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# ABSTRACT

of the dissertation work submitted for the scientific degree of Doctor of Sciences

# PHYSICAL-CHEMICAL BASIS OF IMPROVING THE EFFICIENCY OF PREPARATION AND TRANSPORTATION OF OIL MIXTURES

Speciality: 3354.01 - Construction and exploitation of oil-gas pipelines, bases and storage

Field of science: Technical sciences

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"AZƏRBAYCAN DÖVLƏT NEFT VƏ SƏNAYE UNİVERSİTETİ" PUBLİK HÜQUQİ ŞƏXS
ELMİ KATİB

## GENERAL DESCRIPTION OF THE WORK

**Relevance of the dissertation work and degree of development**: Mixing of crude or commercial oil without taking into account the variety of physical and chemical indicators, as well as rheophysical properties and its transportation through the pipeline system creates various difficulties and complications and leads to the generation of additional costs. Thus, "incompatibility" of mixing of oils with different rheophysical-chemical parameters can cause abnormal changes of values of practically important parameters of dispersed oil system, various clogs in pipelines and formation of asphaltene-resin-paraffin deposits. It is for this reason that some oils can be considered as "undesirable" pairs at mixing. Therefore, the interaction of oils with different physical and chemical properties during mixing, as well as improving the efficiency of technological processes during their collection, preparation for transportation in mining conditions remains relevant, being one of the important issues arising from the need of the time.

On the other hand, the increase in the share of production of high paraffin oils causes the implementation of a set of measures in the direction of solving the processes of corrosion and paraffin formation, which are important problems in the system of collection-transportation of this type of oil, as a priority task for oilmen. Thus, the course of intensive paraffinisation process at low temperatures in the system of collection-transportation of high paraffin oils, characterised by high freezing point, does not allow efficient operation of wells, oil collection, preparation for transportation and efficient pipeline transport. This, in turn, leads to a significant complication of the operation process, reduction of the overhaul period, increase in the cost of materials and at the same time the cost of oil.

The presence of aggressive medium in the system of collection-transportation of high paraffin oils causes electrochemical corrosion of the inner surface of the operated equipment, reduces its service life and increases repair costs, causes serious damage to the environment. Corrosion products formed on the inner surface serve as crystallisation centres for paraffin hydrocarbons and serve for formation of oil deposits. The joint solution of problems of paraffin formation and corrosion processes causing energy and oil losses requires development of modern technologies and study of new scientific bases of their application in mining conditions.

It is from this point of view, in spite of carrying out numerous research works, the mentioned problems still remain unsolved and are of great scientific and practical importance.

**Object and subject of the research.** The objects of research in the performed dissertation work were oil samples taken from Muradkhanli, Sangachal Bulla-deniz, Garachukhur, Surakhani, Siyazan, Absheron, Narimanov, Alat-deniz fields and condensate samples taken from Umid field. The subject of research in the thesis work was the study of individual reagents and new compositions based on them.

**Aims and objectives of the research.** The aim of the research is the development of an innovative method of increasing the efficiency of the collection-transportation system of paraffin oils to find ways to increase the efficiency of technological processes in their collection, preparation and transportation and increase the service life of oil intra-mining and commercial transportation pipelines by applying high-quality anti-corrosion reagents to asphaltene-resin-paraffin deposits and corrosion taking into account the factors of interaction and dilution of oils during mixing.

To achieve the goal of the research work the following tasks are planned:

1. Analysis of problems of dilution and mixing of oils at their collection, preparation and transportation and analysis of rheological and quality indicators of oil-water-condensate mixtures in collection-transportation systems;
2. Rheological research of the effect of mixing and dilution of oils on their rheophysical properties and quality indicators;
3. Determination of the amount of ballast water in rheologically complex oils and their mixtures and development of

methods of diagnosing structural changes of oil mixtures taking into account the degree of dilution;

4. Research of the effect of the degree of dilution of oils on their demulsification and the effect of synergism and antagonism at mixing of oils on the processes of their preparation for transportation;

5. Research of bactericidal-inhibiting properties of individual and composite reagents;

6. Study of the effect of depressor additives on the freezing point of high paraffin oil, the process of paraffin deposition in oil, thixotropic properties and effective viscosity;

7. Research of the effect of new compositions on the freezing point of high paraffin oil, corrosion rate in hydrogen sulphide formation waters and the process of salt deposition;

8. Development of technology of application of new composition on high paraffin oil in mining conditions;

**Research methodology.** Various experimental research methods were used to solve the problems posed during the thesis work.

**The main provisions to be defended:**

1. Physics and chemical aspects of diagnosing and increasing the efficiency of the collection, preparation and transport of oil mixtures: - complex results of the analysis of rheological and quality indicators during the mixing of different oils, considering the emulsification factor;

- diagnosis of the “undesirability” of mixing different types of oils based on their solubility capabilities;

- the influence of microscopic structural changes and the quantity of ballast on macroscopic parameters during the mixing of oils;

- an express method for determining the degree of emulsification of oils and their mixtures;

- The technology for preparing rheologically complex oil mixtures, taking into account the saturation of emulsions with water.

2. Comprehensive experimental results from the study of the bactericidal and inhibitory properties of individual and composite reagents;

3. Indicators of research of the effect of depressor additives on the freezing point of high paraffin oil, the process of paraffin deposition in oil, thixotropic properties and effective viscosity;

4. A set of results of research of the effect of new compositions on the freezing point of high paraffin oil, corrosion rate in hydrogen sulfide formation water and the process of salt deposition;

5. Technology of application of the new composition for high paraffin oils in mining conditions;

**Scientific novelty of the research:** By taking into account the factors of interaction and dilution of oils during their collection, preparation and transportation, methods of optimizing and increasing the efficiency of technological processes, as well as the application of single reagents against asphaltene-resin-paraffin deposits and corrosion, in order to increase the service life of intra-mining oil and commercial transportation pipelines, creation of the scientific basis of the development of an innovative method of increasing the efficiency of the collection-transportation system of high paraffin oils constitutes the scientific novelty of the research work.

1. Developed the physicochemical principles for the rational blending of different grades of crude oil.

2. Proposed methods for diagnosing "undesirable" oil blends and their effects on macroscopic parameters during the collection and preparation of oil mixtures.

3. Developed a accelerated method for diagnosing the water content in oil mixtures.

4. Proposed a new approach to the technology of demulsification of oil mixtures.

5. The bactericidal-inhibiting properties of individual and composite reagents have been studied;

6. The influence of depressant additives on the freezing point of highly paraffinic oil, the process of paraffin deposition in oil, thixotropic properties and effective viscosity was studied;

7. The influence of the new composition on the freezing point of highly paraffinic oil, the rate of corrosion in hydrogen sulfide formation water and the process of salt deposition was studied.

8. The preparation of multifunctional compositions against corrosion and salt deposits and the study of their properties were studied.

9. The influence of temperature and the additive "Difron-4201" on the composition and molecular weight distribution of paraffin hydrocarbons was studied.

10. The influence of temperature and a new composition on the kinetics of formation and group composition of paraffin deposits was studied.

11. A technology has been developed for introducing a composition based on "Difron-4201" and MARZA-1 into highly paraffinic oils under field conditions.

**Theoretical and practical significance of the research.**

The scientific level of the new results obtained in the thesis work allows to include them in the relevant reference books, data banks and international scientific information systems.

Practical significance of the work consists in the fact that new multifunctional compositions prepared in laboratory conditions on the basis of local raw materials can be applied with high efficiency to solve the problems of corrosion and paraffin formation in the system of collection-transportation of high paraffin oils. Also, taking into account the effect of synergism and antagonism when mixing oils with different physical and chemical characteristics contributes to the efficiency of the process by preventing complications arising during their transportation, the express diagnostic method developed on the basis of the "droplet sample" test measures the amount of ballast water in rheologically complex oils in mining collection and transportation systems and allows for an immediate evaluation of the saturation limit of water.

**Authorization and publication.** The main results of the dissertation work were presented and discussed at the following conferences.

**Published scientific works:** 31 scientific papers, 5 articles (4 WOS, 1 SCOPUS in scientific journals indexed in international databases) and 7 conference proceedings have been published.

1. Российский государственный университет нефти и газа (национальный исследовательский университет) имени И.М. Губкина» Юбилейной 70-й Международной молодежной научной конференции «Нефть и газ – 2016. (Москва, 2016)
2. Российский государственный университет нефти и газа (национальный исследовательский университет) имени И.М. Губкина» XI Всероссийская научно-техническая конференция «Актуальные проблемы развития нефтегазового комплекса России» (Москва, 2016)
3. İnternational Conference Dedicated to the 90$^{th}$ Anniversary of Academician Azad Mirzajanzade. (Baku, 2018).
4. "Материалы международной научно-практической конференции «Состояние и перспективы эксплуатации зрелых месторождений". (Газахыстан, 2019)
5. XXXIII Международная научно-практическая телеконференция "Российская наука в современном мире" . (Москва, 2020).
6. International conference on "Actual problems of chemical engineering, APCE – 2020, dedicated to the 100th Anniversary of the ASOİU. (Baku, 2020).

**Name of the institution where the dissertation work was carried out.** The dissertation work was carried out in accordance with the plan of scientific research conducted at the department of "Transportation and storage of oil, gas" of Azerbaijan State Oil and Industry University.

**Structure and volume of the dissertation work:** The dissertation work consists of an introduction, 5 chapters and a list of references cited in 356 titles. The work totally includes 420 pages, 395349 (452192) symbols (introduction 15577(17573), chapter I

68641(78580), chapter II 51676 (59816), chapter III 26978(30838), chapter IV 95767 (109741), chapter V 125887 (143430,, conclusions 4426 (4496) 99 figure and graph, 92 table and concludes with abbreviations and conventional symbol.

**Personal contribution of the author:** The main leading role belongs to the author in analysing literature sources, stating the problem, formulating new ideas, planning and carrying out experimental work, explaining and summarising the principal results obtained by various research methods.

## CONTENT OF THE WORK

In the **introduction part** of the dissertation work the relevance of the topic is justified, aims, objectives, the problems to be solved, scientific innovations, theoretical and practical significance of the work, the main provisions to be defended, the structure and volume of the work are reflected. The thesis consists of five chapters.

**The first chapter** systematises and analyses the complexities and specific problems arising from the dilution and mixing of oils with different physical and chemical parameters in the onshore and offshore collection and transportation system. The effect of oil properties and the degree of dilution and mixing on the operational and environmental performance of the collection and transportation system is interpreted, as well as information on the problems of "incompatibility" when mixing different oils.

As a result of research it was found that stability and quality indicators of oils extracted from one field and delivered to the collection network are heterogeneous depending on time. Thus, the construction of collection and transportation networks, as well as the peculiarities of the location of oil production areas do not allow transporting oil produced at the fields to refineries or to the consumer with preservation of its original physical and chemical properties. Since it does not consider it expedient to transport oil separately in collection-transportation systems, it transports it through the oil pipeline in a mixed state. Otherwise, the separate transportation of oil will not only increase the size of the tank farm, but also greatly complicate the management of oil fields and oil pipeline network. For the above reasons, oils with different physical and chemical parameters are mixed and sent for refining or export. As it is known, the factors influencing the price and rheological parameters of oils include its degree of hydration and temperature factor. These factors can significantly change the internal structure and viscosity of the oil. At the same time, it should be noted that mixing of oils with different physical and chemical characteristics, which is considered very important, has a great impact on the properties and quality parameters of oils.

