

Study of Water-Oil Emulsion Breaking by Stabilized Solution Consisting of Anionic Surface Acting Agent – Soda Ash – Polymer (ASP)

S V Kulichkov^a, E G Avtomonov^b, L V Andreeva^c, S F Solomennik^d,
A V Nikitina^e

Far Eastern Federal University, 8 Sukhanova St., Vladivostok, Russia, 690090

E-mail: ^aseku230@yandex.ru, ^bavtomonov@inbox.ru, ^c708738@gmail.com,
^dsfsol@yandex.ru, ^erabota_oos@mail.ru

Abstract. The paper provides a laboratory research of breaking natural water-oil emulsions: - by non-stabilized ASP; by stabilized ASP; by mixture of stabilized and non-stabilized ASP in different proportions and production of refinery water of the required quality with the use of IronGuard 2495 as flocculant. Oil-in-water emulsion is stable. Classic methods are not suitable for residual water treatment: sediment gravity flow; filtration; centrifuge test. Microemulsion formed after ASP application has low boundary tension and high pH. It contributes to transfer of oil phase into a water one, forming oil-in-water emulsion. Alkaline condition has adverse effect on demulsifying ability of agents, flocculation and boundary tension. For breaking of water-oil emulsion at EBU before the interchanger water or water-oil emulsion from the wells that were not APS-treated in ratio of 1:9 shall be delivered. Residual water after EBU must be prepared in water tanks by dilution in great volume.

1. Introduction

Mature assets are characterized by a high water-cut and low recover coefficient. It leads to cost increase for oil production and processing.

ASP water flooding is a method of enhanced oil recovery. It is based on the idea of injection into formation of the solution consisting of surface active agent, soda ash (caustic soda) and polymer. This method allows producing oil that is left in the formation after utilization of the traditional flooding method.

After ASP application the products of flowing wells are characterized by presence of stable microemulsion.

Chemical method of enhanced oil recovery of the formation is based upon utilization of SAA solutions, including solutions of polymers, caustics and mixtures of chemical agents (ASP) in injection wells. In such case the products of flowing wells become caustic (high value of pH medium >9-10), they are characterized by super low value of boundary tension tending to zero and contain hard-breaking microemulsion.

After injection of agents increasing oil recovery of the formation developed, multiple emulsion is delivered to initial water separation units and oil treatment units. Such emulsion is hard to break and consists of a mixture of oil-in-water, water-in-oil and microemulsion. Such emulsions are accumulated on the interface boundary in bulk-capacity tanks for oil, water preparation and are the reason for upset conditions in initial water separation units and oil treatment units.

Zapadno-Salymskoye oilfield is located in the Khanty-Mansiysk Autonomous District (120 km to the south-west of Surgut and 30 km to the west of Salym settlement). It was put in operation in 2005.

In terms of gravity the oils of Zapadno-Salymskoye oilfield are referred to middle oils – 0.876 g/cm³. Asphaltens content is 0.85-1.87 percent, pitches – 8.4-9.8 percent, paraffins – 1.53-1.81 percent, paraffin melting temperature is 63-64°C.

In terms of ratio of paraffin and asphaltic resinous components of oil they are classified as paraffin.



Temperature of the formations being developed is 100-110°C, temperature of water-oil emulsion at well mouth is 70°C. Gas-oil ratio is 45 m³/t.

Produced waters are of low mineral content, their density comprises 1.008-1.011 g/cm³, pH equals to 7.1-7.2.

After ASP application water-oil emulsion produced of 95 percent water-cut represents a stable microdispersed oil-in-water emulsion, and its boundary tension tends to $\sigma \rightarrow 0$ (pH=9.9).

Produced water-oil emulsion after ASP application is characterized by high water-cut of 90-95 percent, pH=9.88, water density of 1.013 g/cm³ and super low values of boundary tension.

Applied ASP solution consists of the following components:

- Enordet surfactant (by SHELL) – 0.43 %;
- Isobutanol – 2.0 %;
- Soda – 2.0 %;
- Sodium Chloride – 1.1 %;
- FLOPAAM polymer (by SNF) – 0.25 %
- Soda (2%) forming a part of ASP contributes to CaCO₃ sedimentation of pump elements.

To determine the possible ways to solve these problems the following laboratory test were performed:

- water-oil emulsion breakdown:
 - by non-stabilized ASP;
 - by stabilized ASP;
 - be mixture of stabilized and non-stabilized by ASP in different proportions;
- water-oil emulsion breakdown and production of refinery water of required quality with the use of IronGuard 2495 as flocculant.

Pilot tests for breakdown of water-oil emulsion treated by ASP solution were performed on pilot plant Emulsion Breaking Unit (EBU).

