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STUDY OF THE EFFECT OF DEMULSIFIERS ON THE GROUP COMPOSITION OF TRANSPORTED AZERBAIJANI CRUDE OILS

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Muradkanly,Buzovna,Bulla,viscosity, demulsifiers, crude oil emulsion.

A B S T R A C T

The article presents the results of the study of oil dehydration processes in the Muradkanly, Bulla and Buzovna. The results of experiments on selection of demulsifiers for oil dehydration are presented, the choice of optimal demulsifiers, using which a representative oil sample with a residual water content of 0,1 wt % is developed, is justified.The most effective demulsifiers are selected on the basis of laboratory studies taking into account the properties of raw materials and are specified during experimental and industrial tests on the current technology. Crude oil treatment temperature is increased, light oil fractions are converted into gaseous phase, which entails increase of gas quantity, increase of oil losses from gas entrainment and decrease of commercial oil output. In the article, the application of new types of emulsifiers in the future is considered more appropriate..

1. INTRODUCTION

During the development of oil fields, oil production is carried out from associated formation waters. As development time increases the water content of the well products is also growing. This is often It is connected with the commissioning of reservoir pressure maintenance systems. As the water content of the water-oil emulsion increases, a problem arises its further discharge in order to prepare oil to commercial conditions for subsequent transport. To do this, oil must be prepared for the purpose of achievement of quality, according to the regulatory documents on content: associated petroleum gas, commercial water, mechanical impurities and chloride salts. With the increase in watering of oil field products appear additional difficulties in primary oil preparation, due to forming water-oil emulsions with high aggregative stability; high viscosity.

Water-oil emulsions are polydisperse systems consists of globules of different diameters. Oil emulsion viscosity-non-additive property.

$$\mu_e \neq \mu_o + \mu_w$$

where e $\mu_e$emulsion viscosity; $\mu_o$oil viscosity; in$\mu_w$viscosity of water.

The viscosity of the water-oil emulsion is not subject to the Newton law and depends on many parameters, such as: type of water-oil emulsion, emulsion temperatures, oil and commercial water content, size of globules dispersed medium.

In addition, dissolved gases, suspensions and mechanical impurities, unstable colloidal systems, can also contain calcium and magnesium bicarbonates. The latter are often called salts temporary stiffness, due to

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the possibility of their destruction during heating according to diagram:

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O,$$
$$Mg(HCO_3)_2 \rightarrow MgCO_3 + CO_2 + H_2O$$

carbon dioxide is released and insoluble precipitate is formed. Insoluble carbonate precipitates reduce working section of field piping, which should be taken into account when designing objects. Sulfur, phosphorus and other compounds are able to dissolve in oil, while the formation of complex compounds.
(Goroshko 2003).

2. LITERARATURE REVIEW

Natural emulsion stabilizers include those contained in oil asphaltenes, resins and paraffins.

Components of molecules of surfactants are polar group and carbon radical. One of the main criteria for distinction emulsions are disperse phase concentrations: slightly concentrated, concentrated, highly concentrated. (Sorokin et al. 2007). Low-concentrated characterized by a dispersed phase content of not more than 20%; concentrated from 20 to 74% and highly concentrated more than 74%. Water-oil emulsions of the type age over time water in oil, which is the result of an increase in adsorption on interfacial limits of emulsifiers product water and increase of strength and thickness emulsifier layer (Mineev et al. 2004). Possible collisions of commodity water globules at aging of the emulsion does not lead to fusion, which is caused by the formation of them surfaces of strong hydrophobic films. To eliminate this phenomenon it is necessary to break the hydrophobic film and then replace it with hydrophilic. Commercial, unlike fresh water, is able to form emulsions with greater aggregate resistance. (Persiyantsev, 2000).

Usually on at wellheads, highly dispersed emulsions of the reverse type are formed according to cause of adsorption of natural stabilizing materials on interfacial surfaces the globe.