It is known that as a result of macroscopic deposition of solid phase on the inner surface of pipelines operated in the system of collection and transportation of produced oil mixtures, plugs regularly occur. It should be noted that the "incompatibility" of mixing oils of different properties leads to the formation of deposits on the inner surface of pipelines, as well as to abnormal changes in the quality indicators of the mixture and simultaneously the values of concentration of viscosity, freezing point, volume and other parameters that are considered practically important. Various difficulties arise during transportation of oils with complex rheological properties, mixed with each other, with light oil products or with solvents. There are also known cases of imbalance during storage, delivery and reception of such mixture. This is why some oils and oil products can even be considered "undesirable" substances from this point of view. Therefore, it is not considered proper to mix different oils without certain studies, in which case the value of the product may also be reduced. When collecting, preparing and transporting oil mixtures with different rheo-physical-chemical properties and degree of dilution, the properties they will have are not taken into account and no studies in this direction are carried out for Azerbaijani oils. One of the most important factors manifested in mixtures is that the additivity rule, which is a traditional method of determining quality indicators and parameters characterising physical-chemical properties of oil mixtures, gives incorrect results that differ significantly from the results of experimental tests. It is the above mentioned that determines and makes it necessary to study and widely investigate the problems arising when mixing oils with different physical-chemical parameters taking into account the degree of dilution.

This chapter also discusses the rational mixing of oils based on their solubility and the development of a diagnostic method for identifying undesirable mixtures.

It should be noted that laboratory experiments are used to determine the solubility of crude oil. The results of numerous laboratory experiments show that the ratio of aromatic compounds to products within asphaltenes is governed by the presence of asphaltenes in the crude oil. From the results of quantitative analysis and simultaneously using the relative concentration and degassing data of the crude oil, an accurate model of its solvent can be constructed. Consequently, the solubility of one or more crude oils can be determined and this is discussed in detail in this thesis. In determining the solubility of any crude oil, it is important to obtain data from quantitative analyses of that oil. The ratio of aromatic compounds to saturation products in oil products can be determined using the relationship between expulsion value and concentration. In this work, in order to study the solubility of oils, crude oils produced in different fields of Bulla, Garachukhur and Siyazan were used as an example of Azerbaijani oils. It is established that mixing of oils results in deposition and significant anomalous changes in quality parameters. According to the results of experiments it is established that the deposition of asphaltenes from crude oil occurs at a certain solubility limit. This limit is called the crisis solubility of crude oil. Asphaltenes the solubility of which is higher than the critical threshold remain in solution and no deposition occurs. Given that the solubility of crude oil is the ratio of saturation products to aromatic compounds. At this time, paraffin titration is used to mix crude oil to determine the solubility of the crisis. As a result of the research, non-additive solubility properties were observed when mixing the components depending on the proportions **(figure 1)**. The figure shows the corresponding changes in solubility when the above oils are mixed in a certain proportion. As can be seen from the figure, the highest solubility 37 is observed for the mixture of oils in the given ratio of BO:GO:SO=1:3:1. When the oils are mixed in the ratio of BO:GO:SO=1:1:8, the lowest solubility value is 26,5[1].

Experimental results showed that at a certain solubility limit there is deposition of asphaltenes from oil, and non-additive solubility

[1]İsmayılov, Q.Q. Həlletmə qabiliyyətinə görə neft qarışıqlarının "azruolunmaz"lığının diaqnostikası / Q.Q. İsmayılov, M.B. Adıgözəlova, F.B. İsmayılova// Azərbaycan Neft Təsərrüfatı,-2018.-№11, -s.36-39.

properties are observed when mixing components depending on their proportions.

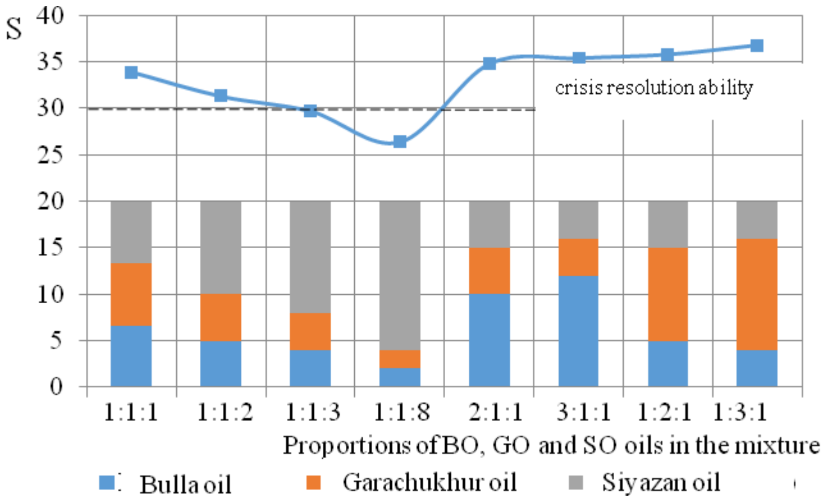


**Figure 1. Change in solubility during mixing of oils**

In general, it has been observed that when oils are mixed, their chemical composition significantly affects the quality parameters. The diversity of chemical composition causes the deposition of mechanical mixtures, asphaltenes, resins, paraffin compounds when mixing oils. In addition, it has been observed that mixng of oils increases the mass fraction of high molecular weight compounds such as asphaltenes and resins in the mixture compared to the original composition. The reason for this increase may be due to the chemical composition of the oils. Experimental results of ballast settling experiments have shown that the settling process can last for months. The bulk of the ballast subsides in the first few days. A hypothetical model for quantifying and assuming the amount of accurately deposited ballast is proposed. A mathematical model for determining and predicting the amount of settled ballast is proposed and its application in mountain conditions is found appropriate.

**In the second chapter** the results of laboratory tests of the effect of mixing and dilution of oils of different types on their rheo-physical-chemical properties and quality indicators are given. This chapter also presents the results of studying the physical-chemical properties of various oils and oil-condensate-water mixtures, as well as the results of the effect of dilution and mixing of condensate with oil on the efficiency of the processes of their collection and preparation for transportation.

In laboratory conditions qualitaty indicators of concentration, viscosity values and quantity of water, mechanical mixture, chloride salts of mixed oil samples taken from different wells and collecting tank of “Jafarli” field of Muradkhanli were determined through known methods and they differed significantly from each other. During the process, it was found that the oil from well No. 43 was anhydrous while the oils taken from wells No. 28, 37 and the reservoir had hydration degree of 15, 40 and 52 per cent respectively. The rheological properties of the different oil samples taken for the study were studied on a viscometer “Reotest-2” after artificial increase in the degree of hydration. The experimental results showed that the oil samples are non-Newtonian fluids and increase in the degree of dilution causes a significant increase in their viscosity. Also, in all oil samples after a certain value of the dilution degree, a sharp decrease in shear stress was observed in the flow curves despite the increase in the velocity gradient. In the mixed oil samples taken from the well and reservoirs No. 28, 37, 43, taken for the experiment, the saturation limit by the dilution degree was 70, 80, 40 and 80 %, respectively[2]. Condensate from the Umid field and oil from the Bulla field were used in laboratory conditions to study the dependence of rheological and quality parameters of oil-condensate-water mixtures on the amount of condensate and water. Physical-chemical properties of condensate and oil are very different from other **(table 1)**.

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[2]Nurullayev, V.X. Neftlərın sulaşma dərəcəsının onların reolojı parametrlərınə təsırının tədqıqı / V.X.Nurullayev, M.B. Adıgözəlova, R.Q. Nurməmmədova // Azərbycan Ali Texniki Məktəblərinin Xəbərləri, -2022.№1(12), -s.4-14.

According to the results of rheological studies it was found that the flow curves of oil, condensate and their mixtures in different mass fractions of condensate for all systems are nonlinear, do not cross the origin of coordinates and tend to cut shear stress axis. Also in the process of research, the concentration of oil-condensate-water mixture, freezing point, value of kinematic viscosity and the amount of water, mechanical mixtures and chlorine salts in the mixture was determined. It was found that when mixing with oil with a dilution degree of 75%, the additivity rule for the qualitaty indicators of the product is not fulfilled in most cases. In order to study the effect of water content on the rheological properties of oil-condensate mixture, the rheological properties of anhydrous and mixtures with different degrees of hydration were studied with the help of viscometer at 5 and 20$^0$C, as well as flow curves constructed on the basis of the results were studied. By analysing the results, it was found that the value of degree of dilution has a significant effect on the flow curves. It was found that as the dilution degree increases, the viscosity of the system first increases and after a certain dilution, it decreases sharply.

At present, there is no field of science and technology, industry where computers are not widely spread. Such a wide spread of computer is due to the fact that the need for calculations, optimisation and control of technological processes, scientific fields, etc. for various purposes is very great. Mathematical modelling as an important field of science for the application of computers in various fields of science and technology, in industry was established in the early 20$^{th}$ century and is being developed at present. Further it is widely used in other fields as well as in oil industry. Considering this point, the application of statistical mathematical models in studying the effect of reagent concentration, test temperature and velocity gradient on the effective viscosity of oil of Muradkhanli field without reagent and in the presence of reagent is of special importance.

The impact of reagent concentration $x_1$, test temperature $x_2$ and velocity gradient $x_3$ on the effective viscosity of oil from Muradkhanli field without and in the presence of reagent has been studied and its statistical mathematical model has been created.

**Table 1**

**Physico-chemical characteristics of "Umid" field condensate and "Bulla" field oil**

| Mass fraction of condensate, $B_k$ | 0 | 0,02 | | 0,04 | 0,06 | 0,08 | 0,1 | 0,2 | 0,4 | 0,6 | 0,8 | 0,98 | 1,0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\rho^{5}_{mix.}$, kg/m³ | 981 | 983 | | 980 | 975 | 972 | 967 | 940 | 907 | 871 | 847 | 822 | 821 |
| $\rho^{20}_{mix.}$, kg/m³ | 976 | 976 | | 973 | 969 | 964 | 962 | 934 | 895 | 859 | 833 | 810 | 806 |
| Freezing temperature, °C | 13 | 16 | | 15 | 14,5 | 14 | 13,5 | 10 | 7 | 4 | 1 | -1 | -1,6 |
| Mechanical mixture, % | 0,368 | 0,367 | | 0,366 | 0,365 | 0,364 | 0,363 | 0,361 | 0,355 | 0,348 | 0,342 | 0,334 | 0,335 |
| Chlorine salts mg/dm³ | 1133,67 | 1097,1 | | 1053,216 | 1038,58 | 1031,274 | 1015,15 | 886,476 | 667,24 | 378,84 | 195,734 | 37,884 | 7,314 |
| Kinematic viscosity, sSt | 5 °C | doesn't flow | doesn't flow | doesn't flow | doesn't flow | doesn't flow | doesn't flow | doesn't flow | doesn't flow | doesn't flow | doesn't flow | doesn't flow | doesn't flow |
| | 20 °C | doesn't flow | doesn't flow | doesn't flow | doesn't flow | doesn't flow | doesn't flow | 122,5 | 40,40 | 18,90 | 10,30 | 7,60 | 7,60 |

The minimum effective viscosity (y) is taken as the output function (criterion) in the planning matrix. The equation of the mathematical model of the process has the form of a Taylor series polynomial dividing function. *The coefficients of the regression model* were determined on the basis of Student's criterion. Then the adequacy of the constructed mathematical model to the process was checked. Adequacy was determined on the basis of Fisher's criterion. In order for the created mathematical model to be adequate to the process, the condition $F_{calcul.} \leq F_{table}$ was fulfilled. The same method of mathematical modelling and optimisation was applied for both the remaining options. These operations were carried out on the basis of a computer programme.

Statistical mathematical models of the process were obtained in the form of the following (1-3) equations:

$$y = 0.348 + 0.002x_1 - 0.003x_2 + 0.003x_1 \cdot x_2 + 0.002x_1 \cdot x_3 + 0.007x_1 \cdot x_2 \quad (1)$$

$$y = 0.055 + 0.002x_1 - 0.003x_2 + 0.001x_3 + 0.002x_1 \cdot x_3 + +0.002x_2 \cdot x_3 - \quad (2)$$

$$y = 0.062 + 0.001x_1 + 0.001x_3 + 0.002x_1 \cdot x_2 + 0.001x_1 \cdot x_3 + +0.001x_1 \cdot \quad (3)$$

Based on the statistical mathematical models of the process (1-3), their optimal mode parameters were found:

$x_1 = 402$ $x_2 = 18{,}5$ $x_3 = 436{,}2$ $y = 0{,}35$

$x_1 = 88.4$ $x_2 = 20.3$ $x_3 = 144.6$ $y = 0{,}063$

$x_1 = 1.054$ $x_2 = 6.07$ $x_3 = 144.6$ $y = 0{,}058$

The "complex" optimisation method was used to determine the optimum mode parameters of the process. As a result, the created regression model of the process (1-3) allows to analyse many variants of process parameters. This, in turn, makes it possible to predict the course of the technological process.

