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REOPYSICAL-CHEMICAL PROPERTIES AND BEHAVIOR OF A PHASE FROM CONTAINING WAX, ASPHALTENE, REZIN OF CRUDE OIL

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ABSTRACT

Modern views on a state problems are considered the wax, asphaltene, rezin of deposits (WARD) in the oil-field equipment and possible methods of her decision. In work, the major factors influencing on are listed formation of WARD. The special attention, is paid to a group chemical composition of initial raw materials and mutual influence of separate high-molecular components of oil on structurization in oil system at low temperatures. Influence of structural and group composition of oil on the formation mechanism, structure and WARD properties is, shown. The short list of the existing methods of prevention and removal of WARD from the oil-field equipment is given. The chemical methods connected with use of various additives, reagents and eliminators are in more detail considered. The short characteristic of the main classes of the chemicals used at a solution of the problem of prevention and removal of WARD is given. It is, shown that for the choice most ways of prevention and removal of deposits, effective from the chemical point of view organic substances receiving adequate idea of structure is necessary, properties and structure of initial oil and the formed deposits. Below the wax appearance temperature these aggregates evidently act as cementing species in extended networks of wax crystals. The optical absorption measurements revealed an increase of a vertical concentration gradient in the samples, heated to the above specific temperatures, which may be indicative of some phase separation in the studied crude oil.

KEYWORDS: Crude oil; wax, asphaltenes; nanocolloids; fluid; anomalies.

1. INTRODUCTION

Development of oil industry of Russia at the present stage is characterized by decline in quality of a source of raw materials. In overall balance of the developed fields the fields which have entered a late stage of development prevail and, as a result, considerable deterioration in their structure, increase in a share of hardly removable reserves of oil, flood of layers and production of wells is observed. So at production paraffinic a crude oil serious problem, defiant complications in work of wells, the oil-field equipment and pipeline communications, education the wax, asphaltene, rezin of deposits (WARD) which formation leads to decline in production is system and overall performance of pump installations. Formation of emulsions at an exit from a well together with the accompanying reservoir water strengthens draft education.

It is known that fight against WARD in processes of oil production is conducted on two to the directions: prevention (or prevention) deposits; removal already the created deposits. The choice of optimum ways of fight from asphalt pitch paraffin deposits and efficiency of various methods depends on many factors, in particulars, from a way of oil production, the thermobaric mode of a current, structure and properties of the got production. Despite a big variety of methods of fight against WARD, problem it is still far from permission and remains to one of the most important in domestic oil-extracting branch [1-5].
The factors influencing formation of WARD.

Intensity of formation of WARD in system of transport, collecting and preparation of oil is influenced by a number of factors, basic of which are: pressure decrease in the field of a face and the violation of hydrodynamic balance of gas-liquid system connected with it; intensive gas emission; reduction of temperature in layer and a trunk of a well; change of speed of the movement of gas-liquid mix and its separate components; composition of hydrocarbons in each phase of mix; ratio of volumes of phases (oil-water).

The roughness of walls and existence in system of solid impurity promote also allocation from paraffin oil in a firm phase. Except the specified major factors on intensity of a parafinization pipelines at transportation of the flooded production of wells water content of production and size pH reservoir waters can exert impact, and influence of these factors is ambiguous and can be various for different fields [6-8].

2. LITERATURE REVIEW

Influence of a chemical composition of oil on process of formation of WARD.

WARD formed in different wells differ from each other on a chemical composition depending on group hydrocarbonic structure crude oil, got on these wells. But at all possible variety of structures for all deposits it is established that contents in them asphaltic and paraffin components will be the return: the more in WARD the share of asphalt of resinous substances, the less will contain paraffin that in turn will be defined by their ratio in oil. Such feature is caused by nature of mutual influence of the paraffin, pitches and asphaltene, which are in crude oil until their allocation in deposits.

WARD formed in different wells differ from each other on a chemical composition in As have shown pilot and practical studies before paraffin is emitted for surfaces of the borehole equipment, his crystals make transformation of the structures so that, connecting among themselves, will organize a continuous lattice like a wide tape. In such form adhesive properties of paraffin amplify many times over, and his ability to stick to firm surfaces considerably is intensified.

However if oil contains rather large number of asphalten (4-5% and above), their depressor action affects. Asphaltene can to act as the germinal centers. Paraffin molecules participate in a sokristallization with alkils chains of asphaltene forming dot structure. That is formation of a continuous lattice doesn't happen. As a result of such process paraffin is redistributed between a set of the small centers and release of paraffin on a surface is significantly weakened.

