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STUDY OF INFLUENCE OF DEMULSIFIERS ON COMPLEX IN RHEOLOGY OIL DEHYDRATION KINETICS

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ИССЛЕДОВАНИЕ ВЛИЯНИЯ РЕАГЕНТОВ-ДЕЭМУЛЬГАТОРОВ НА КИНЕТИКУ ОБЕЗВОЖИВАНИЯ РЕОЛОГИЧЕСКИ СЛОЖНОЙ НЕФТИ

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One of the relevant challenges in development of oil fields is a challenge to increase efficiency of oilfield treatment of hydrocarbons. Solution for that challenge can significantly improve level of oil treatment, reduce hydrocarbon losses with drainage water and thereby improve ecology of the environment and make additional profit for an enterprise. A system of gathering and treatment of water and oil of Karazhanbas field, influence of surface active agents (surfactants) on water-oil emulsions under conditions of the field are studied in the paper. In addition, a chemical demulsifier which has the most efficient properties for field treatment of well production at Karazhanbas field is chosen. Results of laboratory studies of water-oil emulsion, physical and chemical analysis of water composition and new chemical demulsifiers, recommended for pilot tests at Karazhanbas field, are presented. Analisys of results of laboratory studies shows that all test chemicals are inferior to a base demulsifier Randem-2208 by a degree of dehydration. Base demilsifier is inferior to demulsifiers Victory-2, 3 and Rauan-2050 by a degree of desaltation. It is established that demulsifier Victory-1 in comparison with base and other demulsifiers does not show a high demulsifying ability. In coparison with base Randem-2208 demulsifier Victory-2 showed the lowest demulsifying ability with degree of dehydration equal to 60.67 %. In comparison with the base product Randem-2208 demulsifier Victory-3 provides quite good dehydration. Compared to base demulsifier Randem-2208 demulsifier Rauan-2050 has a good demulsifying ability, consumption of demulsifier decreases with increase in water saturation in oil. At the same time, goal-based increase in water saturation of prepeared rheologically complex oil to its ultimate value allows to reduce consumption of demulsifier in several times with no reduce in efficiency oil dehydrationl.

Ключевые слова:
подготовка нефти, вода, водонефтяная эмульсия, вязкость, плотность, химические реагенты, обезвоживание, деэмульгатор, поверхностно-активное вещество, кинетика, хлористые соли, реологические свойства, физико-химические свойства, химический состав, эффективная дозировка, расход реагента.

Одной из актуальных проблем разработки нефтяных месторождений является повышение эффективности нефтепромысловой подготовки углеводородов. Решение этой проблемы может значительно повысить степень подготовки нефти, уменьшить потери углеводородов с дренажной водой, тем самым улучшить экологию окружающей среды и принести дополнительную прибыль предприятию. В работе были изучены система сбора и подготовки воды и нефти месторождения Каражанбас, влияние поверхностно-активных веществ (ПАВ) на водонефтяные эмульсии в условиях данного месторождения. Кроме того, был избран химический реагент-деэмульгатор, имеющий наиболее эффективные свойства для промысловой подготовки продукции скважин месторождения Каражанбас. Приведены результаты лабораторных исследований водонефтяной эмульсии, физико-химического анализа состава воды, новых химических реагентов-деэмульгаторов, рекомендуемых для опытно-промысловых испытаний на месторождении Каражанбас. Анализируя результаты лабораторных исследований, можно сделать вывод, что по степени обезвоживания все испытуемые химические реагенты уступают базовому реагенту-деэмульгатору «Рандем-2208», а по обессоливающим свойствам базовый деэмульгатор уступает деэмульгаторам марки «Victory-2, 3» и «Rauan-2050». В ходе анализа установлено, что деэмульгатор марки «Victory-1» по сравнению с базовым и другими деэмульгаторами не проявляет высокую деэмульгирующую способность. Деэмульгатор марки «Victory-2» по сравнению с базовым «Рандем-2208» показал наименьшую деэмульгирующую способность, степень обезвоживания составляет 60,67 %. Деэмульгатор «Victory-3» по сравнению с базовым продуктом «Рандем-2208» обеспечивает достаточно хорошее обезвоживание. У деэмульгатора марки «Rauan-2050» по сравнению с базовым деэмульгатором «Рандем-2208» хорошая деэмульгирующая способность, с ростом водонасыщенности нефти его расход уменьшается. При этом путем целенаправленного повышения водонасыщенности подготовленной реологически сложной нефти до предельного ее значения можно в несколько раз уменьшить расход деэмульгатора, не снижая при этом эффективность процесса обезвоживания нефти.