**The third chapter of the thesis** is dedicated to providing mixing of oils characterised by complex rheological properties, and at the same time improving the efficiency of such processes as collection, preparation and transportation, taking into account the degree of their hydration. It should be noted that in the course of research we developed an express method for determining the percentage of ballast water in oils and their mixtures, as well as the maximum degree of water dispersion in oil in mining conditions. The impact of the degree of dilution on the demulsification process of anomalous oils and oil-condensate mixtures without reagents and in the presence of reagents was studied. In laboratory conditions the impact of the reagent "Alkan-318" on demulsification of high paraffin oils, and also on process of deposition of paraffins at transportation of this kind of oils was investigated. It is established that the reagent "Alkan-318" is multifunctional and has an effective complex effect.

Nowadays the process of oil demulsification in mining conditions is one of the most important technological processes, and increasing the economic efficiency of this process remains an urgent problem due to the requirement of time. The effect of the degree of dilution on the efficiency of demulsification of oils with complex rheological properties was studied on oil samples of the Muradkhanli field. In the experimental process the reagent "Disolvan-4411" was used as demulsifier. The process was carried out at temperatures of 20, 40, $60^0$C and oil samples of different dilution degrees were used. The efficiency of demulsification of oil emulsions with demulsifier was estimated by the method of "bottle test" by the amount of water released from the stable oil-water system as a function of time. Emulsion samples were sedimented after thermochemical reaction and after a certain time interval the dynamics of water separation from oil and sedimentation were monitored. On the basis of analysis of dependence of oil emulsions stability on the degree of their dilution and consumption characteristics of demulsifier reagent providing their disintegration, it was established that the efficiency of demulsification process strongly depends on the amount of water phase in the oil and the degree of its dispersibility. As the amount of water in demulsified oils increases, the demulsifier consumption decreases. The process of demulsification of various mixtures of oil and condensate with the use of domestically produced “Alkan-202” as a demulsifying reagent was studied. For this purpose the mixture of condensate “Umid” with initial dilution of 36% and oil “Alat-Sangachal-Bulla” (50:50%) was artificially diluted with formation water to different degrees of dilution (50, 60, 70, 80%) and then the possibility of demulsification of these systems was considered. According to the results of demulsification of these mixtures at $60^0$C at dilution degrees of 50, 60, 70 and 80%, it was found that the dilution factor significantly affects the demulsification of oil-condensate mixture. Thus, with the increase of dilution percentage the degree of mixture dehydration increases, and at this time emulsions decompose relatively quickly.

In order to study the impact of oil mixing on their demulsification in laboratory conditions we studied separate oil samples and the process of their mixtures dehydration. According to the generally accepted “bottle test” method the efficiency of demulsification of two oil samples differing in rheological, physical and chemical properties and degree of dilution, and their mixtures in different proportions were determined. As a result of tests carried out both without and with the reagent, the rates of emulsion disintegration were determined. The mass fractions of these oils (0:1; 0,15:0,85; 0,3:0,7; 0,4:0,6; 0,5:0,5; 0,6:0,4; 0,7:0,3; 0,85:0,15 and 1:0) change in demulsifier consumption at different values and the degree of dehydration was analysed. For example, if the reagent consumption for the mixtures at the proportions indicated for the degree of emulsion degradation of 60% is 17 and 10 g/t, the change in reagent consumption for other concentrations of mixed oil is observed with cases of increase and decrease. For example, while there is a positive synergy in the reagent consumption for demulsification of a 50:50% mixture, a negative synergy is observed for a ratio of 60:40%.

Emulsification of water in oil, or in other words, the degree of dispersion, is a crucial characteristic of water-oil emulsions and determines their primary properties. However, due to a number of objective reasons, it is not always possible to precisely determine the varying degree of water dispersion in oil under field conditions.

In light of this, laboratory studies were conducted using the "drop test" method to determine the dispersion of water in oil or the water content in oil. The laboratory studies indicate that the "drop test" method is sufficiently informative and is advisable for use as a rapid analysis to assess the ability of rheologically complex field oils to disperse water[3].

For the research, a high-viscosity, heavy crude oil extracted from well No. 64 of the "Alyat-Deniz" field (SMO-63) of the N.G.D.U. named after N. Narimanov was selected. The physicochemical properties of the oil were determined under laboratory conditions according to the relevant GOST standard. The determined values for density, freezing point, as well as the amounts of water, chloride salts, mechanical impurities, paraffin, resins, and asphaltenes were 931 kg/m³ at 28°C; 34% water, 1300.16 μg/dm³ chloride salts; 0.20% mechanical impurities; 5.5% paraffin; 2.2% resins; and 7.1% asphaltenes, respectively.

For the laboratory investigations of oil with varying degrees of water content, the samples were homogenized, placed into a closed crucible, and re-mixed. Afterward, a drop sample was taken with a pipette and deposited on pre-prepared filter paper.

The drop sample was allowed to sit at the specified temperature until the oil stopped dripping (approximately 20-30 minutes). Experiments were conducted at two temperatures: 5°C and 20°C, with the waiting time being consistent.

Based on the size and color of the stain on the filter paper, the percentage of water dispersed in the oil was initially assessed. The analysis of the obtained results shows that for the oil, the dispersion

[3]Адыгезалова, М.Б., Нурмамедова, Р.Г., Халилов, Р.З. Диагностика эффективности эмульсации нефтей на основе «капельной пробы»// Российский государственный университет нефти и газа имени И.М. Губкина» Юбилейной 70-й Международной молодежной научной конференции «Нефть и газ – 2016, -18-20 апреля, -с. 349.

capacity (DC) increases with the enlargement of the intermediate annular zone. A narrowing of this zone is characterized by an increased percentage of water in the oil. When the oil is fully saturated with water (in other words, when the dispersion of water is complete), this zone no longer exists on the filter paper.

**The fourth chapter of the work** analyses the results of scientific research of corrosion processes occurring on the inner surface of equipment operated in the oil industry and at the same time identifies the issues to be solved. It is known that the inner surface of equipment operated in the oil industry is subjected to corrosion under the influence of formation water with an aggressive medium. The degree of aggressiveness of formation water is determined by its constituent components. Thus, the presence in formation water of molecular oxygen, carbon dioxide, hydrogen sulphide, ionic mineral salts and, most importantly, sulphate-reducing bacteria increases the rate of corrosion of the internal surface of the equipment.

**In this chapter of the dissertation** the bactericidal-inhibiting properties of new reagents with the conventional names MARZA-1, MARZA-2, M-2 in various aggressive media are studied. Also in this chapter the results obtained at research of bactericidal-inhibiting properties of the composition prepared on the basis of resin MARZA-1 and Gossypol and with the conditional name M-1 are reflected. At the same time the efficiency of protection of five new compositions based on MARZA-2 against corrosion and salt deposits was studied. All five new reagents are of organic origin and can be produced industrially on the basis of local raw materials.

In laboratory conditions the corrosion protection efficiency of MARZA-1 reagent in the media with hydrogen sulphide, carbon dioxide and both gases for 24 and 240 hours was studied. According to the results of numerous laboratory experiments it was established that as the concentration of MARZA-1 in the medium increases, the corrosion rate decreases and the effect of the reagent increases. As the test period increased, a weakening of the corrosion rate was observed, which can be explained by the fact that the coating formed from the corrosion products on the surface of the samples fulfils a protective function by shielding the metal surface **(table 2)**.

The effect of reagent MARZA-1 in nutrient medium "Postgate-B" on strains of species of sulfate-reducing bacteria "Desulfomicrobium" and "Desulfovibriode-sulforicans" taken from produced water of the field developed by "Bibieybatneft" OGPD of "SOCAR" was studied. It was found that although the amount of biogenic hydrogen sulfide in the medium MARZA-1 sharply decreases, the process of sulfate reduction does not stop completely. Consequently, the reagent cannot completely stop the exchange process of sulfate-reducing bacteria in the nutrient medium.

In the process of research the bactericidal-inhibiting properties of the composition of reagents MARZA-1 and Gossypol resin in the ratio of 10:1 (conventional name M-1) were studied. $H_2S$, $CO_2$, $H_2S+CO_2$ were used as aggressive media causing corrosion. The experimental results showed that the highest protection effect is observed at 100 mg/l of the composition, and in case of diesel fuel solvent this effect is 98% in $H_2S$ medium, 96% in $CO_2$ medium, 98% in $H_2S+CO_2$ medium, and in case of paraffin it is 97%, 94% and 99%, respectively.

On medium with both sulphate-reducing bacteria, the highest effect of the composition was observed at a concentration of 120 mg/L (95-99%)[4].

Thus, compared with the reagent MARZA-1 prepared composition M-1 had a higher anticorrosive and bactericidal effect in these media, which can be explained by the occurrence of synergistic effect. Anticorrosive effect of MARZA-2 reagent in neutral, acidic and alkaline media was studied in laboratory conditions and according to the results of numerous experiments corrosion rate and efficiency of reagent protection in the studied media were determined.

[4]Гурбанов, Г.Р. Исследование универсального комбинированного ингибитора для нефтегазовой промышленности / Г.Р.Гурбанов, М.Б.Адыгезалова, С.М.Пашаева // Изв. вузов. Химия и хим. технология, - 2020. -V.63. №10, -с.78-89.

**Table 2**

**Protective effects of MARZA-1 reagent in various aggressive environments**

| Environment | $C_{inh.}$. mg/l | K, $g/m^2 \cdot hour$ | Retardation factor,γ | $K_p$ , mm/il | Protection effect, Z, % |
|---|---|---|---|---|---|
| $H_2S$ | - | 0,4326 | - | - | - |
| | | 0,1874 | - | - | - |
| | 3,0 | 0,0506 | 8,54 | 0,0566 | 88,3 |
| | | 0,0504 | 3,71 | 0,0564 | 73,1 |
| | 5,0 | 0,0328 | 13,18 | 0,0367 | 92,4 |
| | | 0,0329 | 5,69 | 0,0368 | 82,4 |
| | 7,0 | 0,0190 | 22,76 | 0,0212 | 95,6 |
| | | 0,0163 | 11,49 | 0,0182 | 91,3 |
| | 10,0 | 0,0086 | 50,3 | 0,0096 | 98,0 |
| | | 0,0080 | 23,42 | 0,0089 | 95,7 |
| $CO_2$ | - | 0,2418 | - | - | - |
| | | 0,06231 | - | - | - |
| | 3,0 | 0,0573 | 4,21 | 0,0641 | 76,3 |
| | | 0,0247 | 2,52 | 0,0276 | 60,22 |
| | 5,0 | 0,0430 | 5,62 | 0,0481 | 82,2 |
| | | 0,0187 | 3,33 | 0,0209 | 69,86 |
| | 7,0 | 0,0232 | 10,42 | 0,0259 | 90,4 |
| | | 0,0080 | 7,78 | 0,0089 | 87,15 |
| | 10,0 | 0,0125 | 14,34 | 0,0140 | 94,8 |
| | | 0,0032 | 11,47 | 0,0035 | 94,83 |
| $H_2S$ +$CO_2$ | - | 0,3416 | - | - | - |
| | | 0,7612 | - | - | - |
| | 3,0 | 0,0792 | 4,31 | 0,0887 | 76,8 |
| | | 0,1364 | 5,58 | 0,1527 | 82,07 |
| | 5,0 | 0,0526 | 6,49 | 0,0589 | 81,6 |
| | | 0,0796 | 4,56 | 0,0891 | 89,54 |

| | | | | | |
|---|---|---|---|---|---|
| | 7,0 | 0,0290 | 11,77 | 0,0324 | 91,5 |
| | | 0,0246 | 30,94 | 0,0275 | 46,76 |
| | 10,0 | 0,0109 | 31,33 | 0,0122 | 96,8 |
| | | 0,0058 | 131,24 | 0,0064 | 99,23 |

***Note***: the experiment duration is 24 hours (velocity) and 240 hours (denominator).

It was found that when the amount of reagent varies in the range of 3-10 mg/l, the corrosion rate in neutral medium is 0.0782-0.0078 $g/m^2 \cdot hour$, the protection effect is 90-99%, the corrosion rate in acidic medium is 0,3430-0.00 g/ $m^2 \cdot hour$, the protection effect is 88-100%, and the corrosion rate in alkaline medium is 0.1843-0.0410 $g/m^2 \cdot hour$, the protection effect is 82-96%.