Pitches, owing to the structure, on the contrary, promote creation of conditions for formation of tape units of paraffin crystals and their sticking to a surface and the presence interfere with impact of asphaltene on paraffin, neutralizing them. As well as asphaltene, pitches influence the size of temperature of saturation by oil paraffin, however nature of this influence opposite: with growth of their mass contents temperature of saturation increases in oil (if, for example, to increase presence of pitches from 12 to 32%, then temperature of saturation will increase from 22 ºC to 43 ºC).

Crude oil saturation temperature paraffin is in direct dependence on mass concentration of pitches and in the return from concentration of asphaltene.

Therefore, process of a, education paraffin depends on a ratio asphaltene (A) and resinous (R) connections as a part of crude oil.

With increase in the A/R parameter temperature of saturation will decrease – associates of asphaltene in crude oil are less stabilized because of a lack of the stabilizing components (pitches). As leads to reduction of temperature of saturation, process of crystallization of paraffin such crude oil is suppressed with associates, and adjournment of paraffin doesn't happen; at the A/R small values on the contrary, saturation temperature increases – asphaltene don't make impact on a paraffin education, paraffin is freely emitted from crude oil. Mechanism of formation of WARD.

The parafinization mechanism is understood as set of processes, leading to accumulation of a firm organic phase on an equipment surface. At the same time, formation of deposits can happen or due to coupling with a surface of already ready, formed in a stream particles of a firm phase, or due to emergence and growth of crystals directly on a surface equipment.

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The probability of fixing of particles of paraffin on an equipment surface in the conditions of the operating well is almost insignificant – the paraffin particle can be fixed on an equipment wall, but provided that originally she will get stuck on her purely mechanically.

At transportation of oil on the pipeline the following processes proceed. Crude oil comes to the pipeline and contacts to the cooled metal surface. At the same time there is a gradient of temperatures directed perpendicular to the cooled surface to the center of a stream. Due to turbulization of a stream oil temperature in volume decreases. At the same time two processes in parallel proceed: allocation of crystals of n-alkanes on a cold surface; crystallization of n-alkanes in volume of crude oil.

Release of paraffin not in itself, but their adjournment on a surface of pipes and the equipment in the direction of a heat transfer is almost important. Such deposits are formed at observance of a number of conditions: existence in crude oil of high-molecular hydrocarbons, first of all metane row. Decrease in temperature of a stream to values at which there is a loss firm phase; existence of a substrate with the lowered temperature on which hydrocarbons crystallize and to which they are so strongly linked that a possibility of failure of deposits by a stream at the set technological mode it is practically excluded. By researches of the last years it is authentically established that direct link between the content of paraffin and intensity of his adjournment isn't present. Lack of such communication is caused, first of all, by essential distinction of structure solid hydrocarbons – paraffin, namely, distinction in ratios of aromatic, naphthenic and metane connections in high-molecular part hydrocarbons which at standard methods of research of crude oil isn't defined.

Meanwhile, it is proved that distinctions as a part of solid hydrocarbons generally and predetermine features of formation of paraffin deposits. The content of hydrocarbons with branched structures aromatic is higher, naphthenic and the izoalkans, the less strong appear paraffin deposits as connections of this kind possess the increased ability to keep crystal educations liquid weight.

Hydrocarbons of a metane row – especially high-molecular paraffin, on the contrary are easily allocated from solution with formation of dense structures. It is clear, that friable and semi-fluid crystal deposits rather easily can be removed with a natural stream of liquid in use of wells, without causing any complications, and, on the contrary, the dense and strong deposits created generally from n-alkanes create serious complications for which elimination many means and work are spent. Structure and WARD properties.

Usually under the term paraffin unites all hydrocarbonic part deposits. Though in this part n-paraffin (metane hydrocarbons, or alkanes with a direct chain), in it contains naphthenic (cyclanic) and aromatic hydrocarbons with long alkils chains in smaller quantity. Structure of paraffin hydrocarbons microcrystalline, naphthenic with long alkils radicals form macrocrystalline structure.