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Introduction

The challenge of increase in efficiency of field treatment of oil is on the front barrier to overcome because that could significantly increase the efficiency of field treatment of oil, decrease hydrocarbon losses along with drainage water and, thereby, improve the ecology of the environment and bring additional profit to an enterprise [1-7].

As is known, field treatment of oil, its demulsification are carried out under the influence of temperature. Oil is heated and a chemical agent is supplied [8-14]. The higher the temperature the lower the viscosity of oil and the bigger the difference in densities of water and oil. Temperature of demulsification depends on properties of oil and conditions of a process itself. A combined effect of temperature and chemical agent initiate coalescence, i.e. intensive fusion of water droplets into larger ones, capable of falling off quickly and separating themselves from oil under the action of gravity. In laboratory experiments the influence of main factors such as temperature, concentration of agents, amount of stirring and settling time were studied carefully.

Challenge statement

A technological method of demulsification intends to ensure production of maximum amount of dehydrated oil with lowest irreducible water saturation and with a minimum consumption of a demulsifier. All mentioned should be achieved under considered conditions of economical consumption of fuel and steam, safety of equipment and equipment of an installation. Since increased temperature increases fuel consumption, reduces capacity of an installation and increases loss of valuable light fractions the process should be carried out economically with slight heating of an emulsion. However, the heating value should ensure demulsification process at a sufficient rate [15-25].

Solution for the challenge

As is known, water-oil emulsions belong to typical representatives of complex heterogeneous and polydisperse systems. Recent studies have shown that in addition to basic physical and chemical property such as viscosity emulsions are also characterised by water saturation [26-28]. In particular, studies of rheological characteristics of artificially created emulsions based on high-viscosity anomalous oil of Muradkhanly field on a rotational Rheotest-2 viscometer at temperatures of 20, 40 °C showed that from 22 to 80 % of water saturation system viscosity, as expected, increases with increasing water cut (Fig. 1, *a*, *b*). As can be seen from these figures complete saturation of oil with water occurs at 80 % of water content.

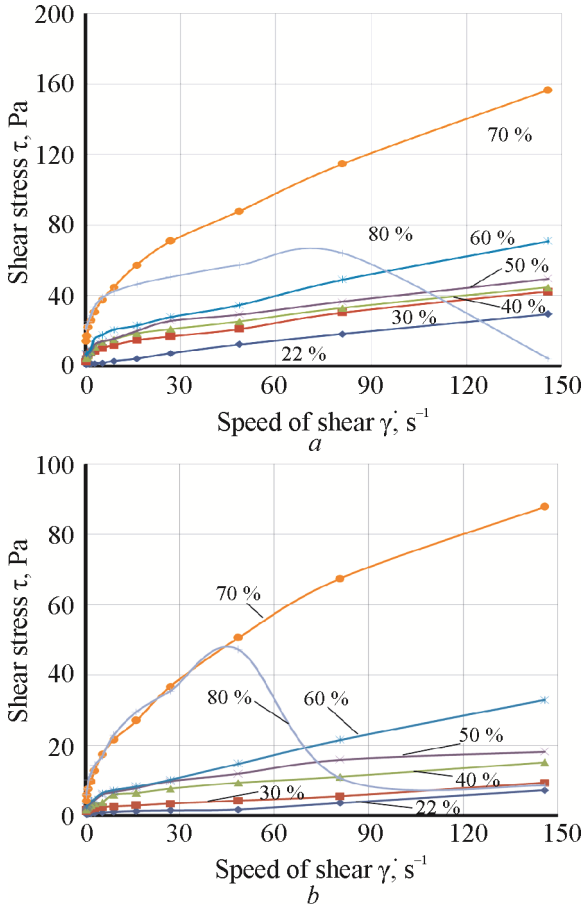


Fig. 1. Graphs of a function of shear stress versus shear speed during flow of Muradkhanly oil at different water content such as *a* – *T* 20 °C; *b* – *T* 40 °C

There are on oil fields of Azerbaijan foreign demulsifier "Disolvan" (Switzerland) and the domestic "Alcan" were widely used.