Thus, as a result of comparative analysis of the results obtained from laboratory tests, it was found that the amount of 10 mg/l of MARZA-2 reagent is effective for all three media, and its anti-corrosion effect is 96-100%.

Significant reduction of corrosion rate in all studied aggressive media can be explained by the property of the reagent to hydrophobise the metal surface.

Thus, during the process the reagent screens active centres with high energy on the metal surface and isolates them from the aggressive medium, making the corrosion process passive. Experimental results suggest that MARZA-2 reagent has a strong inhibitory property in all three media.

From mining experience it is known that sulphate-reducing bacteria are the cause of severe corrosion of the internal surface of the equipment in operation. For this reason, the effectiveness of MARZA-2 reagent against these bacteria was studied according to the known standard NASE methodology. As a nutrient medium
"Posgate-B" medium was used. It should be noted that when the activity of sulfate-reducing bacteria stops, the activity of biocenosis formed by other physiological groups of microorganisms in the medium also stops.

The process was carried out for fifteen days by alternate dilution method. Sulfate reducing bacteria used in laboratory studies

were taken from formation water produced with oil from operating wells of "Bibihaybatneft" OGPD of "SOCAR".
Experiments were carried out in 3,0, 5,0, 7,0 and 10 mg/l solutions of MARZA-2 reagent at 28-30$^0$C in the volume of $10^3$ vol/ml of sulfate-reducing bacteria. After fifteen days of experiments, the bactericidal effect of the reagent was calculated and it was found that the bactericidal effect of MARZA-2 reagent in the concentration range of 3.0-10 mg/l was in the range of 50-85%. In general, the results of numerous laboratory experiments confirmed that MARZA-2 reagent is multifunctional and has bactericidal-inhibiting properties **(figure 2)**.

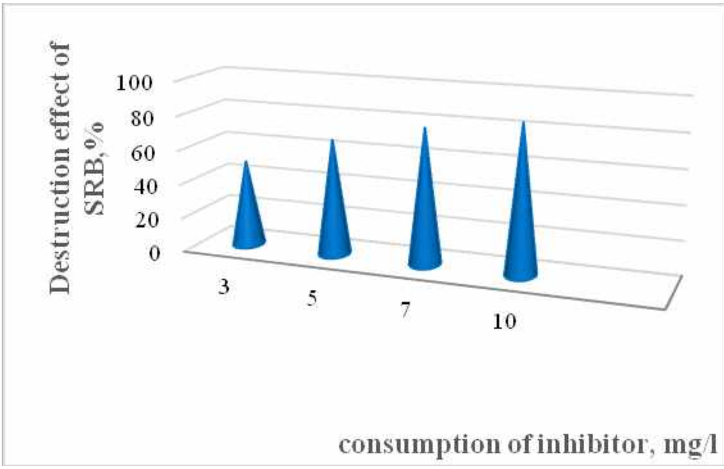


**Figure 2. Effect of destruction of SRB reagent MARZA-2**

Taking into account that separate reagents MARZA-1, MARZA-2, which can be produced in industry on the basis of local raw materials, and the composition of MARZA-1+Gossypol resin have highly effective bactericidal-inhibiting properties, it is economically feasible to use them can be attributed to the protection against corrosion of the inner surface of equipment operated in the oil industry.

In the course of research work on the basis of synergism principles five new compositions with conditional names P-1, P-2, P-3, P-4, P-5 of MARZA-1 and MARZA-2 bactericidal-inhibiting reagents were created and their bactericidal and corrosion-protection effect in hydrogen sulphide formation waters was studied in laboratory conditions.

Two strains of sulfate-reducing bacteria “Desulfomycrobium” and “Desulfovibriodesulforicans” were used to study the bactericidal properties of the compositions. In laboratory conditions, the effect of the new compositions on the incubation period of sulfate-reducing bacteria was studied for fifteen days, using nutrient medium “Postgate B”, where intensive reproduction of bacteria is possible. Comparative analysis, laboratory studies were carried out on nutrient media without composition and with the addition of composition. From the analysis of the results of experiments it was found that the greatest bactericidal effect of P-series compositions occurs at a concentration of 10 mg/l of composition P-3 (99%).

It is known that the cause of electrochemical corrosion of the internal surface of oil industry equipment is production water produced together with oil. The main component of formation water is various dissolved gases, mineral and organic salts, mechanical mixtures and, most importantly, hydrogen sulphide. Therefore, produced water is considered as a strong electrolyte medium in terms of corrosion. In view of the above, the effect of new P series formulations on the corrosion rate of formation water samples taken from well No1082 of “Bibieybatneft” OGPD of SOCAR was studied and their anti-corrosion effects were calculated. The protection level ranges from 85-98% for P-1, 92-99% for P-2, 95-99% for P-3, 75-92% for P-4 and 72-90% for P-5. The best anti-corrosion effect is shown by compositions P-2 and P-3 and at a concentration of 10 mg/litre (99%). **Table 3** shows a comparative analysis of corrosion protection and bactericidal action of individual reagents MARZA-1, MARZA-2 and new compositions of P-series based on them.

Thus, on the basis of the comparative analysis of the values of corrosion protection and bactericidal effects of individual reagents and P-series compositions given in table 3, the following conclusions can be drawn.

1. Compared to MARZA-1 and MARZA-2 compositions P-1, P-2, P-3 have higher corrosion protection and bactericidal effects.

2. Among the compositions of the P series the greatest value both in terms of corrosion protection and bactericidal effect is the composition P-3.

**Table 3**

**Comparative analysis of bactericidal-inhibitory (in acidic environment) properties of MARZA-1, MARZA-2 and P-series compositions**

| conventional name of reagents | concentration of reagents, mg/l | corrosion protection effect,% | bactericidal effect% |
|---|---|---|---|
| MARZA-1 | 3,0 | 88,3 | 57 |
| | 5,0 | 92,4 | 67 |
| | 7,0 | 95,6 | 82 |
| | 10 | 98,0 | 87 |
| MARZA-2 | 3,0 | 88 | 50 |
| | 5,0 | 90 | 67 |
| | 7,0 | 93 | 78 |
| | 10 | 95 | 85 |
| P-1 | 3,0 | 85 | 59 |
| | 5,0 | 90 | 74 |
| | 7,0 | 97 | 81 |
| | 10 | 98 | 85 |
| P-2 | 3,0 | 92 | 84 |
| | 5,0 | 96 | 88 |
| | 7,0 | 98 | 92 |
| | 10 | 99 | 94 |
| P-3 | 3,0 | 95 | 93 |
| | 5,0 | 97 | 96 |
| | 7,0 | 99 | 97 |
| | 10 | 99 | 99 |
| | 3,0 | 75 | 56 |
| | 5,0 | 86 | 70 |

| | | | |
|---|---|---|---|
| P-4 | 7,0 | 90 | 78 |
| | 10 | 92 | 81 |
| P-5 | 3,0 | 72 | 50 |
| | 5,0 | 84 | 65 |
| | 7,0 | 88 | 72 |
| | 10 | 90 | 76 |

3. Widespread use of P-3 composition for corrosion protection of the internal surface of equipment used in the oil industry is considered more appropriate.

Bactericidal-inhibitory properties of the reagent of organic origin and conventional name M-2 were studied in laboratory conditions by conducting numerous experiments. At the same time reagent quantities of 10, 15, 20 and 25 mg/l were used. Anti-corrosion effect of reagent M-2 was studied in three different aggressive media: hydrogen sulphide, carbon dioxide, hydrogen sulphide + carbon dioxide. After processing the results of six-hour laboratory experiments, it became clear that the greatest anti-corrosion effect in all three aggressive media is observed at a concentration of 25 mg /l reagent. The corrosion protection effect is 98 % in the medium with hydrogen sulphide, 92,7 % in the medium with carbon dioxide and 94,8 % in the aggressive medium with both gases **(figure 3).**

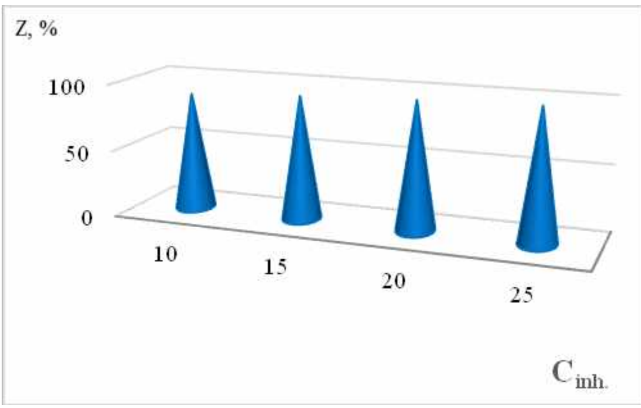

**Figure 3. Protection effect of reagent M-2 in hydrogen sulfide environment**

In the laboratory, the effect of reagent M-2 on sulfate-reducing bacteria was also studied for seven days and its bactericidal effect at different concentrations was calculated **(table 4)**. As can be seen from table 4, as the concentration of reagent M-2 in the nutrient medium with the characteristic of intensive reproduction increases, the number of bacteria, the amount of biogenic hydrogen sulfide decreases, and the bactericidal effect of the reagent increases. Thus, when changing the concentration of reagent M-2 in the range of 10-25 mg/l, the number of bacteria varies from 107 to 101, the amount of hydrogen sulfide from 270 to 5,4 mg/l, and the value of the bactericidal effect of the reagent varies from 70 to 98%.

**Table 4**

**Bactericidal effect of reagent M-2**

| concentration, mg/l | number of bacteria (cell count /ml) | the amount of $H_2S$, mg/l | bactericidal effect, % |
|---|---|---|---|
| 0,00 | $10^7$ | 270 | - |
| 10 | $10^5$ | 80 | 70 |
| 15 | $10^3$ | 60 | 78 |
| 20 | $10^2$ | 22 | 92 |
| 25 | $10^1$ | 5,4 | 98 |

Thus, it is found that high bactericidal effect is observed at the concentration of M-2 reagent 25 mg/l. The results of experiments suggest that reagent M-2 has high bactericidal-inhibiting properties.

Currently, the main energy source for humanity, which is at a technologically advanced stage, remains oil due to its physical and chemical properties. Countries of the world with developed oil industries produce millions of tons of oil every day. Electrochemical corrosion processes caused by asphaltene-resin-paraffin deposits, salt deposits, corrosive media, and microorganisms in the production, storage, treatment, and transportation of oil through pipelines create complex problems petroleum engineers. This is because that the above factors cause premature failure of the lifting pipes of the elevator, oil-well tubing, rod pumps, injection lines and other linear pipelines, tanks, oily pipelines and main pipelines at all stages of the collection, and transportation system. Problems caused by scale, and corrosion aggression leads to failure not only of equipment, devices, pipes, etc., made of precious metals and their alloy, but also violate the ecological balance of nature. It should be noted that the growth of oil production and refining since the end of the twentieth century has exacerbated the problem of salt deposition and corrosion in general.

