARIOUS COMPOSITIONS ON CORROSION RATE OF STEEL IN FORMATION WATER AND FREEZING TEMPERATURE OF HIGH-PARAFFIN MODEL OIL

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The effects of Gossypol resin and NDP-6 reagents and Z-1 composition (the mixture of NDP-6+Gossypol resin at the ratio of 9:1) on the corrosion rate of steel in the formation water and the freezing temperature of high-paraffin model oil were investigated for the first time under laboratory conditions. In the experiments, a model oil sample prepared in a ratio of 2:1 of commercial oils from Narimanov and Absheron fields of SOCAR was used as a research object, and a formation water sample taken from well No. 1082 of "Bibiheybatneft" OGPI, SOCAR was used as an electrochemical corrosion medium. It was determined that the new composition had a more effective impact on the corrosion rate in H_2S-containing formation water and the freezing temperature of high-paraffin oil sample than individual reagents. Thus, the highest efficiency for gossypol resin was observed at a concentration of 110 mg/l, when the corrosion rate was 0.09 $g/m^2{\cdot}h$ (corrosion protection efficiency of 98%). The most effective indicator for NDP-6 depressant additive was 1000 g/t, and the freezing temperature of high-paraffin model oil was stated to decrease from $+16^0C$ to -2^0C. However, the strongest effect has been observed for the Z-1 composition. Thus, the composition with a concentration of 700 g/t reduces the corrosion rate in the formation water from 4.30 $g/m^2{\cdot}h$ to 0.04 $g/m^2{\cdot}h$ (corrosion protection efficiency of 99%) and the freezing temperature of model oil from $+16^0C$ to -9^0C.

Keywords: corrosion, corrosion efficiency, high-paraffin model oil, formation water, freezing temperature.

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Introduction

Corrosion protection of units and facilities exploited in the oil industry remains an urgent problem, and the damage caused by corrosion to the world economy is measured in billions of dollars per year.

It is known that the elements with corrosion aggressiveness, including sulfur and oxygen compounds, hydrogen sulfide, carbon dioxide, molecular oxygen, as well as mineral salts dissolved in formation waters, cause corrosion of facilities during exploitation. Hydrogen sulfide containing in the formation water is extremely dangerous for the units and facilities. This compound not only is highly reactive but also causes hydrogen embrittlement in metal [1–3]. Although the process of 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 [3,4]. 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. For this reason, the issue of selecting, checking and wide application of chemical reagents for reducing the speed of the corrosion process and even stopping it completely remains relevant.

On the other hand, at the last stage of the development of oil fields, the processes of asphaltene-resin-paraffin deposits formation in the well-storage-

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transportation system are considered one of the serious and urgent issues. Asphaltene-resin-paraffin deposits are formed in the systems of oil extraction, storage and preparation for transportation. The amount and nature of this deposit changes as a result of the impact of many factors such as pressure, mode, temperature drop, oil degassing and others in the well bottom, well body and surface storage-transportation systems. The temperature drop is the most important of these factors. Currently, the oils produced in Republic of Azerbaijan are diverse ccording to their physical-chemical indicators and rheological properties. This diversity shows itself in the indicators such as viscosity, the amount of resin, asphaltene and paraffins and others [5]. Most of the oils produced in Azerbaijan contain asphaltene, resin and paraffin to some extent. In this regard, the process of those components deposition in the well bottom and pipelines is inevitable.

The main rheological parameter of oils is viscosity. Viscosity characterizes the fluidity of oil, and paraffinic oils belong to the group of high viscosity oils. With an increase in viscosity, the frictional pressure increases, fluidity deteriorates, and as a result, energy loss occurs. Pipeline transportation of paraffinic oils creates a number of difficulties in this regard. The main goal in oil extraction is the development of technological processes that will reduce the energy loss and at the same time prevent additional losses of hydrocarbon raw materials. The most important factor affecting viscosity is temperature. An increase in temperature lowers the viscosity, which eliminates the difficulty of transporting high-viscosity oils. In this regard, high paraffin oil and oil products are transported by heating method. However, this method is inconvenient because it is expensive from an economic point of view [6,7].