Technical documentation regulates high efficiency of these agents. However, usually in

field conditions real efficiency of mentioned demulsifiers is much lower than the regulated one. That is caused by the fact that at the stage of development and production of agents it is extremely difficult to take into account all the factors that affect their efficiency due to changes in the composition and water saturation of oil produced.

Demulsifying agents Victory-1, 2, 3, Rayan-2050, Randem-2208 of Karazhanbasmunai JSC intended for application at facilities of production, collection, treatment and transportation of crude hydrocarbon were tested in laboratory conditions. Demulsifiers of Victory are multi-type, suitable for destruction of various types of water-oil emulsions. They are composite based on surfactants dissolved in organic solvents. The test demulsifier Rauan-2050 is a composite based on block copolymers of ethylene oxide and propylene dissolved in organic solvents and is intended for dehydration and desalting of oil emulsions during collection and treatment of oil in fields. The demulsifier was developed by RauanNalko TOO and is produced according to ST TOO 7585-1915-38-36-2012.

Efficiency of demulsifiers was determined according to a method of ST AO 000840001829-04-14 The method for conducting laboratory tests to assess demulsifying activity of chemical agents by bottle test method [29], the essence of which is visual observation of emulsion stratification and water separation in glass vessels (bottles-sedimentation tanks). The investigated product was added in various dosages into a water-oil emulsion, poured into 100-millimeter settling tanks. Then dynamics of water separated from the emulsion were recorded. To assess stability of an emulsion under study, the experiment includes a dummy experiment in which an emulsion is treated under the same conditions without addition of a demulsifier. Testing of demulsifiers was carried out using a water-oil emulsion of the Karazhanbas field at temperature of 90 °C. At the end of the tests the content of chloride salts in oil was determined by titrating the water extract in accordance with GOST 21534-76 [30].

Dehydration degree of demulsifier was calculated by the formula

$$P = \frac{V_1}{V} 100\ \%,$$

where V_1 is volume of water, separated after thermostat control, %; V is content of bound water in a sample, %.

The effective dosage was determined according to the following criteria:

– approximate (indicative) assessment of efficiency at specific consumptions 150, 200, 240, 300 g/tonne;

– clarification of the optimal effective dosage of a demulsifier at specific consumption 220-260 g/tonne.

Tables 1-5 and Fig. 2-7 show results of study of kinetics of water coming of the test demulsifiers under conditions of Karazhanbas field. The analysis of laboratory studies has shown that oil of the field taken from a well and gas-measuring unit is homogenious, similar in chemical composition and properties. Oil relates to a paraffin-type (average 3.7 % by weight), high-resin (average 19 % by weight), high-sulfur and in terms of chloride salts and mechanical impurities belong to the third group.

Since demulsifier Randem-2208 is already used at facilities of the Karazhanbas field, it is considered as the basic one and is an agent-demulsifier for comparison. Based on results of tests (Table 1 and Fig. 2), it is obvious that there is no adverse effect on the process of treatment, dehydration and desalting of oil during adding into the initial water-oil emulsion of amount of 240 g/tonne. Dehydration level is 63.27 %, residual content of chloride salts is 2.44 g/l.

Results of the study (Table 2 and Fig. 3) show that Victory-1 demulsifier during adding into a water-oil emulsion of the Karazhanbas field does not show a high demulsibility in comparison with other sorts of Victory demulsifiers. Maximum specific consumption of 300 g/tone corresponds to

Table 1

Results of study of kinetics of approximate and specified effective dosage of Randem-2208 demulsifier at 90 °C of test temperature