In the countries of the world oil industry, up to five times more formation, water is extracted than produced oil. This amount is even higher if we consider the injection of water into the reservoir in the reservoir pressure maintenance system. As you know, formation waters, being electrolytes, contain hydrogen sulfide, carbon dioxide, oxygen, microorganisms, mineral salts of various compositions, including sodium chloride, calcium chloride, magnesium chloride, sodium carbonate, sodium bicarbonate, calcium bicarbonate, sulfates, sulfides, boron compounds, organic substances (compounds of naphthenic acid, etc.). Iron, aluminum, and silicon oxides are also found in some formation waters. It is known from the composition of associated water that it plays the role of both an agent of scaling and electrochemical corrosion of oil field equipment.

Protecting metal equipment used in the oil industry from corrosion and scale is an urgent issue. The combined damage caused by these problems to the global economy amounts to billions of dollars a year.

In the course of the thesis work, twelve compositions combining the properties of protection against corrosion and salt deposits were prepared **(table 5).**

The results of numerous experiments carried out in laboratory conditions showed that only two of the twelve new compositions - compositions C-5 and S-5 - have a high protection effect against both salt deposits and corrosion **(tables 6-9).**

As can be seen from the tables, when the concentration of both formulations is increased from 20 mg/l to 100 mg/l, the protection effect against salt deposition increases. At concentration of 100 mg/l this effect is 98% for C-5, 99% for S-5.

As can be seen from the results shown in table 8 and table 9, when the concentration of C-5 and S-5 formulations is varied between 20-100mg/l, the corrosion protection effect varies between 86-99% and 89-100%, respectively[6]. As can be seen from the results shown in table 8 and table 9, when the concentration of C-5 and S-5 formulations is varied between 20-100mg/l, the corrosion protection effect varies between 86-99% and 89-100%, respectively[5].

**Table 5**

**Component composition and conventional names of compositions**

| № | Component composition | Component ratio,% | Conventional name |
|---|---|---|---|
| 1 | МАРЗА-2+gossipol+ kerosene | 5:45:50 | СЕSСЭ - С1 |
| 2 | МАРЗА-2+gossipol+ kerosene | 7:43:50 | СЕSСЭ - С2 |
| 3 | МАРЗА-2+gossipol+ kerosene | 9:41:50 | СЕSСЭ – С3 |
| 4 | МАРЗА-2+gossipol+ kerosene | 11:39:50 | СЕSСЭ – С4 |
| 5 | МАРЗА-2+gossipol+ kerosene | 13:37:50 | СЕSСЭ – С5 |
| 6 | МАРЗА-2+gossipol+ kerosene | 15:35:50 | СЕSСЭ – С6 |
| 7 | МАРЗА-2+gossipol+ diesel fuel | 5:45:50 | СЕSСЭ - S1 |
| 8 | МАРЗА-2+gossipol+ diesel fuel | 7:43:50 | СЕSСЭ - S2 |
| 9 | МАРЗА-2+gossipol+diesel fuel | 9:41:50 | СЕSСЭ – S3 |
| 10 | МАРЗА-2+gossipol+diesel fuel | 11:39:50 | СЕSСЭ – S4 |
| 11 | МАРЗА-2+gossipol+diesel fuel | 13:37:50 | СЕSСЭ – S5 |
| 12 | МАРЗА-2+gossipol+diesel fuel | 15:35:50 | СЕSСЭ – S6 |

**Table 6**

**Protective effect of C-5 composition against calcium salts**

| № | concentration, mg/l | protection effect, % |
|---|---|---|
| 1. | 20 | 85 |
| 2. | 30 | 89 |
| 3. | 40 | 91 |
| 4. | 50 | 93 |
| 5. | 70 | 96 |

| | | |
|---|---|---|
| 6. | 100 | 98 |
| 7. | 120 | 90 |

[5]Gurbanov, G.R. Investigation of the efficiency of the composition containing gossypol resin against corrosion and scaling / G.R.Gurbanov, M.B. Adigezalova // Izvestiya Vysshikh Uchebnykh Zavedenii Khimiya i Khimicheskaya Tekhnologiya, -2022, V. 65. № 12, -c. 76-84.

**Table 7**

**Protective effect of S-5 composition against calcium salts**

| № | concentration, mg/l | protection effect, % |
|---|---|---|
| 1. | 20 | 88 |
| 2. | 30 | 91 |
| 3. | 40 | 93 |
| 4. | 50 | 96 |
| 5. | 70 | 98 |
| 6. | 100 | 99 |
| 7. | 120 | 90 |

**Table 8**

**Corrosion protection effect of C-5 composition**

| № | concentration, mg/l | protection effect, % |
|---|---|---|
| 1. | 20 | 86 |
| 2. | 30 | 90 |
| 3. | 40 | 92 |
| 4. | 50 | 92 |
| 5. | 70 | 95 |
| 6. | 100 | 99 |
| 7. | 120 | 89 |

**Table 9**

**Corrosion protection effect of S5 composition**

| № | concentration, mg/l | protection effect, % |
|---|---|---|
| 1. | 20 | 89 |

| | | |
|---|---|---|
| 2. | 30 | 91 |
| 3. | 40 | 93 |
| 4. | 50 | 94 |
| 5. | 70 | 97 |
| 6. | 100 | 100 |
| 7. | 120 | 89 |

Thus, in the study of twelve compositions of complex effect, compositions C-5 and S-5 have the highest effect against salt deposits and corrosion.

**In the fifth chapter of the dissertation** asphaltenes, resins, paraffins, which are the main components of high paraffin oils, and deposits formed by them, the main factors affecting their formation, as well as the results of scientific research carried out in the direction of the solution of this problem were systematised and analysed, and a general conclusion was made. It is shown that researchers' opinions on the mechanism of asphaltene-resin-paraffin deposits formation, as well as factors affecting it, are ambiguous.

Recently there are a lot of theories correctly explaining from modern views the formation of paraffin deposits accumulated on the inner surface of oil pipelines, and the most widespread of them is the theory explaining the process of formation of asphaltene-resin-paraffin deposits from the point of view taking into account the crystallisation temperature of solid paraffin-naphthenic hydrocarbons. It is shown that this theory does not take into account such determining factors as adhesion, adsorption and the impact of resin-asphaltene components on dispersed oil systems. Also, another theory states that asphaltene-resin components have a significant effect on the waxing process on the internal surface of equipment. The research scientists who put forward this theory base the process of asphaltene-resin-paraffin deposit formation on the coagulation, aggregation and micelle-forming properties of naphthenic hydrocarbons and asphaltenes in a dispersed oil system.

From numerous scientific researches it is known, that both in our republic and in foreign countries the difficulties arising in the system of collection-transportation of high-paraffin oil, and research

works carried out in the direction of their elimination, show that corrosion and paraffin deposition processes, really necessary for effective transportation of this type of oil, should be eliminated.
However, in published scientific articles, as well as in dissertations carried out in this direction, in order to improve the efficiency of the system of collection and transportation of high paraffin oils, a group of authors separately considers it appropriate to eliminate corrosion, and others only paraffin deposition. Proceeding from the fact that it is more expedient to develop an efficient technology for the simultaneous elimination of both factors that create complications, namely corrosion and paraffin deposition processes, in order to obtain a higher effect from an economic point of view in the collection and transportation system of high-paraffin oils, research work was carried out in this direction during the fulfillment of the dissertation work. For this reason domestic and foreign reagents against corrosion and paraffin deposition were selected and their protection effect was determined in laboratory conditions.

In this chapter the freezing temperature, thixotropic properties, effective viscosity of the model oil prepared in laboratory conditions, and the additives “Difron-4201” and “Difron-3970” produced by the company “EKOS-1” of the Russian Federation, as well as the formed asphaltene-resin-paraffin deposits experimental results related to the effect are given. At the same time, in the fifth chapter the effect of a new composition based on “Difron-4201” and MARZA-1 on the freezing point of high paraffin oil and corrosion rate in hydrogen sulphide formation waters is considered and the development of new technologies in the transportation of high paraffin oil is reflected. Physical-chemical parameters of model high-paraffin oil selected for the study are given in **table 10**.

**Table 10**

**Physico-chemical characteristics of high-paraffin oil**

| № | parameters | quantification | method of determination |
|---|---|---|---|
| 1 | The amount of water in the sample, % | 0.2 | SS 2477-2014 |

| | | | |
|---|---|---|---|
| 2 | Density $\rho_4^{20}$ kg/m$^3$ | 894.3 | SS 3900-85 |
| 3 | Amount of paraffin, % | 11.6 | SS 11851-85 |
| 4 | Amount of resin, % | 10.2 | SS 11851-85 |
| 5 | Amount of asphaltene, % | 5.2 | SS 11851-85 |
| 6 | Freezing temperature, °C | +16 | SS 20287-91 |
| 7 | Melting point of paraffin,$^0$ C | 57 | SS 11858-83 |
| 8 | Sulfur content, % | 0.22 | SS 1437-75 |
| 9 | A/Q | 0.509 | - |

It should be noted that this oil sample was prepared from commercial oils of Narimanov and Absheron fields in the ratio of 2:1.

In the course of the thesis work selection and evaluation of the efficiency of depressor additive was carried out based on the effect on the freezing point of oil. The impact of depressor additives on the freezing point of high paraffin oil was carried out according to the method RD 39-3-812-82, the additives "Difron-3970" and "Difron-4201" were used as reagents.

Analysis of the results of numerous laboratory tests showed that the depressor additive "Difron-4201" has a more effective impact on the freezing point of high-paraffin oil compared to "Difron-3970". It should be noted that the greatest effect is observed at a concentration of both additives of 900 g/t. The depressor additive "Difron-3970" in the specified concentration reduces the oil freezing point from +16$^0$C to +7$^0$C, and the depressor additive "Difron-4201" to +5$^0$C **(figure 4)**.

It is for this reason that during the research works the depressor additive "Difron-4201" was used to affect other rheological parameters of high paraffin oil.

In connection with the commissioning of high-paraffin oil fields in developed countries of the world oil industry, including our country, the struggle against asphaltene-resin-paraffin deposits accumulating on the inner surface of pipelines and other operated equipment has become more acute. Therefore, effective fight against paraffin deposits is considered to be one of the most important decisive issues. Thus, asphaltene-resin-paraffin deposits not only worsen technical and economic indicators of the processes of production, storage, transportation of oil through pipelines, but also increase energy demand and increase the probability of accidents. In other words, accumulation of asphaltene-resin-paraffin deposits on the inner surface of the equipment used in the system of downhole collection-transportation of high paraffin oils leads to technological complications, production reduction, equipment failure and equipment in operation until the end of its service life.

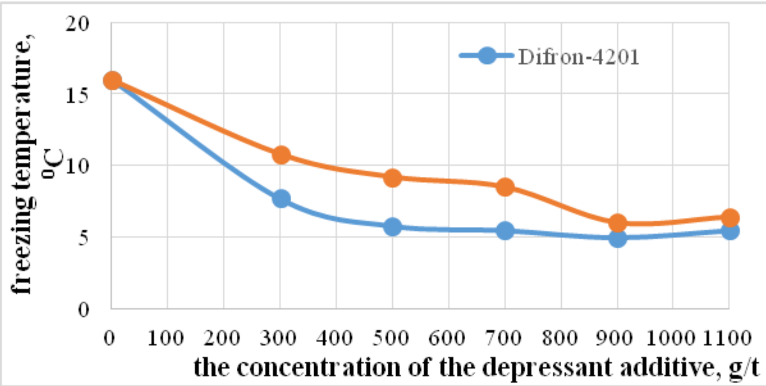


**Figure 4. Effect of depressor additives on the freezing temperature of high paraffinic oil**

Despite the existence of numerous methods to combat asphaltene-resin-paraffin deposits, the most optimal method in terms of cost-effectiveness and simplicity of application technology is the use of depressor additives in the transportation and storage of high paraffin oils in difficult geotechnological conditions of the oil industry. It should be noted that the method of using depressor additives against asphaltene-resin-paraffin deposits differs from other methods not only in technological efficiency. At the same time in this method the effect obtained by adding the reagent at temperatures above the starting temperature of crystallisation of paraffin hydrocarbons does not depend on the thermohydrodynamic conditions of oil movement through the pipeline. That was the reason for the dissertation work to study the effect of the depressor additive "Difron-4201" on the process of formation of paraffin deposits in high paraffin oil in laboratory conditions. For this purpose the "Cold finger" method, which is used to assess the effectiveness of depressor additives and determine the optimal rate of consumption, was applied. The "Cold finger" method is a method based on deposition of paraffin deposits from moving oil on a cold metal surface.