The pitches which are a part of WARD are presented first of all by the neutral pitches emitted by means of silica gel and chloroform (four-chloride carbon). These are semi-fluid, sometimes semisolid dark brown or black color of substance. The relative density of pitches is from 0,99 to 1,08 g/cm^3. The molecular mass of pitches can reach 1200. They are well dissolved in all oil products and organic solvents, except for ethyl and methyl alcohols. On average pitches contain up to 15-17% of oxygen, sulfurs, nitrogen.

With increase of molecular mass of pitches the content of oxygen, sulfur and nitrogen decreases. A basis of structure of molecules of pitches is the flat condensed polycarbocyclic grid consisting mainly from benzene rings. This structural grid can contain naphthenic and heterocyclic rings (five and six-membered). The peripheral part of the condensed system of WARD pitches is replaced on hydrocarbonic radicals (aliphatic, cyclic and mixed). The nature and the number of these deputies strongly depends on properties of oil. Deputies can include functional groups (-OH, -SH, $-NH_2$, =CO, etc.). When heating to 260-350 °C of pitch begin to be condensed and turn into asphaltene.

With increase of concentration in pitch solution, on the one hand, slow down growth of crystals, and with another, – promote deformation of a surface of crystals and emergence on them the new centers of crystallization. Extent of manifestation of this or that tendency is defined by the nature of pitches and causes the corresponding form and the size of crystals of solid hydrocarbons.

On modern representations of an asphaltene are the polycyclic aromatic strongly condensed structures with short aliphatic chains in the form of dark-brown amorphous powders. Density of asphaltene is slightly more than unit. In the asphaltene contains (% of masses.): 80... 86% of carbon, 7... 9% of hydrogen, to 9% of sulfur and oxygen, and to 1,5% of nitrogen. Asphaltene don't crystallize and can't be divided into individual components or narrow fractions. When heating higher than 300-400 ºC they don't melt, and decay, forming carbon and flying products. Asphaltene are the heaviest and polar components of crude oil. Asphaltene are very inclined to association, their particles of a polidispers and therefore molecular weight depending on a method of definition can fluctuate from 2000 to 4000 a.e.м. Asphalthen are considered as products of consolidation of pitches. The particle of asfalten represents itself a micelle which kernel consists of the high-molecular polycyclic condensed connections of mainly aromatic character, and the adsorptive layer is formed by low-molecular surface-active connections, including pitches and naphthenic acids which together with aliphatic components of oil, form a solvate cover of a micelle [9-11].

3. RESEARCH METHODOLOGY

Apparently, still nobody seriously thought that the properties of micellar colloids attributed to asphaltene carried them to a new class of disperse systems. Namely, the disperse systems consisting of the firm particles dispersed in a liquid phase are colloidal suspensions whereas systems in which the disperse phase is formed on reversible process an education micelle represent associative colloids. Associative, or micellar colloids, as a rule, have a rich phase variety: from the elementary isotropic micellar phases to elaborate supramolecular nanostructures.

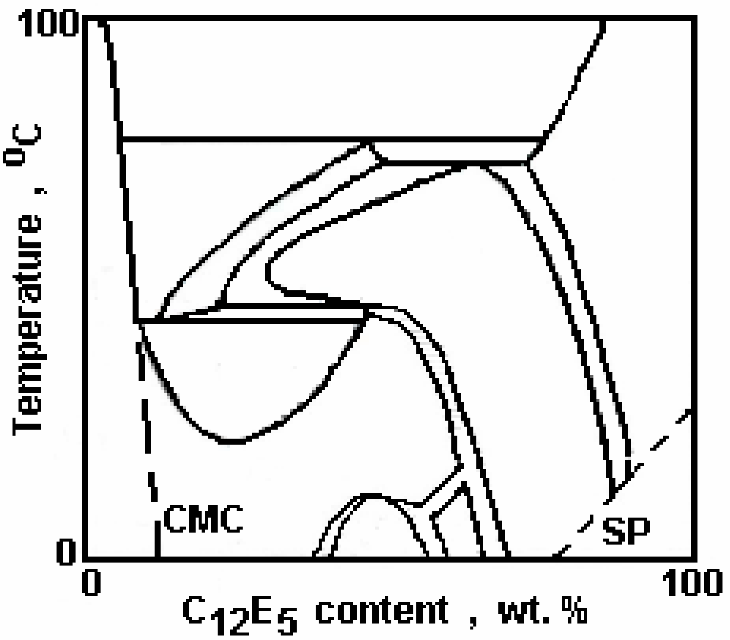

Figure 1: Complex T-with the phase chart of associative colloids in to binary system water-surfactant. Shaped critical borders – traditional curves of critical concentration a micelle of education (SMS) and solubilities.