No	Product	Dosage, g/tonne	Amount of water released, %											Degree of dehydration, %	Irreducible water content, %	Content of chloride salts, mg/l
			Time, min													
			5	10	15	20	30	40	50	60	75	90	120			
Estimated effectiveness, a value of bound water is 44,6 %																
1	Dummy sample	0	0.00	0.00	0.00	0.00	0.00	0.41	0.82	0.82	1.64	3.28	4.10	9.19	90.81	8090.9
2	Randem-2208	150	0.00	2.46	12.30	18.04	22.14	22.96	23.78	24.60	26.24	27.06	27.06	60.67	39.33	2764.2
3	Randem-2208	200	0.00	3.90	11.70	17.16	22.62	22.62	23.40	24.18	24.96	25.74	25.74	57.71	42.29	2976.3
4	Randem-2208	240	0.00	2.49	12.45	20.75	24.90	26.56	27.39	27.39	28.22	28.22	28.22	63.27	36.73	2436.7
5	Randem-2208	300	0.00	3.20	13.60	19.20	22.40	24.80	25.60	26.40	27.20	27.20	27.20	60.99	39.01	2648.1
Specified efficiency, a value of bound water is 42 %																
1	Dummy sample	0	0,00	0.00	0.00	0.00	0.00	0.80	0.80	0.80	1.20	1.60	2.40	5.71	94.29	13045.9
2	Randem-2208	220	0.00	8.00	13.60	16.00	19.20	21.60	22.40	22.40	22.40	23.20	24.00	57.14	42.86	6319.1
3	Randem-2208»	260	0.00	8.20	13.94	17.22	20.50	22.14	22.96	23.78	24.60	24.60	25.01	59.55	40.45	6664.6

Table 2

Results of study of kinetics of approximate and specified effective dosage of Victory-1 demulsifier at 90 °C of test temperature (a value of bound water is 55.6 %)

No	Product	Dosage, g/tonne	Amount of water released, %											Degree of dehydration, %	Irreducible water content, %	Content of chloride salts, mg/l
			Time, min													
			5	10	15	20	30	40	50	60	75	90	120			
1	Dummy sample	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.80	3.20	5.76	94.24	5940.9
2	Victory-1	150	0.00	0.00	0.08	1.60	4.80	7.20	8.00	10.40	12.80	15.20	18.40	33.09	66.91	3193.5
3	Victory-1	200	0.00	0.00	0.08	3.95	7.11	9.48	10.27	12.64	14.22	15.01	18.17	32.68	67.32	3269.6
4	Victory-1	240	0.00	0.00	0.08	5.60	9.60	12.00	15.20	16.00	18.40	20.80	23.20	41.73	58.27	2587.4
5	Victory-1	300	0.00	0.00	0.16	5.77	7.96	10.61	12.25	12.87	14.20	15.91	17.16	30.86	69.14	3566.0

Table 3

Results of study of kinetics of approximate and specified effective dosage of Victory-2 demulsifier at 90 °C of test temperature

No	Product	Dosage, g/tonne	Amount of water released, %											Degree of dehydration, %	Irreducible water content, %	Content of chloride salts, mg/l
			Time, min													
			5	10	15	20	30	40	50	60	75	90	120			
Estimated effectiveness, a value of bound water is 54 %																
1	Dummy sample	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.80	1.60	2.40	4.44	95.56	7118.3
2	Victory-2	150	0.00	0.00	2.31	6.16	8.47	18.48	24.64	27.72	30.03	30.80	31.57	58.46	41.54	2245.6
3	Victory-2	200	0.00	0.00	3.16	7.90	18.96	26.07	30.02	30.81	31.60	32.39	32.39	59.98	40.02	2141.3
4	Victory-2	240	0.00	0.00	2.34	7.80	13.26	26.52	29.64	30.42	31.20	31.98	32.76	60.67	39.33	2099.8
5	Victory-2	300	0.00	0.00	2.46	9.84	22.14	28.70	30.34	31.98	33.62	34.44	34.44	63.78	36.22	2038.8
Specified effectiveness, a value of bound water is 42 %																
1	Dummy sample	0	0.00	0.00	0.00	0.00	0.00	0.80	0.80	0.80	1.20	1.60	2.40	5.71	94.29	5940.9
2	Victory-2	220	0.00	7.20	11.20	13.60	16.00	19.20	20.00	20.80	21.60	21.60	22.40	53.33	46.67	2120.7
3	Victory-2	260	0.00	6.56	9.84	13.94	16.40	18.86	19.68	21.32	21.32	22.14	22.14	52.71	47.29	2778.5

Table 4

Results of study of kinetics of approximate and specified effective dosage of Victory-3 demulsifier at 90 °C of test temperature