Laboratory tests were carried out at "Cold finger" temperatures of $0^0$C, $5^0$C, $10^0$C, $15^0$C, $20^0$C, $25^0$C, $30^0$C for two hours. The mass of paraffin deposits collected on the surface at each "Cold finger" temperature for 0, 20, 40, 60, 80, 100, 120 minutes was determined by weighing on analytical scales.

Laboratory experiments were conducted on oil samples with the addition of 300, 500, 700, 900, 1100 g/t of the depressor additive "Difron-4201" and the efficiency of the depressor additive was calculated on the basis of the following mathematical dependence.

where: K- depressor additive efficacy;

$m_1$ – the mass of ARPD in the environment without additives;

$m_2$ – the mass of ARPD in the medium containing the depressant additive;

**Figure 5** shows the efficiency of the depressor additive against oil deposits at a temperature of $5^0$C in the "Cold finger".

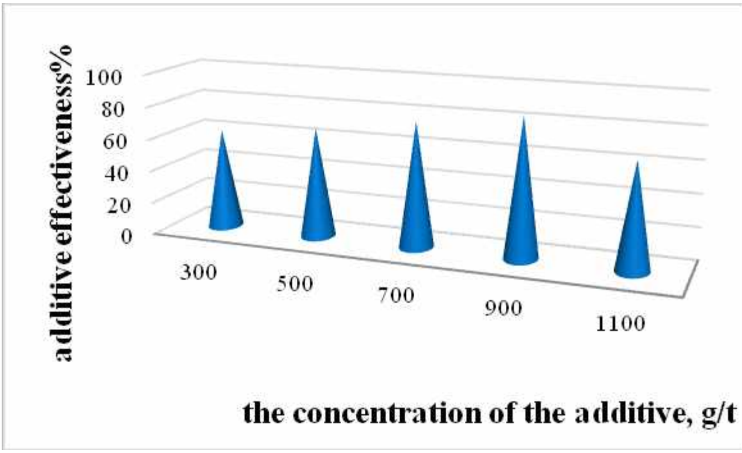


**Figure 5. Effectiveness of "Difron 4201" against paraffin precipitation**

As can be seen from figure 5, the depressor additive “Difron-4201” can be used as an effective agent against asphaltene-resin-paraffin deposits in high paraffin oils at low temperatures, and its optimal consumption rate is 900 g/t[6].

It is known that high paraffin oils are rheologically complex fluids prone to structure formation at low temperatures (thixotropic properties) and belong to inhomogeneous and non-equilibrium disperse systems. The reason why oils with a high paraffin content have thixotropic properties is due to the presence of components such as paraffin, asphaltene and resin, which tend to form structure. The study of rheological properties of high paraffin oils with thixotropic properties shows that non-Newtonian properties are formed in oil at low temperatures due to asphaltene, resin and paraffin components in the dispersed state. At that, resin components of oil give it elasticity, and paraffin components give it nonlinear viscous properties.

It should be noted that the value of rheological parameters of thixotropic oils changes during their flow and subsequent suspension. During the flow the paraffin structure of oil is destroyed, and at its stopping it is restored again. In other words, thixotropy is the ability to restore the dispersed structure of a high paraffin dispersed oil system over time.

Thixotropic properties of high-paraffin oil were studied according to SS 1929-87 at temperatures of $10^0$C, $15^0$C, $20^0$C on a rotational viscometer "Reotes-2". Laboratory experiments were carried out both without additives and with different amounts of depressor additive "Difron-4201" on highly paraffinised samples.

It was determined that with increasing concentration of the additive the area of the hysteresis loop decreases, and the largest decrease occurs at a concentration of 900 g/t of the depressor additive "Difron-4201".

The correct determination of various rheological properties of oils with different physical-chemical parameters is of great importance

[6]Гурбанов, Г.Р. Исследования влияние депрессорного присадка «Дифрон-4201» на формирование парафиноотложения в лабораторных условиях / Г.Р.Гурбанов, М.Б.Адыгезалова, С.Ф С.М.Пашаева [и др.] // Азербайджанского нефтяного хозяйства, - 2020. №12, - с. 30-36.

to prevent energy losses that will be noticeable in practice when calculating their flow mode, as well as to improve the efficiency of their transportation through the pipeline. In particular, the correct determination of the ultimate shear stresses and effective viscosity of viscoplastic oils is very important for both theoretical work and practical applications. Therefore, the effect of the depressor additive "Difron-4201" on a number of rheological parameters of high paraffin oil was studied in laboratory conditions. The experiments were carried out on a "Reotes-2" viscometer in a wide range of temperatures ($6^0$C, $8^0$C, $10^0$C, $12^0$C, $15^0$C, $20^0$C, $30^0$C, $40^0$C, $50^0$C) and in the range of velocity gradient from 0.1 to 35 $s^{-1}$ . Experiments were carried out on oil samples without additives and with 300, 500, 700, 900, 1100 g/t of the depressor additive "Difron-4201". The values of rheological parameters of the investigated high paraffin oil were determined by the Bulkley-Herschel model. The results of experiments showed that when the concentration of depressor additive is increased up to 900 g/t, the value of ultimate shear stress of oil decreases to 15 at $6^0$C; 16.5 at $8^0$C; 18.3 at $10^0$C; 46.3 at $12^0$C- and 65.2 at $15^0$C. Also, the value of the effective viscosity of oil decrease to 5.6 at $6^0$C; 2.6 at $8^0$C; 2.8 at $10^0$C; 3.8 at $12^0$C and 5.1 at $15^0$C in the specified concentration intervals.

Using the results of the experiments conducted to study the rheological properties, a graph of the dependence of the ultimate shear stress of high paraffin oil on temperature and concentration of the depressor additive "Difron-4201", the dependence of the oil consistency index on temperature and concentration of the depressor additive "Difron-4201", the non-Newtonian index of oil on temperature and the dependence on the concentration of the depressor additive "Difron-4201" was constructed.

According to the results of experiments, in order to find out the effect of structure and phase transitions occurring in high paraffin oil on its structural and mechanical properties when changing the concentration and temperature of depressor additive "Difron-4201", a graph characterising the following dependences was constructed **(figure 6)**.

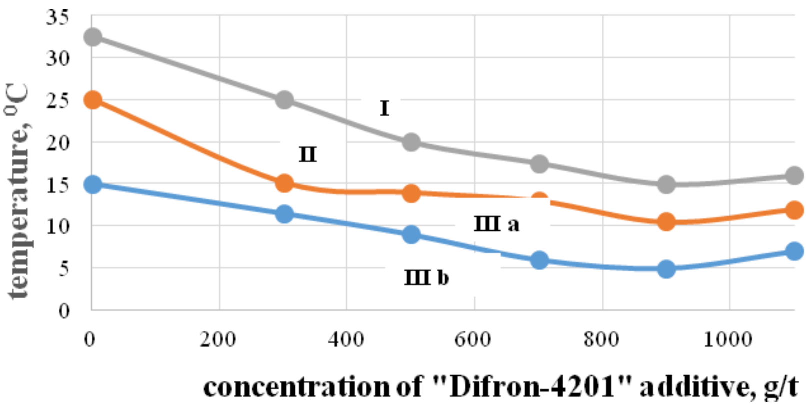


**Figure 6. Structure and phase transitions of high-paraffin model oil at different concentrations of "Difron-4201" depressant additive**

The curves (1,2,3) in the figure divide the graph into the following areas.

I. The field characterising the molecular-disperse state of the system
II. The field characterising the freely dispersed state of the system
III. The field characterising the coherent-dispersed state of the system.

Field III can be divided into two zones.

1. A soft gel zone with temperature from $T_\tau$ to $T_d$
2. A gel zone solidified below the temperature $T_d$

Curve I in the figure shows the dependence of paraffin crystallisation onset temperature, curve II the onset temperature of non-linearly viscous plastic nature and curve III the oil freezing temperature on the concentration of depressor additive "Difron-4201". As can be seen from the figure, the value of all three parameters decreases with increasing concentration of the depressor additive "Difron-4201", but a relative increase is observed at a concentration of 1100, and the greatest decrease occurs at an additive concentration of 900 g/t. The composition and properties of asphaltene-resin-paraffin deposits depending on the temperature of high paraffin oil and adsorbing surface have been studied. In the course of the research it was found that the change in the temperature of high paraffin oil and "Cold finger" affects the group composition of paraffin deposits. Decreasing the temperature of the oil leads to a decrease in the amount of resins and asphaltenes. When lowering the temperature of model oil and "Cold finger" to temperatures close to the freezing point of oil, there is a change in the composition and molecular-mass distribution of n-alkanes in oil deposits due to the release of low-molecular-weight paraffin hydrocarbons. When the depressor additive "Difron-4201" is added to the model oil, a decrease in the share of paraffin hydrocarbons with the number of carbon atoms C17-C40 in the deposition and an increase in the number of n-alkanes with a lower value of molecular weight is observed. The amount of resins and asphaltenes in the group composition of deposits decreases. Such changes in the composition of oil deposits lead to improvement of their rheological properties.

In the course of the dissertation work the effect of composition of “Difron-4201” and “Difron-4201+Marza-2=90:1” (conventional name M-3) on dynamic viscosity of oils of Muradkhanli and Sangachal fields was studied. The results obtained showed that the new composition M-3 at a concentration of 900 g/t has a more effective impact compared to the depressor additive “Difron-4201” **(tables 11-12)**[7].

Thus, in Muradkhanli oil sample the dynamic viscosity of the new composition in comparison with “Difron-4201” additive decreases 2 times at $20^0$C, 1.8 times at $10^0$C, 2.2 times at $5^0$C and 2, 2.1 and 2 times, respectively, in Sangachal oil sample.

In laboratory conditions the effect of Gassypol resin-based composition (conventional name M-4) on the kinetics of deposition

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[7]Gurbanov, H.R Research of the rheo-physical and chemical properties of commercial oil through the use of additives / H.R Gurbanov, G.N. Abdullayeva, G.A. İsayeva Processes of petrochemistry and oil refining, 2022, V.24,№3,p. 413-418.

**Table 11**

**Influence of M-3 composition on dynamic viscosity of Muradkhanli field oil**

| driving tension σ, Pa | dynamic viscosity without and with the addition of 900 g/ton M-3 composition, sPz | | | | | |
|---|---|---|---|---|---|---|
| | $20^0$C | | $10^0$C | | $5^0$C | |
| | commercial oil | oil with additive | commercial oil | oil with additive | commercial oil | oil with additive |
| 18.09 | 652.1 | 281.1 | 938.8 | 391.2 | 1234.3 | 561.0 |
| 21.71 | 396.8 | 165.3 | 625.9 | 240.7 | 678.1 | 308.2 |
| 21.94 | 246.8 | 94.9 | 397.3 | 141.9 | 406.7 | 184.8 |
| 25.34 | 127.8 | 42.6 | 243.4 | 76.1 | 260.8 | 108.6 |
| 27.57 | 78.8 | 30.3 | 135.4 | 42.3 | 177.1 | 73.8 |
| 31.19 | 48.8 | 16.3 | 81.0 | 27.0 | 104.1 | 34.7 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 34.81 | 27.6 | 6.0 | 48.5 | 17.3 | 69.3 | 23.1 |
| 37.04 | 15.2 | 5.8 | 30.7 | 9.0 | 44.2 | 13.0 |
| 48.74 | 13.7 | 3.6 | 19.5 | 5.4 | 31.1 | 9.7 |
| 55.99 | 7.5 | 1.9 | 12.0 | 3.2 | 18.5 | 5.4 |
| 63.23 | 5.6 | 1.2 | 7.5 | 2.5 | 10.6 | 3.5 |
| 70.48 | 3.9 | 0.8 | 5.2 | 1.3 | 6.9 | 2.0 |

formation and composition of oil deposits in high paraffin oil was studied.