The intensity of ARPD formation in the transport system, collection and preparation of oil is affected by a number of factors, the main of which are pressure decrease in the bottom area and associated disturbance of the hydrodynamic equilibrium of the gas-liquid system; intensive gas emission; decreasing of temperature in the formation and wellbore; changing a speed of the gas-liquid mixture and its separate components; composition of hydrocarbons in each phase of the mixture; the ratio of the volumes of each phases (oil-water) (Tronov, 1970; Kayumov et al., 2006). With increasing speed of oil, intensity of the deposits first increases, which explain the increase in flow turbulence and, consequently, an increase frequency of formation and detachment of bubbles from the surface of the tube, floating the suspended particles of paraffin and asphaltic substances (ARS) (Sorokin et al. 2009). In addition to these main factors, the intensity of the paraffinization of pipelines during the transportation of flooded wells production may be affected flooded production (Nebogina et al. 2008) and the pH of the formation water (Goroshko, 2003).

ARPD, formed in different wells differ from each other in chemical composition depending on the hydrocarbon composition group of the oils produced at these wells. But with all the possible variety of compositions for all deposits is established that the content of asphaltic and paraffinic components will be the inverse: the more paraffin, the proportion of asphaltic substances, the less paraffin will be contained, which in turn, are determined by their ratio in the oil. This feature is due to the nature of the mutual influence of paraffins, resins and asphaltenes in oil until the moment of their allocation to deposits (Sharifullin, 2006).

As experimental and practical studies have shown, before the paraffin is released on the surface of the downhole equipment, its crystals transform their structures so that, by joining together, they organize a continuous lattice like a wide band. In this form, the adhesive properties of paraffin increased many times, and its ability to adhere to solid surfaces is significantly intensified. However, if oil contains a sufficiently large amount of asphaltenes (4-5% and higher), their depressor effect is affected. The formation of a continuous lattice does not occur, since asphaltenes themselves act as germinal centers and as a result of this, the release of paraffins on the surface significantly weakened.

Resin, because of its structure, on the contrary, create conditions for forming banded aggregates of paraffin crystals and their adhesion to surfaces and by its presence prevent the effects of asphaltenes on the paraffin, neutralizing them. Like asphaltenes, the resin affects the paraffin oil saturation temperature, but the nature of this influence is the opposite: with the growth of their mass content in the oil saturation temperature increases (if, for example, the presence of resins increase from 12% to 32%, the saturation temperature will increase from 22 ºC to 43 ºC) (Baimukhametov, 2005). Saturation temperature of paraffin oil is directly dependent on the mass concentration of the resin and in the reverse concentration of asphaltenes. Consequently, the process of paraffin formation depends on the ratio of asphalt (A) and resin (R) compounds in the composition of oil. As the parameter A/R increases, the saturation temperature will decrease - associates of asphaltenes in oil are less stabilized due to a lack of stabilizing components (resins), which leads to a decrease in the saturation temperature, the crystallization of paraffins of such oils is suppressed by associates, and paraffin deposition does not occur; at small values of A/C on the contrary, the saturation temperature increases -

asphaltenes have no effect on paraffin formation, paraffin is freely released from oil (Goroshko, 2003).