No	Product	Dosage, g/tonne	Amount of water released, % Time, min 5	10	15	20	30	40	50	60	75	90	120	Degree of dehydration, %	Irreducible water content, %	Content of chloride salts, mg/l
Estimated effectiveness, a value of bound water is 44 %																
1	Dummy sample	0	0.00	0.00	0.16	2.40	3.20	4.00	4.80	4.80	5.60	6.40	7.20	16.36	83.64	6749.2
2	Victory-3	150	0.08	4.74	8.69	11.85	15.01	21.33	22.91	25.28	26.07	26.07	26.07	59.25	40.75	2457.0
3	Victory-3	200	0.00	2.46	5.74	9.84	13.94	20.50	22.14	24.60	24.60	25.42	26.24	59.64	40.36	2367.0
4	Victory-3	240	0.16	4.00	7.20	10.40	15.20	18.40	21.60	24.00	24.80	25.60	26.40	60.00	40.00	1109.7
5	Victory-3	300	0.04	3.28	7.38	11.48	17.22	23.78	27.06	27.88	28.70	28.70	29.52	67.09	32.91	725.0
Specified effectiveness, a value of bound water is 42 %																
1	Dummy sample	0	0.00	0.00	0.00	0.00	0.00	0.80	0.80	0.80	1.20	1.60	2.40	5.71	94.29	5940.9
2	Victory-3	220	0.00	7.20	13.60	16.80	20.80	22.40	23.20	24.00	24.00	24.00	24.00	57.14	42.86	1556.2
3	Victory-3	260	0.00	8.20	13.94	16.40	21.32	23.78	23.78	24.60	25.42	25.42	25.42	60.52	39.48	1093.4

Table 5

Results of study of kinetics of approximate and specified effective dosage of Rauan-2050 demulsifier at 90 °C of test temperature (a value of bound water is 42 %)

No	Product	Dosage, g/tonne	Amount of water released, % Time, min 5	10	15	20	30	40	50	60	75	90	120	Degree of dehydration, %	Irreducible water content, %	Content of chloride salts, mg/l
1	Dummy sample	0	0.00	0.00	0.00	0.00	0.00	0.80	0.80	0.80	1.20	1.60	2.40	5.71	94.29	5940.9
2	Rauan-2050	100	0.00	2.40	5.60	9.60	12.00	13.60	15.20	15.20	16.00	16.80	17.60	41.90	58.10	3626.3
3	Rauan-2050	150	0.00	4.00	8.00	9.60	12.80	14.40	16.80	17.60	17.60	18.40	19.20	45.71	54.29	3231.4
4	Rauan-2050	200	0.00	8.00	12.00	13.60	16.80	20.00	21.60	22.40	23.20	24.00	24.80	59.05	40.95	2650.1
5	Rauan-2050	220	0.00	7.20	8.80	12.00	16.80	20.00	20.80	22.40	23.20	24.00	24.80	59.05	40.95	1154.7
6	Rauan-2050	240	0.00	7.29	9.72	12.96	18.63	21.06	21.87	23.49	25.11	25.11	25.92	61.71	38.29	709.8
7	Rauan-2050	260	0.00	5.67	8.10	12.15	17.82	20.25	21.12	22.64	24.14	25.10	25.10	59.76	40.24	1007.6
8	Rauan-2050	300	0.00	8.10	11.34	15.39	20.25	21.68	22.30	23.11	23.98	24.72	24.72	58.86	41.14	1105.3

dehydration level of 30.86 %, residual water content in oil is 69.14 %. The content of chloride salts in oil is decreased from 5.94 to 3.57 g/l. When a demulsifier is added into a water-oil emulsion released water does not get cloudy, there is no clear interface and intermediate layer, no precipitation formed, but there is adhesion to test tube walls.

As a result of evaluation of effectiveness of Victory demulsifiers Victory-2 and Victory-3 were chosen to clarify the optimal effective dosage during futher studies.

There is a decrease in content of chloride salts in doses of 240 and 300 g/tonne in more that 3 times (from 7.12 to 2.04 g/l) if Victory-2 demulsifier is added to oil emulsion (Table 3 and Fig. 4). At the same time, degree of dehydration reaches a maximum value at 300 g/tonne and is 63.78 %, while the same effect is achieved using 240 g/t of the base agent. Released (separated) water does not cloud, there is a clear interface between the phases, no intermediate layer and no sediment is formed. Adhesion to the test tube walls is not established.