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. It is known that small additions of surfactants significantly weaken or prevent the formation of dispersed spatial structures formed by paraffin crystals. It has been established that resinous components, which differ in polarity depending on the type and composition of oil, and natural depressants that reduce the freezing temperature of oil and its products, can lead to both positive and negative depressant effects of the participation of resins in the system [8].

Depressant additives prevent its formation by affecting the structure of bulk crystalline lattices. As a result, the rheological properties of the oil improve, the freezing temperature decreases, and the frictional pressure losses decrease. Chemical reagents can also be used for hydrotransport of high-viscosity oils [9].

The mechanism of effect of depressant additives has not been fully elucidated at present. It is believed that the additive adsorbs on the surface of the formed crystals, and as a result, their growth occurs only outside. The crystals are needle-shaped and branched, and the thickness is comparable to the length and width. The solution contains surface crystals with various modifications, which reduces the probability of their convergence [10].

The difference in the effect of additives is explained by the diversity of their composition and technology of their introduction into oil. Their use in the general technological stage consists of heating, preparation of liquid solutions and dosing of oil through dispensers. It is important to take into account the individual tendency of oils to additives from a technological point of view. In other words, the additive with the most effective efficiency should be selected for each oil experimentally. When determining the optimal properties of the depressant, it is also an economic necessity to choose the minimum concentration that ensures its maximum depressant effect [11].

As mentioned, during corrosion, the smoothness of the inner surface of the pipeline is lost 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 solve the problems of paraffin deposition and corrosion at the same time in order to increase the efficiency of high-paraffin oils in the storage-transportation system. More precisely, it is necessary to prepare such a reagent or composition, which at the same time has a high effect against both corrosion and paraffin deposition.

Thus, thee research objective is to investigate the properties of individual reagents and new compositions under laboratory conditions.

Experimental

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

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

Table 1

Physicochemical properties of model oil

Parameter	Value	Method of determination
The amount of water in the sample, %	0.2	SS 2477-65
Density, ρ_4^{20}, kg/m^3	894.3	SS 3900-85
Amount of paraffin, %	11.6	SS 11851-85
Amount of resin, %	10.2	SS 11851-85
Amount of asphaltene, %	5.2	SS 11851-85
Freezing temperature, ^{0}C	+16	SS 20287-91
Melting point of paraffin, ^{0}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

Ions	Concentration of ions, mg/l	Equivalent concentration of ions, mg-eq/l	Equivalent amount, %
Na^++K^+	31298.987	1304.12	46.57
Ca^{2+}	1122.24	56	1.9998
Mg^{2+}	486.4	40	1.4284
Fe^{3+}	2561.58	853.86	–
Cl^-	49010.49	1382.52	49.37
SO_4^{2-}	28.81	0.60	0.0214
CO_3^{2-}	0.00	0.00	0.0000
HCO_3^-	1037.00	17.00	0.6071
H_2S	15	–	–

During the experiment, Gossypol resin, NDP-6 depressant additive, and a composition with conventional name Z-1 prepared on their basis in a ratio of NDP-6+Gossipol resin=9:1 were used as individual reagents.

Gravimetric tests under laboratory conditions were carried out in accordance with the requirements of the state standards SS 9.502-82 and SS 9.506-87; and St3 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 introduced into the flask separately. 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^{0}C with constant mixing with a rotation speed of 800 rpm for six hours. 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 weighed again on an analytical balance. Then the corrosion protection efficiency of Gossypol resin and Z-1 reagents was calculated.

Determination of the freezing temperature of oil under laboratory conditions was carried out according to the methodology of ISO 1041-2015.

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^{0}C; depressant additives of different concentrations were added to it, and gradually cooled to a temperature of 30–40^{0}C (for comparison, no additive was added to a test bottle). Then 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 45^0 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.