As an example, in figure- 1 the complex phase chart in coordinates temperature – concentration is shown for nonionic surfactant – monododecsilt air of pentaethylene glycol ($C_{12}E_5$) in water. We will note that on the phase chart there are closed phase areas (the closed contours) corresponding to implementation so-called returnable phase transitions [12,3].

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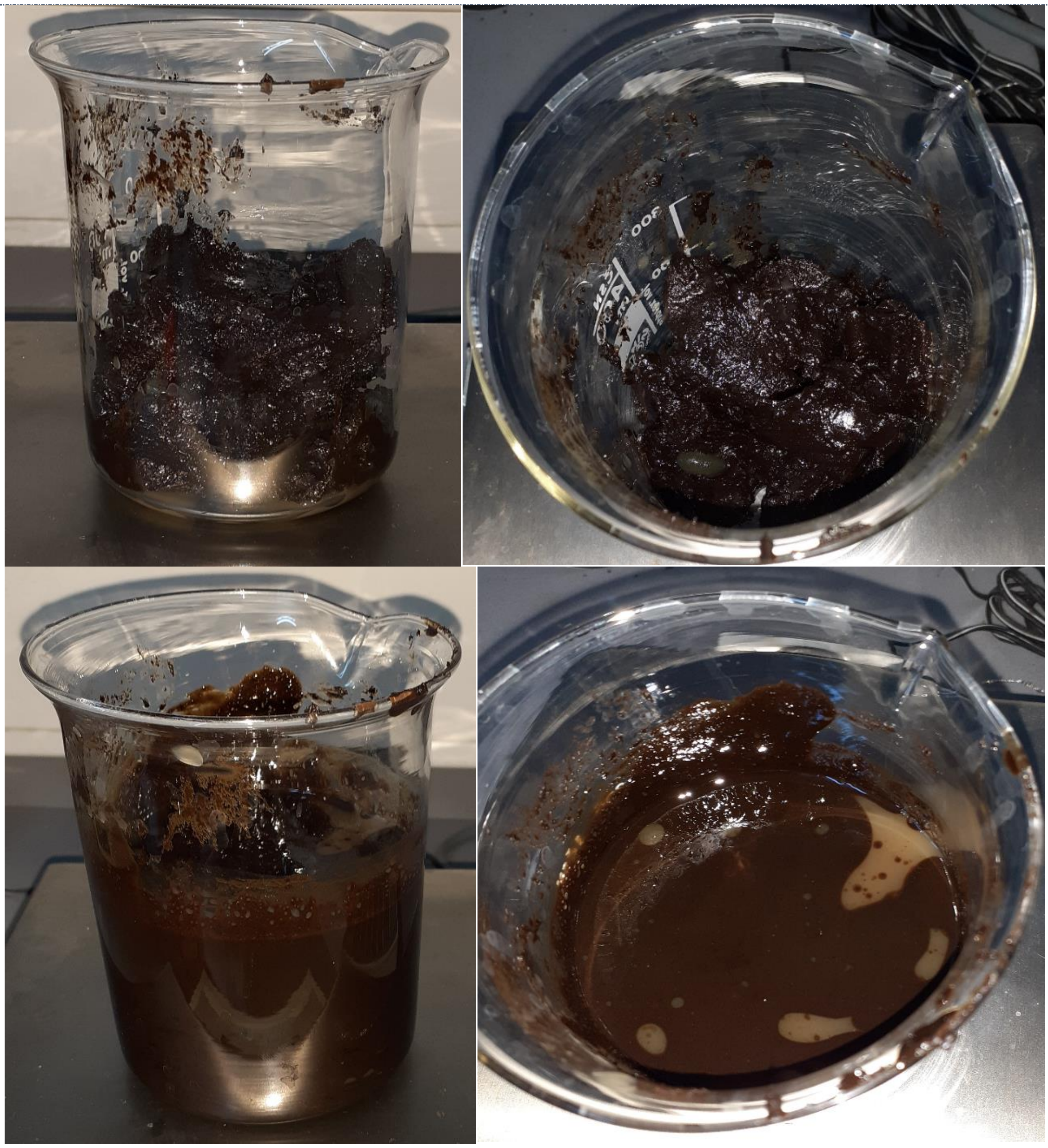

Figure 2: Wax, asphaltene, rezin of deposits (WARD) emulsions formed.