**Table 13 shows** the results of deposit formation at different temperatures and at different times for "Cold finger" oil without reagent and with the addition of composition (700 g/t). As can be seen from the table, the amount of paraffin deposits changes inversely proportional to temperature and directly proportional to time. Most of the paraffin deposits are formed at $20^0$C and is 28.7%.

However, at the same temperature the amount of deposits in the oil, to which the composition is added, decreases by 4 times, and the protection effect of the reagent is 76%.

**Table 12**

**Influence of M-3 composition on the dynamic viscosity of Sangachal i oil**

| driving tension σ, Pa | dynamic viscosity without and with the addition of 900 g/ton M-3 composition, sPz | | | | | |
|---|---|---|---|---|---|---|
| | 20 $^0$C | | 10 $^0$C | | 5 $^0$C | |
| | commercial oil | oil with additive | commercial oil | oil with additive | commercial oil | oil with additive |
| 18.09 | 657.1 | 273.8 | 751.0 | 312.9 | 1126.6 | 512.1 |
| 21.71 | 401.6 | 154.5 | 469.4 | 195.6 | 625.9 | 284.5 |
| 21.94 | 218.9 | 78.2 | 287.8 | 110.7 | 375.4 | 170.6 |
| 25.34 | 144.2 | 48.1 | 156.4 | 55.9 | 208.6 | 231.8 |
| 27.57 | 72.8 | 22.8 | 83.3 | 27.8 | 114.6 | 71.6 |
| 31.19 | 40.4 | 12.7 | 52.0 | 5.8 | 69.4 | 43.4 |
| 34.81 | 27.6 | 11.5 | 34.6 | 15.8 | 41.5 | 34.6 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 37.04 | 13.3 | 4.4 | 19.1 | 7.3 | 28.7 | 23.9 |
| 48.74 | 6.7 | 3.0 | 11.4 | 5.7 | 19.5 | 13.9 |
| 55.99 | 3.7 | 1.5 | 6.9 | 2.9 | 13.3 | 8.3 |
| 63.23 | 2.1 | 0.9 | 5.6 | 2.8 | 8.3 | 4.6 |
| 70.48 | 1.3 | 0.3 | 3.0 | 1.1 | 5.2 | 2.6 |

With increasing oil temperature the protection effect of the composition decreases and makes 57% at 30$^0$C, 39% at 40$^0$C and 6.5% at 50$^0$C[8].

As can be seen from table 13, the rate of paraffin deposits formation depends significantly on the oil temperature. Thus, increasing the temperature from 20$^0$C to 30$^0$C causes a decrease in the rate of formation of paraffin deposits by 1.75 times, up to 40$^0$C by 2.3 times and up to 50$^0$C by 3.5 times. In all studied temperature ranges, the highest rate of deposition occurs in the first five minutes of the process.

[8]Адыгезалова, М.Б. Комбинированного ингибитора для нефтегазовой промышленности//Журнал Практика противокоррозионной защиты.- Т.25.- 2020. №2 (25), с.34-44.

**Table 13**
**From high-paraffin oil to the surface of the "cold tube". amount of collected sediment (mass, %)**

| time, minute | temperature, $^0$C | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 $^0$C | | 30 $^0$C | | 40 $^0$C | | 50 $^0$C | |
| | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| 5 | 17.6 | 5.3 | 13.0 | 5.9 | 12.3 | 7.5 | 6.1 | 5.3 |
| 10 | 20.2 | 6.3 | 13.6 | 6.5 | 13.2 | 8.0 | 6.2 | 5.8 |
| 15 | 24.3 | 7.1 | 15.7 | 7.3 | 14.1 | 8.5 | 6.0 | 5.8 |
| 30 | 26.8 | 7.3 | 17.7 | 8.3 | 15.0 | 8.9 | 7.6 | 6.3 |
| 50 | 28.7 | 7.3 | 19.8 | 8.5 | 15.5 | 9.5 | 7.8 | 7.3 |

1-high paraffinic oil without reagent.
2- high paraffin oil with added composition.

As the duration of the process increases, the rate decreases by 3-4 times depending on the temperature.

Due to the effect of the composition the depositon rate in high paraffin oil decreases **(table 14)**. Compared to reagent free oil, the rate is reduced by an average of 2.3 times in the temperature range of 20-30$^0$C.

However, at temperatures of 40-50$^0$C the rate of deposition formation decreases by a factor of 1.5 in reagent free and reactant-added oil, and this also depends on the temperature factor.

**Table 14**

**The rate of sediment formation in crude oil**

| time, minute | 5 | 10 | 20 | 30 | 40 | 50 |
|---|---|---|---|---|---|---|
| $T_{oil}$ $^0$C | sedimentation rate; Дm/Дt, g/min. | | | | | |
| 20 | 3.15 | 1.85 | 1.26 | 1.1 | 1.0 | 0.7 |
| 30 | 2.3 | 1.25 | 0.8 | 0.7 | 0.5 | 0.4 |
| 40 | 1.75 | 1.2 | 0.75 | 0.6 | 0.55 | 0.3 |
| 50 | 0.75 | 0.42 | 0.36 | 0.3 | 0.28 | 0.2 |

**Table 15**

**Rate of sedimentation in composite oil**

| time, minute | 5 | 10 | 20 | 30 | 40 | 50 |
|---|---|---|---|---|---|---|
| $T_{oil}$ $^0$C | sedimentation rate; Дm/Дt, g/min. | | | | | |
| 20 | 1.4 | 0.8 | 0.6 | 0.5 | 0.4 | 0.3 |
| 30 | 0.8 | 0.6 | 0.4 | 0.3 | 0.2 | 0.17 |
| 40 | 0.7 | 0.5 | 0.3 | 0.2 | 0.18 | 0.14 |
| 50 | 0.5 | 0.3 | 0.2 | 0.18 | 0.14 | 0.12 |

It should be noted that in order to choose a more favourable method of controlling asphaltene-resin-paraffin deposits, it is important to know information about the kinetics of deposit formation, as well as the group composition of oil deposits. Table 15 shows the group composition of deposits formed at 30$^0$C.

Depending on the accumulation of oil deposits, the group composition of asphaltene-resin-paraffin deposits does not remain constant and changes. From the analysis of experimental results it is established that the amount of paraffin hydrocarbons in the deposits obtained during the first 5-15 minutes in the initial oil, sharply increases and practically does not change in the subsequent periods **(table 16)**. This dependence affects the deposition rate. On the other hand, the PH/AR ratio in the initial oil increases from 1.2 to 2.2 with time. This indicates that the deposits contain paraffin and paraffin hydrocarbons play a crucial role in the deposition process. However, after application of the composition, the amount of paraffin hydrocarbons in ARPD decreases by 8-13% depending on time compared to the initial oil.

The MKP of paraffin hydrocarbons in deposition samples taken within 30 minutes in crude oil is practically unchanged. However, an increase in the percentage of low-molecular-weight n-alkanes is observed 60 minutes after the start of the test.

**Table 16**

**Group composition of precipitates formed at 30$^0$C temperature**

| sediment sample | time, min | amount of components, % | | | | |
|---|---|---|---|---|---|---|
| | | WFH | PH | resin | asphaltene | PH/ ARC |
| Oil | | 81.1 | 8.7 | 3.1 | 4.1 | 1.2 |
| Primary oil | 5 | 62.27 | 38.8 | 13.3 | 14.3 | 1.6 |
| Oil | | 64.45 | 34.1 | 12.1 | 13.6 | 1.5 |
| Primary oil | 10 | 64.43 | 50.3 | 10.7 | 15.6 | 2.3 |
| Oil | | 64.46 | 43.8 | 13.5 | 12.7 | 1.7 |
| Primary oil | 15 | 69.06 | 50.9 | 11.5 | 9.8 | 2.4 |
| Oil | | 64.66 | 43.8 | 15.8 | 7.6 | 1.9 |
| Primary oil | 30 | 71.26 | 50.2 | 12.1 | 6.9 | 2.6 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Oil | | 64.96 | 46.2 | 19.1 | 6.0 | 1.8 |
| Primary oil | 50 | 66.96 | 54.2 | 16.3 | 8.2 | 2.2 |
| Oil | | 70.26 | 47.3 | 12.1 | 9.7 | 2.2 |

WFH- wide fraction of hydrocarbons
PK-paraffin hydrocarbons
ARC-asphaltene-resin components

Judging from the change in the composition of paraffin hydrocarbons as a function of time, it can be said that the amount of oil droplets is formed firstly by solid n-alkanes and at the last stage by low molecular weight n-alkanes. The obtained result is consistent with the results of group composition of oil deposits. Thus, in the deposition formed at the beginning of the test, the amount of asphaltene components that retain solid paraffin hydrocarbons in the ARPD increases. However, as the amount of solid hydrocarbons decreases, this leads to a decrease in the percentage of asphaltenes in the deposition (within 30-60 minutes). The percentage of MKP of n-alkanes in the deposition produced after 5-50 minutes from the composite oil has different properties. In the first five minutes compared to the initial oil, the mass fraction of oil with low carbon atom number increases, followed by high carbon atom number. During 5-30 minutes of the experiment compared to the oil without the reagent, the added composition causes an increase in the concentration of low molecular weight hydrocarbons and a decrease in the concentration of solid n-alkanes **(table 17)**.

**Table 17**
**Dependence of PH composition in oil sediment on sediment formation time**

| sediment samples | time, min | mass fraction ,% | | |
|---|---|---|---|---|
| | | У$C_{12}$ – $C_{16}$ | У$C_{17}$ – $C_{33}$ | У$C_{12}$ – $C_{16}$ /\|У$C_{17}$ – $C_{33}$ |
| Primary oil | 5 | 27.06 | 73.1 | 0.37 |
| Oil + composition | 5 | 30.9 | 64.9 | 0.48 |
| Primary oil | 10 | 25.6 | 73.9 | 0.35 |

| | | | | |
|---|---|---|---|---|
| Oil + composition | 10 | 28.6 | 70.7 | 0.40 |
| Primary oil | 15 | 25.1 | 75.5 | 0.33 |
| Oil + composition | 15 | 30.8 | 68.2 | 0.45 |
| Primary oil | 30 | 25.5 | 72.7 | 0.35 |
| Oil + composition | 30 | 31.5 | 67.3 | 0.47 |
| Primary oil | 50 | 29.4 | 70.4 | 0.42 |
| Oil + composition | 50 | 13 | 79.5 | 0.16 |

The composition retains a significant part of paraffin hydrocarbons in the oil volume during the specified period. Therefore, their amount is less in the composite oil compared to the reagent-free oil.

The amount of solid hydrocarbons in the deposition formed from the composite oil in 60 minutes is significantly higher than in the deposition collected in 5-30 minutes. The occurrence of this difference in deposition composition is probably due to the reduced ability of the solid hydrocarbons of the composite to retain in the oil volume, causing the solid PHs to move into the deposition together.