Results and discussion

The effect of gossypol resin on the corrosion rate of formation water was investigated and the corrosion protection efficiency was calculated. As is seen from Table 3 and Fig. 1, as the concentration of gossypol resin increases, an increase in the impact effect is observed. According to the results obtained from the laboratory experiments, it can be noted that the highest effect of gossypol resin on the corrosion

Table 3

Protection effect of gossypol resin in H_2S formation water

C_{inh}, mg/l	K, g/m^2·hour		Inhibition factor, γ	Protective effect, Z, %
	inhibitor free	with an inhibitor		
0.0	4.30	–	–	–
50	4.30	0.43	10	91
70	4.30	0.26	16.54	94
90	4.30	0.13	33.08	97
110	4.30	0.09	47.78	98

process was at a concentration of 110 mg/l, the corrosion protection efficiency being 98%.

The effect of NDP-6 depressant additive on the freezing temperature of high-paraffin oil was investigated and the efficiency of the effect on the freezing temperature was calculated (Table 4 and Fig. 2).

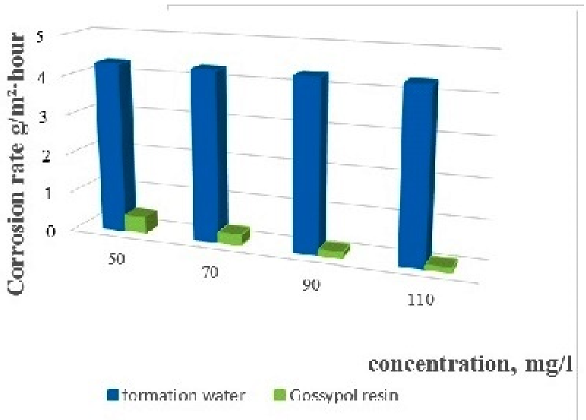

Fig. 1. The effect of gossypol resin on corrosion rate in H_2S-containing formation water

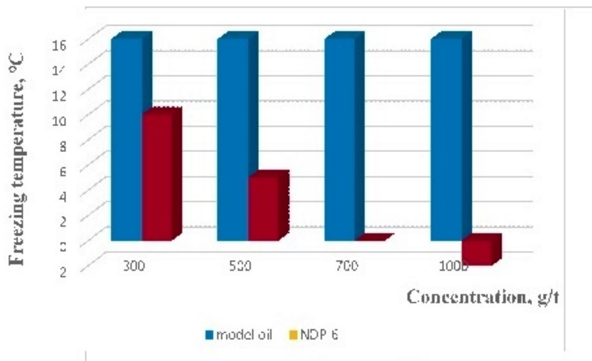

Fig. 2. Effect of NDP-6 depressant additive on freezing temperature of model oil

As is seen from Table 4 and Fig. 2, an increase in the impact effect was observed as the concentration of the depressant additive increased. 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 $+16^0$ to -2^0C, and the effect on the freezing temperature is 113%. In addition, the effect of Z-1 composition on the corrosion process in formation water and the freezing temperature of model oil were studied (Table 5 and Fig. 3).

Table 4

The effect of NDP-6 depressant additive on freezing temperature of model oil

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

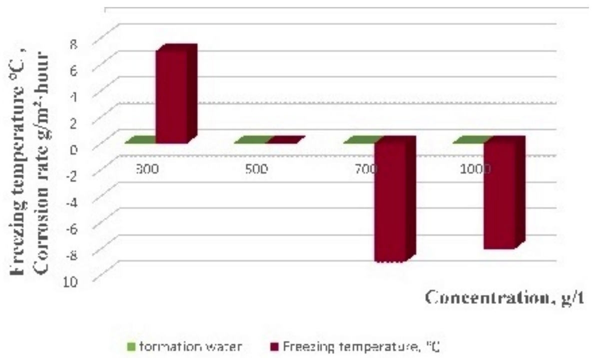

Fig. 3. The effect of composition on corrosion rate and freezing temperature

As is seen from Table 5 and Fig. 3, due to the effect of the composition at concentrations of 300, 500, 700 and 1000 g/t, the corrosion rate in formation water was decreased from 4.30 g/m^2·hour to 0.04 g/m^2·hour and the freezing temperature of model oil decreased from $+16^0$C to -9^0C. Based on the results obtained from the experiment, it can be noted that the optimal concentration of the Z-1 composition was 700 g/t for both processes, and at this concentration, the corrosion protection effect was 99%