The mechanism of "paraffinization" understood as the set of processes leading to the accumulation of a solid organic phase on the surface of the equipment. In this case, the formation of deposits can occur either due to the adhesion to the surface of already prepared, solid particles formed in the flow of particles, or due to the appearance and growth of crystals directly on the surface of the equipment (Zevakin et al., 2008). The probability of fixation paraffin particles on the surface of equipment under the conditions of an operating well is practically negligible- paraffin particle can be fixed on the equipment wall, but on the condition that, initially, it will get stuck on it mechanically (Sharifullin et al., 2006). During transportation of oil by pipeline, the following processes occur. Oil enters the pipeline and contacts the cooled metal surface. This gives rise to a temperature gradient directed perpendicularly to the cooled surface toward the center of the flow. Due to flow turbulence, the oil temperature in the volume reduced. In this case, two processes proceed in parallel; the isolation of n-alkane crystals on a cold surface; crystallization of n-alkanes in the volume of oil. Practically important is not the release of paraffins, but their deposition on the surface of pipes and equipment in the direction of heat transfer (Sergienko, 1959). Such deposits formed under a number of conditions: the presence of high-molecular hydrocarbons in the oil, primarily the methane series; reduce the flow temperature to values at which there is a loss of the solid phase; the presence of a substrate with a lower temperature, on which hydrocarbons crystallize and with which they are so firmly entangled that the possibility of stripping deposits by flow at a given technological regime is virtually eliminated. Studies of recent years have reliably established that there is no direct relationship between the content of paraffin and the intensity of its deposition (Ibragimov et al., 1986). The absence of such a connection is due, first of all, to a significant difference in the composition of solid paraffin hydrocarbons, the difference in the proportions of aromatic, naphthenic and methane compounds in the high-molecular part of hydrocarbons, which is not determined by standard methods of studying the oils. Meanwhile, it is proved that the differences in the composition of solid hydrocarbons that mainly predetermine the features of formation of paraffin deposits. The higher the content of hydrocarbons with branched aromatic, naphthenic and iso-alkane structures, the less strong are the paraffin deposits, because this type of connection has an increased ability to retain crystalline formations of a liquid mass. Hydrocarbons of the methane series - especially high-molecular paraffins, on the contrary, are easily released from the solution with the formation of dense structures. It is clear that the loose and semi-liquid crystalline deposits can relatively easily be removed by the natural flow of liquid during the operation of the wells without causing any complications, and conversely, dense and strong deposits formed mainly from n-alkanes create serious complications in liquidation of which consumes a lot of resources and labor (Petrova et al., 2005).

Oil dispersed systems are classified as a class of colloids in which asphalt-resinous substances is dispersed in the maltten environment. It is obvious that the physico-chemical and technological properties of oils are largely due to intermolecular interaction in the systems "asphaltene-resin" and "maltenes-resin-asphaltenes."

As a rule, the structure of resins and asphaltenes considered in the form of "sandwich" structures, which are parallel napthenoaromatic layers, connected together by the formation of complexes with charge transfer. It is generally accepted that resins and asphaltenes are paramagnetic liquids, and oil and oil products thermodynamically stable paramagnetic solutions. Asphaltenes are a combination of many associates, depending on the degree of homolytic dissociation of diamagnetic particles. The change in the concentration of paramagnetic resins and asphaltenes in oil is associated with a change in the structure of combinations of associates (Ibragimov, 2003): Chemical and physico-chemical processes involving ARS has a collective nature. Asphaltenes are not individual components, but form associative combinations in the center of which stable free radicals are located. The appearance of a solvate shell from diamagnets is an indispensable condition for the existence of paramagnetic particles in solutions. The formation of solvate shells weakens the attraction forces of paramagnetic molecules and prevents their recombination as a result of thermal movement. Resins consist of diamagnetic molecules, some of which are capable of transition into an excited triplet state or undergo homolysis. Therefore, resins are a potential source of asphaltenes. The properties of ARS are not determined by elemental composition, but the degree of intermolecular interaction of the components. The intensity of ARPD formation depends on the prevalence of one or several factors that can vary over time and depth, so the amount and nature of the deposits are not constant.

Thus the knowledge of the composition of ARTD is of practical importance for determining the optimal methods of controlling them, in particular, for the selection of chemical reagents. This selection is often carried out on the basis of the type of ARTD (Sharifullin, 2006).

3. RESEARCH METHODOLOGY

We analyzed the physical and chemical properties of Azerbaijani crude oils. Physicochemical properties of emulsions of some Azerbaijani crude oil deposits are presented in table 1.

Difference in diameters of globules of commercial water and different characteristics streams result in dispersal and emulsification during mining water-oil emulsion is caused by viscous and dynamic forces. The formation of the water-oil emulsion occurs during production and transportation of oil. Often, water-oil emulsions are different in their own way properties and physicochemical properties.

Table 1. Physicochemical properties and emulsions of some deposits of Azerbaijan.