Results of Victory-3 demulsifier, presented in Table 4 and Fig. 5, show that there is a significant reduction in chloride salts down to 0.73 g/l is observed if the demulsifier is added into a water-oil emulsion. In comaprison with two other demulsifiers (Victory-1 and 2) of the same product line Victory-3 demulsifier is more effective at dosage of 300 g/t, dehydration level reaches a maximum value of

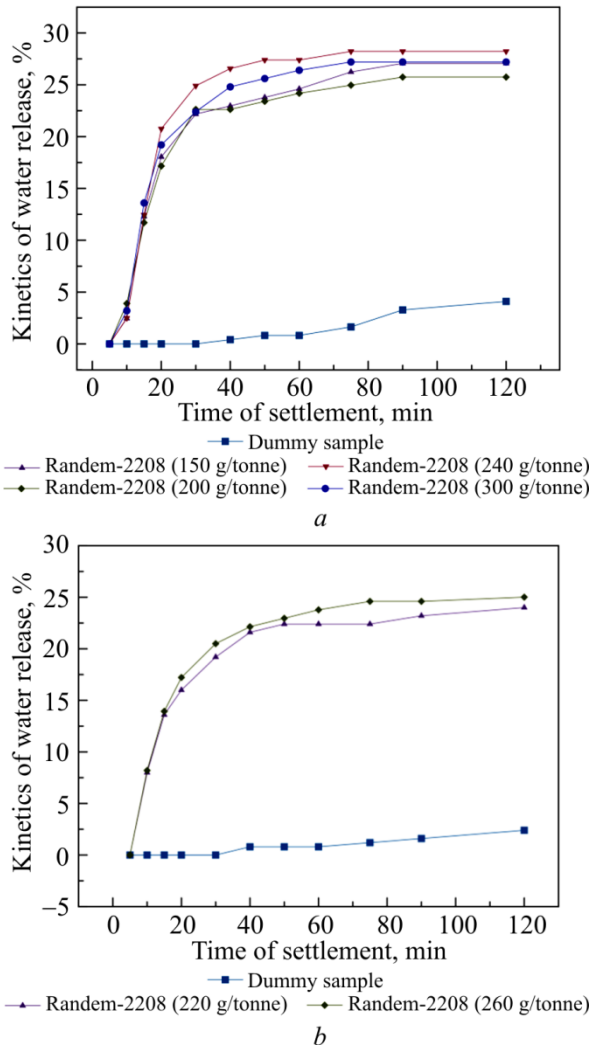


Fig. 2. Kinetics of water release in presence of Randem-2208 demulsifier at bound water values of 44.6 % (*a*) and 42 % (*b*) (see Table 1)