Table 5

The effect of Z-1 composition on freezing temperature and corrosion process

The concentration of depressant additive, g/t	K, $g/m^2 \cdot hour$	Corrosion protection effect, %	Freezing temperature, ^0C	Effect on freezing temperature, %
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

and the efficiency of the effect on the freezing temperature was 163%. In this regard, it can be said that the Z-1 composition had an effective impact on both the corrosion process and the freezing temperature.

Conclusions

1. The effect of NDP-6 depressant additive and Z-1 composition on the freezing temperature of the model oil sample prepared in a ratio of 2:1 of commercial oils of Narimanov and Absheron fields of SOCAR were investigated. An effects of gossypol resin and Z-1 composition on the corrosion process of steel in the formation water sample taken from well No. 1082 of «Bibiheybatneft» OGPI of SOCAR were studied under laboratory conditions. The optimal rate of consumption of the composition was established.

2. It was determined that the freezing temperature of oil at the concentration range of 300–1000 g/t of NDP-6 additive varies between $+10^0C$ ... -2^0C), and the impact effect varies between 38–113%. At 50-110 mg/l of gossypol resin, the corrosion rate in the formation water is 0.43–0.09 $g/m^2 \cdot h$, and the corrosion protection efficiency is between 91–98%.

3. The change in the concentration of Z-1 composition in the range of 300–700 g/t causes a decrease in the freezing temperature of oil from $+7^0C$ to -9^0C, and a decrease in the rate of corrosion from 0.26 $g/m^2 \cdot h$ to 0.04 $g/m^2 \cdot h$. The protection effect varies between 94–99%.

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ВПЛИВ РІЗНИХ КОМПОЗИЦІЙ НА ШВИДКІСТЬ КОРОЗІЇ СТАЛІ В ПЛАСТОВІЙ ВОДІ ТА ТЕМПЕРАТУРУ ЗАМЕРЗАННЯ ВИСОКОПАРАФІНОВОЇ МОДЕЛЬНОЇ НАФТИ

С.М. Пашаєва

Вперше в лабораторних умовах досліджено вплив смоли госипол і реагентів НДП-6 і композиції Z-1 (суміш НДП-6+смола госипол у співвідношенні 9:1) на швидкість корозії сталі в пластовій воді та температуру замерзання високопарафінової модельної нафти. В експериментах в якості об'єкта дослідження використовували модельну пробу нафти, приготовлену в співвідношенні 2:1 з промислових нафт Нарімановського і Апшеронського родовищ SOCAR; пробу пластової води зі свердловини № 1082 НГПІ «Бібіхейбатнефть», SOCAR використовували як електрохімічне корозійне середовище. Встановлено, що нова композиція має більш ефективний вплив на швидкість корозії в H_2S-вмісній пластовій воді та температуру замерзання зразка високопарафінової нафти, ніж окремі індивідуальні реагенти. Так, найвища ефективність для смоли госипол спостерігалася при концентрації 110 мг/л, коли швидкість корозії становила 0,09 г/м^2·год (ефективність захисту від корозії 98%). Найефективнішим показником депресорної присадки НДП-6 було 1000 г/т, а для температура замерзання високопарафінової модельної олії зафіксовано зниження від +16^{0}С до −2^{0}С. Проте найсуттєвіший ефект спостерігався для композиції Z-1. Так, композиція з концентрацією 700 г/т знижує швидкість корозії в пластовій воді з 4,30 г/м^2·год до 0,04 г/м^2·год од (ефективність захисту від корозії 99%) і температуру замерзання модельної нафти від від +16^{0}С до −9^{0}С.

Ключові слова: корозія; корозійна ефективність; модельне високопарафінова нафта; пластова вода; температура замерзання.

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Keywords: corrosion; corrosion efficiency; high-paraffin model oil; formation water; freezing temperature.

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