Parameters	Names of crude oils		
	Muradkanly field	Buzovna field	Bulla field
Density at 20 ^{0}C, kq/m^3	876,8	991,6	973,4
Waters contents, %	41	69	36
Mechanical Impurity, mas. %	5,2	5,9	4,7
Resins, mas. %	18,3	10,8	10,27
Asphaltens, mas. %	4,82	0,13	0,23
Paraffins, mas. %	6,21	2,13	13,34
Density water phase, kq/m^3	1123	1254	1178
Kinematic viscosity at 20 ºC, mm^2/sec	83,1	8,73	15,76

Currently, the processes of destruction of water-oil emulsions are divided into the following types: settling under the action of gravitational forces; coalescing filtration; use of centrifugal forces; electrical impact on globules of water-oil emulsion; increasing the temperature of the water-oil emulsion; use of the effect of intrauterine demulsion; magnetic processing. In the petroleum industry for separation of water-oil emulsion, as generally, capacitive equipment is used in the form of horizontal settling tanks. (Sharifullin et al., 2006).

During operation time of oil fields changes physicochemical composition of water-oil emulsion. This is influenced by many factors such as: hydraulic fracturing, injection of chemical reagents, increasing watering of well products. Modern demulsifier reagents for the preparation of highly viscous oil is usually developed through the creation of new composite demulsifying compositions. Composition of composite mixtures in this case, previously known substances used in various in the fields of science and production - in chemistry, petrochemistry, oil field training, oil refining and other related industries, and also the newly synthesized compounds to which the complex is reported functional features that guarantee the identification of two, three and even several surface-active properties. Use of demulsifiers shows that the use of composites occurs many times more effective than using the compound in pure form (Ismayilov et al. 2016). The object of the study was a commercial water-oil emulsion Muradkanly field. Physicochemical characteristics are given in table 2.

The investigated oil is characterized by a large content of natural emulsifier-stabilizers of water-oil emulsion - resins and asphaltenes. A commercial water-oil emulsion was also used Bulla field. Physicochemical characteristics are given in the table-2. The investigated oil is characterized by a large content of natural emulsifier-stabilizers of water-oil emulsion – resins (Usubaliev et al., 2015).

Table 2. Physical and chemical characteristics of Muradkanly and Bulla field emulsion

Parameters	Muradkanly field, value	Bulla field, value
Density at 20 ^{0}C, kq/m^3	947,3	973,8
Viscosity at 20 ºC, mP·sec	2157,3	2445,8
Waters contents, %	41	36
Resins, mas. %	16,9-18,1	8,1-9,3
Asphaltens, mas. %	3,7-4,5	0,12-0,18
Paraffins, mas. %	3,9-5,8	11,7-12,9
Pour point,ºC	+9	+12

The reagents used in the study are presented in table-3. Dissolvan-4411 - non-ionic demulsifier, manufactured in Germany. Composition: ethylene and propylene oxide dissolved in methanol (Nurullayev, 2016).

Table 3. The main indicators of the demulsifier Dissolvan-4411

Appearance	Yellowish liquid
Density at 20 ^{0}C, kq/m^3	950
Pour point,ºC	- 36
Viscosity at 20 ºC, mP·sec	25
Flash point (closed cup), ºC	11
The pH value (1% in distilled water at 20 °C)	9,0

Based on test results selected by demulsifiers for which optimal dosages. To determine the optimal dosage, a series of tests is carried out with the selected demulsifiers. The analysed emulsion is dosed a demulsifier with at least four dosages, such that at least at one dosage, ensure separation of emulsion into stages cold dehydration till residual water content within 5-10%, on deep dewatering stages - about 1%. As demulsifier of comparison, demulsifier is used, which is used for field preparation of this oil. Based on test results selected by demulsifiers for which optimal dosages. To determine the optimal dosage, a series of tests is carried out with to assess the effectiveness of different types of mixing and coalescing elements were performed by multifactorial experiments in laboratory conditions (Nurullayev et al., 2016).

4. RESEARCH RESULTS AND DISCUSSION

Speed and duration of rotation of elements varied in given ranges of factors and boundaries of study areas, presented in table 4.

Table 4. Factor variation intervals and area boundaries research in experiments with mixing elements

Factors experiments	Min. value factor	Max. value factor
Speed V, (turns, min^{-1}),	133	225
Time t, s	90	540
Water content emulsions,%	41	36
Temperature,°C	60	60
Settling time emulsions after processings, h	3	3
Dosage and grade deemulgator	Dissolvan-4411, 200-600 g/t	Dissolvan-4411, 200-600 g/t

The mixing element in the form of a cut-out sheet was fixed in a stirring device by which the speed is set; duration of its rotation.