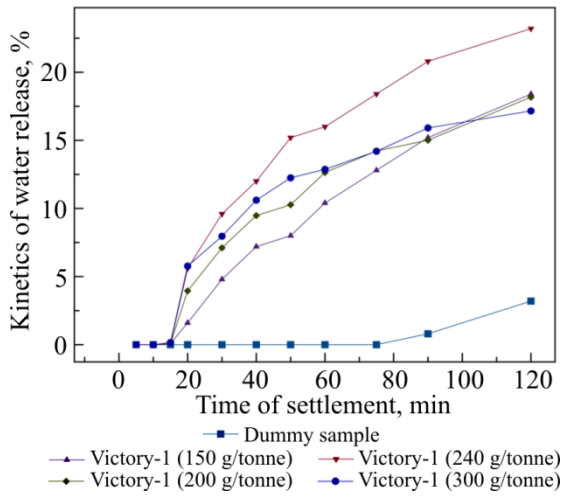


Fig. 3. Kinetics of water release in presence of Victory-1 demulsifier

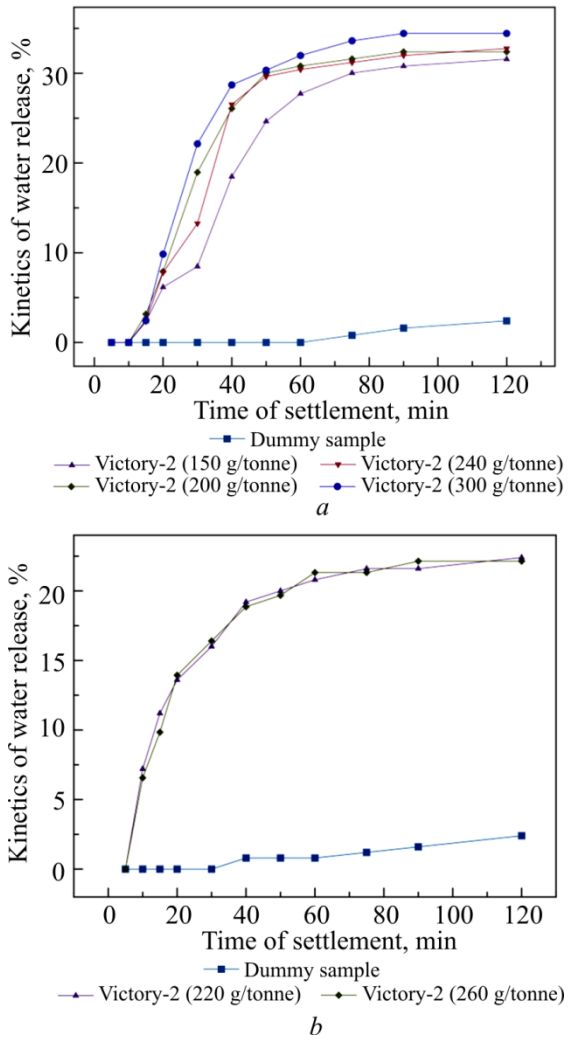
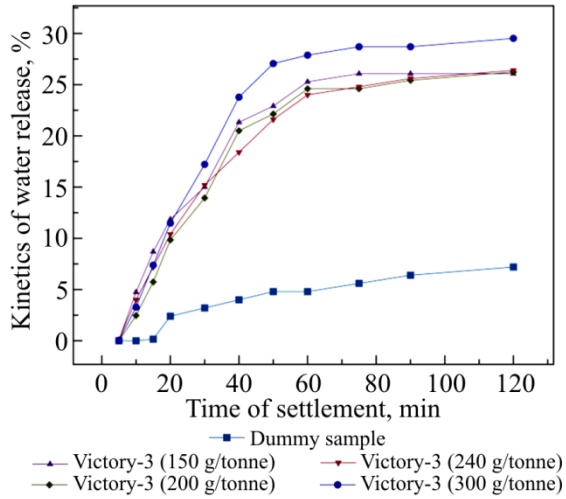


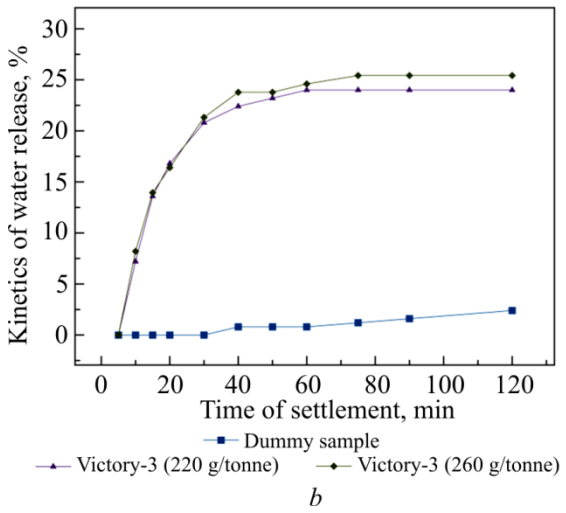
Fig. 4. Kinetics of water release in presence of Victory-2 demulsifier at bound water values of 54 % (*a*) and 52 % (*b*) (see Table 3)

67.9 %. In comparison with the basic demulsifier Randem-2208 Victory-3 does not provide sufficient good dehydration at a specific consumption of 240 g/t. Water released does not cloud if demulsifier is added into the water-oil emulsion. There is a clear interface between the phases, no intermediate layer, no adhesion on test tube walls, but there is a small amount of precipitatation.

There are results of study of kinetics of approximate and specified effective dosage of the demulsifier Rauan-2050 presened in Table 5 and in Fig. 6. In case if the demulsifier is added into the water-oil emulsion then a degree of dehydration at specific rates of 240 and 300 g/tonne was 61.7 %, irreducible water saturation in oil was 38.29 %. Released water does not cloud, there is a clear



a



b

Fig. 5. Kinetics of water release in presence of Victory-3 demulsifier at bound water values of 44 % (*a*) and 42 % (*b*) (see Table 4)