It is important for further discussion that the closed contours on the phase chart demonstrate existence in system of polymorphism; formation of these areas on the phase chart happens to stratifying transition participation (phase transition of the second sort) that is characteristic of existence in the associates directed not covalent (for example, hydrogen) communications.

Surprisingly, as after adoption of the concept of a micelle of education for nanoparticles of asphaltene, researchers of crude oil disperse systems still continued to adhere to outdated ideas of existence of only one critical concentration in surfactants solutions. As a result, no analogies to associative colloids (the difficult phase chart with a set of critical concentration and temperatures) still seriously were studied though, as shown below, both the known experimental data and the last publications contain versatile information which will be coordinated that asphaltene on business, really are associative nanocolloids. The determination of resin asphaltene paraffins was carried out by washing in silogel and is given in the following figure-2.

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Our experiments have allowed to find noticeable changes of properties natural crude oil and upon transition through temperature phase border.

4. RESEARCH RESULTS AND DISCUSSION

We analyzed the physical and chemical properties of Azerbaijani crude oils. The object of the study was a commercial water-oil emulsion Muradkanly, neft dashlari, Suraxani and Bulla field. Physicochemical characteristics are given in table-1.

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 field. The investigated oil is characterized by a large content of natural emulsifier-stabilizers of water-oil emulsion - resins.

The reagents Dissolvan-4411 - non-ionic demulsifier, manufactured in Germany. Composition: ethylene and propylene oxide dissolved in methanol. Based on test results selected by demulsifiers for which optimal dosages. 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.

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Table 1: Physical and chemical characteristics of field emulsion

Parameters	**Muradkanly field, value**	**Bulla field, value**	**Balaxani field, value**	**Neft dashlari field, value**	**Suraxani field, value**
Before the reagent Dissolvan-4411 is injected					
Density at 20 ^{0}C, kq/m^3	947,3	973,8	923,0	904,7	912,8
Viscosity at 20 ºC, mP·sec	2157,3	2445,8	2126,3	1968,4	2021,3
Waters contents, %	41	31	29	24	27
Salts contents, mg/l	534,3	493,8	378,7	329,3	394,9
Sediment contents, %	5,86	4,53	3,98	3,26	3,85
Resins, mas. %	16,9-18,1	8,1-9,3	6,7-8,4	12,4-13,7	13,1-14,9
Asphaltens, mas. %	3,7-4,5	0,12-0,18	0,09-0,14	2,18-3,94	1,79-2,75
Paraffins, mas. %	3,9-5,8	11,7-12,9	0,27-0,43	1,8-2,6	1,43-2,1
Pour point, ºC	+9	+12	-3	-9	-3
After the reagent Dissolvan-4411 is injected					
Density at 20 ^{0}C, kq/m^3	876,4	842,1	887,9	856,9	859,3
Viscosity at 20 ºC, mP·sec	283,4	214,2	1925,4	184,9	192,7
Waters contents, %	0,98	0,76	0,61	0,83	0,79
Resins, mas. %	17,2-18,3	8,7-10,1	7,3-8,9	13,2-14,3	13,6-15,1
Salts contents, mg/l	152,7	138,6	125,3	141,3	139,5
Sediment contents, %	0,009	0,007	0,006	0,009	0,008

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Asphaltens, mas. %	4,1-4,8	0,14-2,3	0,12-0,23	2,94-4,23	1,93-3,21
Paraffins, mas. %	4,6-6,7	12,1-13,4	0,36-0,57	2,3-3,5	1,72-2,87
Pour point, ºC	+9	+12	-36	-45	-21

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 [14].

5. 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-2.

Table 2: 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, ºC	20	20
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. Depending on the water content of the oil emulsion, the dosage is adjusted from 40 to 200 g/t. The results of the experiment are shown in the table-3.

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.

Table 3: 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	30,2
Balaxani	200	7,9	13,2	23,3	26,4
	400	8,3	14,8	25,2	27,3
	600	9,4	15,3	25,8	28,4

Neft dashlari	200	7,9	12,6	22,2	22,9
	400	8,2	13,9	22,4	23,1
	600	9,6	15,1	22,6	23,2
Suraxani	200	7,3	12,8	22,4	25,2
	400	7,8	13,2	2,7	25,9
	600	8,9	13,8	24,9	26,2

6. CONCLUSION

In the oil and gas industry of nanotechnology so far weren't widely adopted, except for processes of oil refining and gas. In oil production and drilling the bigger attention began to be paid to researches and developments of the new nanostructured clever liquids for an intensification of production, oil recovery increase only recently layers and safe performance of drilling operations.