Volume of deemulsifier solution dosed into emulsion suspension is calculated by formula:

$$V = \frac{m \times (100 - w) \times Q}{1000}$$

where V- Volume of deemulsifier, (mkl);
m - is emulsion suspension, qr (ml);
W-initial average watering of emulsion, %;
Q-preset dosage of demulsifier, qr/ton;
Depending on the water content of the oil emulsion, the dosage is adjusted from 40 to 200 g/t. (Usubaliev et al. 2015; Nurullayev 2016).

Table 5. Influence of quantity of deemulgator on efficiency of branches of water at 20 ^{O}C

Crude oil	Reagent flow rate, g/t	Amount of released water,% vol., per time, h			
		0,5	1,0	1,5	2,0
Muradkanly	200	4,0	8,2	12,1	12,1
	400	4,2	8,4	16,9	18,3
	600	5,8	13,0	32,2	40,9
Bulla	200	7,1	12,3	22,3	25,2
	400	7,8	13,5	24,5	27,1
	600	8,1	14,5	25,3	30,1

For maximum dewatering of emulsion with water content of not more than 1% in laboratory conditions it is necessary to provide the following: preliminary heating of emulsion with dosed demulsifier to 40-60 ° C; vigorous mixing in a rotary mixer for 0.5 h at 750-1000 rpm; settling in dividing funnel. The results of the experiment are shown in the table 5.

Figures 1 and 2 show the emulsifier for Muradkhanli and Bulla oils. As can be seen from the figure, the effect of the emulsifier depends on the dry composition of the crude oils.

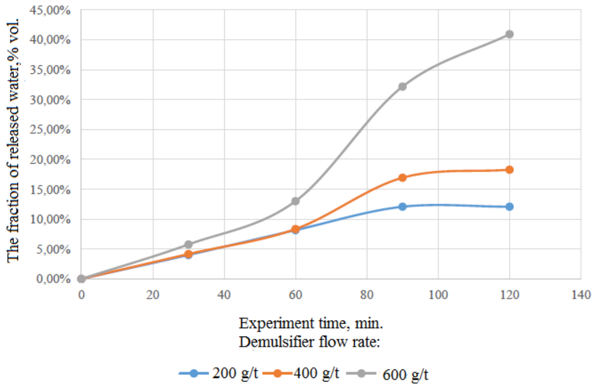

Figure 1. Efficiency of Dissolvan-4411 demulsifier from Muradkanly oil at 20 °C

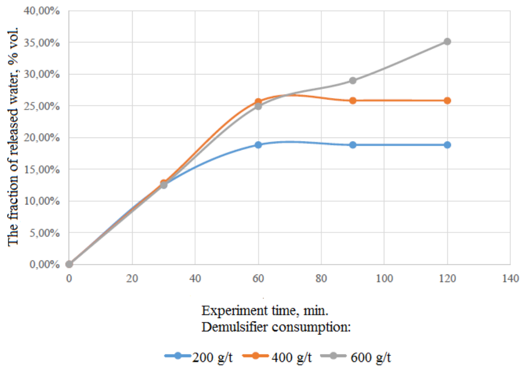

Figure 2. Efficiency of Dissolvan-4411 demulsifier from Bulla crude oil at 20 °C

5. CONCLUSION

Water-oil emulsions are very stable systems, and as a rule, do not delaminate under the influence of gravity alone. Therefore, in order to accelerate the process of breaking the emulsion, along with the sludge, it is simultaneously subjected to other measures aimed at enlarging water droplets, increasing the density difference, and reducing the viscosity of oil. In the experiments described in the article, such measures are: the introduction of a demulsifier and the heating of the emulsion. It has been shown that the most efficient separation occurs when the oil emulsion is preheated. Methods for dehydration of oil in laboratory conditions presented in the work can be used to prepare samples of dehydrated oil for further studies of its physicochemical properties: fractional and hydrocarbon composition, density, sulfur content, analysis of gasoline fractions obtained from oil, kerosene, diesel fuel, fuel oil and their practical application.

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