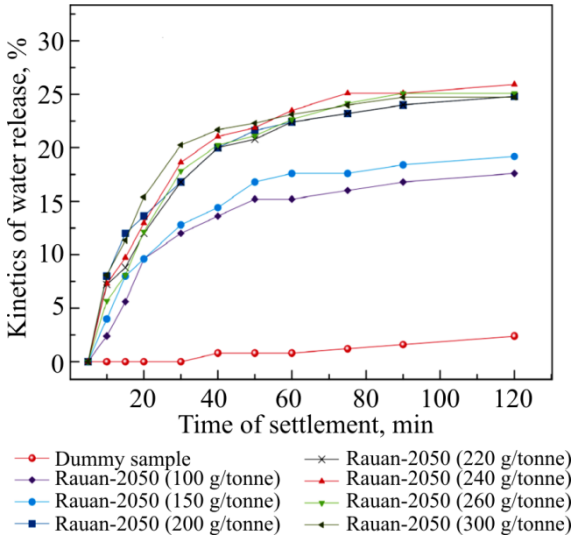


Fig. 6. Kinetics of water release in presence of Rauan-2050 demulsifier

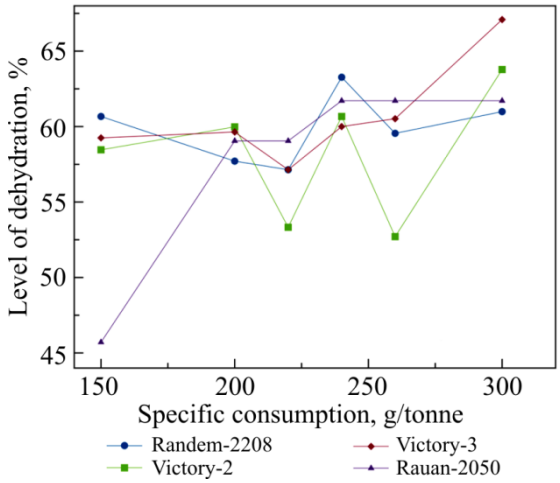


Fig. 7. Function of a level of dehydration versus specific consumption of Randem-2208, Victory-2, 3 and Rauan-2050 demulsifiers

interface between the phases, no intermediate layer, no precipitation forms and adhesion to test tube walls is not established.

There are the same (stable) results in level of dehydration and irreducible water saturation at 240, 260 and 300 g/tonne for Rauan-2050 demulsifier. At the same time the content of chloride salts in oil decreases by an order of magnitude from 5.94 to 0.71 g/l, which is also an indicator of quality of oil treatment.

Conclusion

Analysis of results of laboratory studies (Fig. 7) shows that according to the level of dehydration at technological specific consumption of 240 g/tonne all the test chemicals are inferior to the basic agent-demulsifier Randem-2208. In terms of desalting properties the base demulsifier are inferior to demulsifiers Victory-2, 3 and Rauan-2050.

Thus, an analysis of results of laboratory tests showed the following:

1. The demulsifier Victory-1 does not show high demulsibility in comparison with the base and other demulsifying agents.

2. The demulsifier Victory-2 compared to the basic demulsifier Randem-2208 with technological specific consumption of 240 g/tonne showed the lowest demulsifying ability, level of dehydration is 60.67 %.

3. The demulsifier Victory-3 in comparison with the basic demulsifier Randem-2208 provides quite

good dehydration and desaltation of water-oil emulsion at specific consumption of 220-300 g/tonne.

4. The demulsifier Rauan-2050 in comparison with the basic demulsifier Randem-2208 shows a good demulsifying ability. It has stable results on residual water content in oil and significantly reduces content of chloride salts in oil at specific rates of 220-300 g/tonne. But if the concentration is 240 g/tonne (field one), Randem-2208 has the best demulsifying ability.

Analysis of stability of oil emulsions performed depending on watercut and consumption indicators of agent-demulsifier that provide their stratification, showed that the effectiveness of demulsification is affected by interaction of two factors such as the content of water phase and level of its dispersion. Since oil demulsification using agent-demulsifier is associated with destruction and adsorption displacement by demulsifier of natural stabilizers from the oil-water interface, an increase in water content has a strong effect on agent consumption.

Thus, results of conducted experimental studies show that the higher the water content in oil the lower the consumption of an agent-demulsifier. At the same time, it is possible to reduce demulsifier consumption several times with no reduce in efficiency of oil dehydration through deliberately increase in water saturation of treated complex in rheology oil to its ultimate value.

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