It is known that depressor additives used against paraffin deposits in high paraffin oils in countries with developed oil industry are polymeric substances of organic origin. Due to difficulties in obtaining such substances their selling price is rather high. Therefore, the use of depressor additives in pipeline transportation of high paraffin oils is in most cases less favourable than other available methods. However, despite all this, the method of application of depressor additives has such advantages as significant improvement of rheological parameters of high paraffin oils, stability of the effect of the additive on the oil, simplicity of implementation of the process and low capital costs in implementation. For this reason, based on these advantages, it is important to maintain its reliability by significantly reducing the cost of depressor additives and the operating cost of heating high paraffin oil during the application of the additive. On the other hand, as mentioned above, currently available depressor additives are synthesised on the basis of expensive chemicals, and creation of additives on the basis of cheaper raw materials is not foreseen in the near future. For this reason, in order to maintain the advantage of using depressor additives for high paraffin oils, the development of new application technologies aimed at reducing costs and testing them preliminarily in laboratory conditions is one of the most important issues. On the other hand, one of the important tasks solved in pipeline transportation of high paraffin oils is protection against corrosion of the internal surface of pipelines. It should be noted that one of the factors that increase the viscosity of oil during transportation and impede its flow is the corrosion process occurring on the inner surface of the pipeline. Thus, at corrosion process occurring on the inner surface of the pipeline, violation of surface smoothness, formation of corrosion products increase the rate of paraffin deposition process and oil viscosity, as well as lead to the formation of asphaltene-resin-paraffin deposits by playing the role of crystallization centers of paraffin hydrocarbons.

As already mentioned, corrosion loses the smoothness of the internal surface of the pipeline and the surface becomes rough. At the same time adhesion of paraffin deposits to the surface and increase of their quantity become more intensive. Therefore, in order to increase the efficiency of high-paraffin oil utilisation in the collection-transportation system, it is more expedient to solve the problems of paraffin deposition and corrosion simultaneously on the principles of complex approach. In other words, it is necessary to prepare a reagent or a composition having simultaneously a high effect against electrochemical corrosion and paraffin separation. From this point of view for the first time a new composition from different molar ratios of reagents "Difron-4201" and MARZA-1 for different purposes (conventional name M-5) and freezing temperature of high paraffin oil was prepared and the effect on corrosion rate in selected hydrogen sulfide formation water was studied from well No. 1082 of "Bibiaybatneft" OGPD.

According to the results of numerous laboratory tests it was found that the M-5 composition has a higher effect both on corrosion protection and on freezing temperature reduction of a high paraffin oil sample **(figures 7, 8)**.

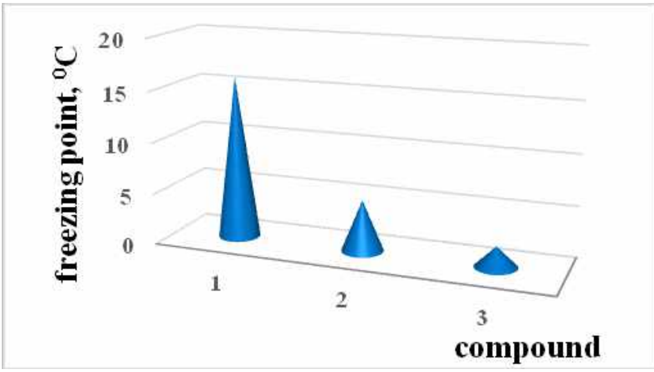


**Figure 7. Effect of M-5 composition on the freezing temperature of high paraffinic oil. 1-oil, 2-oil+900g/t "Difron-4201", 3-oil+M-5 composition**

Thus, if the depressor additive “Difron-4201” reduces the freezing temperature of oil from $+16^0$C to $+5^0$C at a concentration of 900g/t, the new composition reduces the freezing temperature to $+2^0$C.

As it is seen from figure 7, the new composition reduces the corrosion rate in hydrogen sulfide formation waters more than the reagent MARZA-1. Thus, according to the results of numerous laboratory experiments it is established that the new composition has high efficiency of protection against paraffin deposition and corrosion, and also allows to reduce the consumption of depressor additive from 900 g/t to 700 g/t.

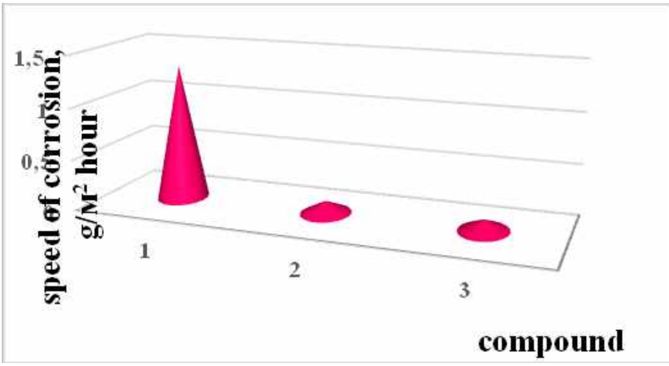


**Figure 8. Effect of M-5 composition on corrosion rate in hydrogen sulphide formation water. 1-formation water, 2-formation water+10 mg/l MARZA-1, 3-formation water+M-5 composition**

The technology of application of the new composition prepared in laboratory conditions to high paraffin oils in mining conditions during pipeline transportation is developed and a new technological diagram for implementation in mining conditions is developed.

When applying the new composition to high paraffin oils it is proposed to use the following technological equipment:

- a tank for preparing the additive solution;
- a tank for storage of the additive solution;
- a tank for storage of MARZA-1 reagent,
- a tank for storage of solvent;
- dosing tank;
- metering pump.

Tanks should be scaled and equipped with a heater.

Technological parameters of the devices should be as follows.

- pressure - atmospheric pressure in tanks;
- temperature of additive solution-35-40$^0$C in tanks;
- oil temperature -50-60$^0$C when adding the additive

**Figure 9 shows** a simple technological diagram proposed for performing the process of injection of oil moving through the pipeline of multifunctional new composition.

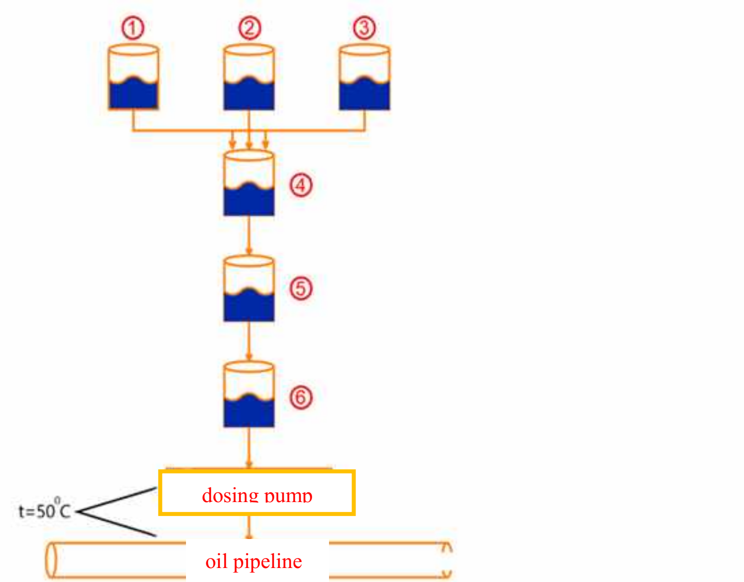


**Figure 9. The principle technological scheme of applying the M-5 composition to high-paraffin oil. 1-capacity for "Difron-4201" additive; capacity for reagent 2-MARZA-1; 3- capacity for solvent; 4-mixer capacity; 5-dosing capacity**

The proposed technology provides simultaneous solution of two main problems -paraffin deposition and internal surface corrosion of equipment causing complications in systems of collection and transportation of high paraffin oils, and also provides high economic efficiency.

## RESULTS AND PROPOSALS

1. As a result of the experimental studies conducted, it has been established that complications arising in the system of well collection and transportation of various types of crude oil are primarily caused by anomalous changes in the rheological

parameters and other quality indicators when mixing "undesirable" dispersed oil systems that do not adhere to the generally accepted rule of additivity.

2. For the first time, through multiple studies using the rapid method developed based on the "drop test," the possibility of predicting the limit of water content in types of crude oil has been determined by analyzing the dynamics of changes in the water-dispersing capacity of these oils.

3. Based on laboratory research, taking into account the factor of incompatibility, it has been established that adherence to the principle of rational blending is necessary when mixing oils to enhance the efficiency of preparing oil mixtures for transportation.

4. It has been demonstrated that, at a certain limit of dissolving capacity, and depending on the ratio of the constituent components, non-additive characteristics of the dissolving capacity for the precipitation of asphaltenes from crude oil are observed.

5. It was found that the interaction of oils during mixing can lead to the formation of various blockages due to anomalous changes in practically important parameters, such as viscosity, freezing point, volume, and others.

6. It has been shown that, based on the transportation data of rheologically complex oil mixtures, the rheological properties of these mixtures (such as relaxation time and viscosity) can be diagnosed.

7. Experimental results indicate that as the water saturation of oil emulsions increases, the consumption of demulsifier reagents during their demulsification decreases. It has been established that the consumption of the applied demulsifier can be significantly reduced without compromising the effectiveness of the dehydration process of crude oils.

8. It is established that bactericidal-inhibiting reagents MARZA-1 and MARZA-2, which can be produced on the basis of local raw materials, and compositions of P series prepared on their basis, have high protection and bactericidal effect due to reduction of corrosion rate to minimum in optimal layers of 10mg/l.

9. As a result of experimental studies it has been established that the optimal concentration of the depressor additive “Difron-4201” significantly affects the freezing point, the process of paraffin deposition, the ultimate shear stress and effective viscosity, as well as structural and mechanical properties of paraffin oil at high temperatures.

10. When studying the effect of the new composition M-5 on the freezing point of high paraffin oil and corrosion rate in hydrogen sulfide formation water in comparison with the components “Difron-4201” and MARZA-1 it was established that the freezing point decreased by 8 times, and the corrosion rate decreased by 132.6 times.

11. In the course of studying the effect of high paraffin oil and the change of “Cold finger” temperature on the group composition of paraffin deposits it was found that the decrease in oil temperature leads to a decrease in the amount of resins and asphaltenes, as well as the temperature of oil and “Cold finger” to temperatures close to the freezing point of oil, and its decrease causes a change in the composition and molecular-mass distribution of n-alkanes in oil deposits due to the separation of low-molecular-weight paraffin hydrocarbons.

12. Experimental studies have shown that when the depressor additive “Difron-4201” is added to high paraffin oil, the percentage of paraffin hydrocarbons with carbon atoms $C_{17}$-$C_{40}$ in the deposits decreases and the number of n-alkanes increases with a lower value of the molecular weight, while the number of resins and asphaltenes increases, and the reduction occurs. Such changes lead to improvement of rheological properties of oil.

13. From the analysis of the results obtained from the dependence of the deposit formation rate on time, it is established that the highest rate is fixed in the first minutes in all temperature intervals, and the amount of oil deposits in the first moments is formed at the expense of solid n-alkanes and, eventually, low molecular weight n-alkanes. It was found that under the effect of the new composition M-4 the rate of deposit formation in oil decreases.

The reason for the decrease in the rate is that the composition retains solid paraffin crystals in the oil volume, which in turn leads to a change in the group composition of the deposition.

14. The results of numerous experiments conducted in laboratory conditions have shown that the new compositions K-5 and D-5 have high efficiency of protection both from salt deposition and from corrosion processes.

15. For the first time the technology of application of multifunctional composition M-5 during transportation of high paraffin oils in mining conditions against internal surface corrosion and paraffinisation process has been worked out, as well as wide application of new compositions against complications that may occur in the system of collection and transportation of high paraffin oils in mining conditions.

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**1.** Исмайылов, Г.Г., Проявление «несовместимости» в нефтяных смесях / Г.Г. Исмайылов , Р.Л. Зейналов , М.Б.Адыгезалова // Теоретическая и прикладная механика,-2016.Т.11.№-4,-с.114-117.

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**In the works carried out with co-authors, the personal work of the author:**

[9], [13], [14], [19] – performed independently.

[10], [16], [18], [20], [21], [22], [23], [24], [27], [30] - statement of the problem, research work and analysis of the results.

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