Our researches have shown that now there are enough facts to consider also oil as associative nanoliquid, by the nature which is object of nanotechnologies. Therefore, and traditional technologies for development of oil and gas fields can (have to) become in fact nanotechnologies in the sense that they have to be optimized or designed anew with the accounting of complex phase charts of the nanocolloids entering oil. As a result, it will allow if not to improve, then at least, to keep thin internal structure natural crude oils (in the latter case it is possible to call such approach oil nanoecology). Moreover, the similar nanoideology, can be necessary and during the work with some macroscopic disperse systems to which emulsions sheeted belong waters in oil. Morphological/phase charts of water oil emulsions find the complex structure reminding some lines of phase charts of natural nanocolloids of oil environments.

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.

7. ACKNOWLEDGEMENTS

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REFERENCES

[1] Bannov P.G. Oil Refining Processes. Moscow, 2000. 224 p.
[2] Usubaliev B.T., Nurullaev V.H., Murvatov F.T. New multifunctional technology based on nanostructural coordination polymers to increase the efficiency of production, transport and oil storage // International scientific-practical conference "Status and prospects of exploitation of deposits" 2019, the Republic of Kazakhstan." Aktau, April 25-26, p. 212-216.
[3] Nurullayev V.Ch., Usubaliyev B.T., Gahramanov F.S. Selectivity in Improvement of Rheological Properties of Crude Oil, American Journal of Applied and Industrial Chemistry, U.S.A. 2019, v. 3, №1 pp. 1-8.
[4] Usubaliev B.T., Nurullaev V.H., Murvatov F.T. and others. Application of new nanostructured coordination polymers for crushing asphalt-resin-paraffin associations in the volume of oil and petroleum emulsion, Bulletin of the Azerbaijan Academy of Engineering, 2020, Vol. 12, № 2, p. 47-57.
[5] Ryabov V.G., Starkova N.N., Tarkhov L.G., Kudinov A.V. Oil and Gas Processing: Tutorial. Perm, 2008. 103 p.

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

[6] Khutoryanskii F.M., Galiev R.G., Kapustin V.M. Deep Dehydration and Desalting of Crude Oil at Refineries. Modern Scientific and Technical Level of the Process. Proceedings of Reports of XVIII Mendeleev Congress on General and Applied Chemistry. Moscow, 2007. Vol. 3, pp. 461.
[7] Sakhabutdinov R.Z., Gubaidulin F.R., Khamidullin R.F. Test Methods for Demulsifying Agents for Oil Field Preparation: Method. Instructions. Kazan, 2009. 35 p.
[8] Procedure for Conducting Laboratory and Pilot Field Testing of Chemical Reagents for Use in Oil and Gas Production and Treatment Processes, ANK Bashneft, 2013. 83 p.
[9] Vinogradov V.M., Vinokurov V.A. Formation, Properties and Methods of Destruction of Oil Emulsions: Method. Directions. Moscow, 2007. 31 p.
[10] Sidorov G.M., Yakhin B.A., Akhmetov R.F. Modeling Process of Static Mixers (Oil-Water) for Desalting Crude Oil and Pilot-Industrial Testing. – Advances in Current Natural Sciences, 2017, No. 2, pp. 152-156.
[11] Ismailov G. G., Kuliev M. M., Nurullaev V. Kh., Keleova I. N., Guliev V. K., Accounting the structural stability of abnormal flows in oil gathering systems network, no. 4,2010, p. 31-33.
[12] Evdokimov, I. N., Eliseev, N. Yu., and Eliseev, D. Rheological evidence of structural phase transitions in asphaltene-containing petroleum fluids, Journal of Petroleum Science and Engineering, 30(3-4), 2001, p. 199-211.
[13] Evdokimov, I. N., Eliseev, N. Yu., and Iktisanov, V.A. 2005. Excess density in oilfield water - crude oil dispersions, Journal of Colloid and Interface Science, 285(2), 2005, p. 795-803.
[14] Ekaterina V. Grokhotova, Nadezhda M. Mukhina, Georgiy M. Sidorov, Study of oil dehydration methods in Kaliningrad region, Oil and gas business, №3, 2019, p. 251-268.