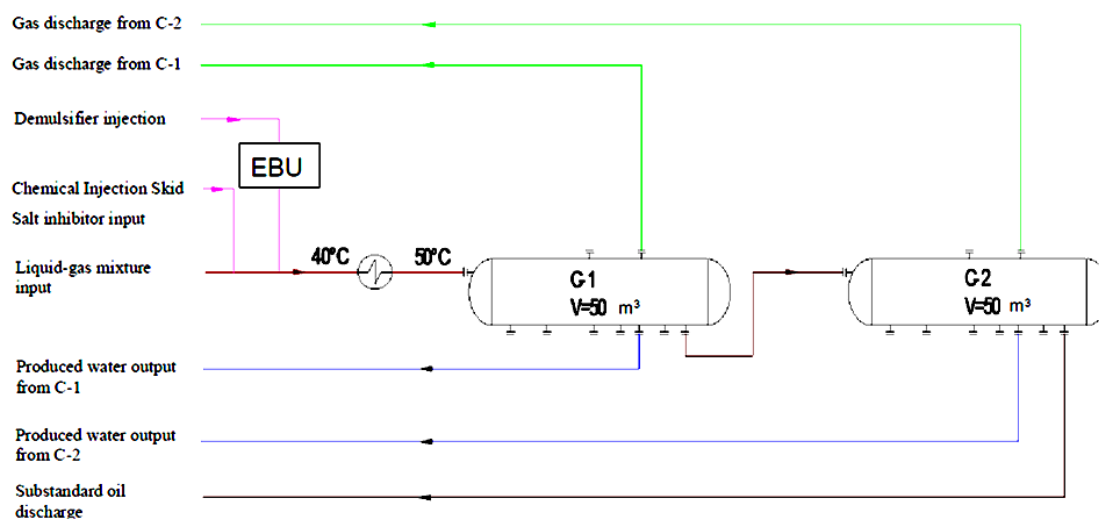


Figure 1. EBU basic diagram.

Water-oil emulsion (water-cut – 95 %, temperature – 15°C) is delivered to EBU.

Oil demulsifier Emulsotron R2601A (specific flow – 50 g/t) and salt inhibitor GYPTRON R4601-C (specific flow – 50 g/m³) are dosed at EBU input. Liquid treated by demulsifier and salt inhibitor arrives to heat interchanger where it is heated to 45 – 50°C, and then directed to two consecutively tied separation plants C-1,2 (V=50 m³ each).

In 75-percent-full separation plants of the first and second stage gas withdrawal takes place and discharge of produced waters. Hold-on time of liquid in separation plants is within 4 – 4.5 hours at 50 °C.

Originally there was almost no water discharge into C-1 due to high content of oil products in refinery water (low value of boundary tension). The more water was discharged, the more oil products were in refinery water – from 1,500 mg/l to 7,258 mg/l.

After first-stage separation in C-1 partially dry and separated liquid arrives to the last stage separation at C-2 where gas is separated and produced water is discharged. Water content in oil after C-2 separation plant is from 8 % to 25 %, chlorides content – 3,125–5,130 mg/l; oil products in refinery water – up to 190,390 mg/l (1.5%).

After EBU oil with different degree of water-cut (%) and chlorides content (mg/l) as well as refinery water were delivered to pre-treatment tanks of oil treatment unit.

Pilot tests for breakdown of water-oil emulsion performed at EBU showed that this scheme and applied chemical agents didn't allow producing oil and water of required quality.

To enhance oil recovery of the formation the laboratory by SHELL selected ASP solution which is capable of forming a stable microemulsion with oil in formation conditions at high temperatures, pressure, high pH and super low boundary tension.

Laboratory tests for water-oil emulsions breaking were carried out by well-known bottle test in accordance with the following technique:

- emulsion sample is taken from the well;
- upon presence, free water is separated from emulsion;
- emulsion sample is carefully mixed;
- water content in emulsion is determined;
- emulsion is poured into graded catchers;
- catchers with emulsion are thermostated in water-bath, in this case at 70 °C and 50 °C;
- demulsifier in commodity form is dosed into the catchers with the help of microliter syringe;
- emulsion treated by demulsifier is manually mixed within three minutes;
- catchers with emulsion treated by demulsifier are placed in water-bath;
- sedimentation temperature for emulsion from Zapadno-Salymkoye oilfield is 70 °C and 50 °C;
- sedimentation time is from 5 to 60 minutes.

The volume of separated water was recorded at set time intervals upon achievement of the preset temperature in catchers.

Content of water separated from water-oil emulsion was calculated according to the formula:

$$W_{\text{sep.}} = \frac{V_i}{V_{\text{orig.}}} \cdot 100 \quad (1)$$

Where V_i - the amount of separated water in a given period of time, ml;

$V_{\text{orig.}}$ – amount of water in original water-oil emulsion, ml;

$W_{\text{sep.}}$ – amount of water separated from emulsion, %.

Content of residual water in oil emulsion was calculated according to the formula:

$$W_{\text{resid. water}} = \frac{W_{\text{orig.}} \cdot 0.01 \cdot V_{\text{samp.}} - V_i}{V_{\text{samp.}} - V_i} \cdot 100 \quad (2)$$

Where V_i is the amount of separated water in a given period of time, ml;

$V_{\text{samp.}}$ – volume of sample taken for de-emulsification, ml;

$W_{\text{orig.}}$ – original water-cut of emulsion sample, %;

$W_{\text{resid. water}}$ – residual water content in oil phase, %

Process efficiency was estimated by the speed of water separation from broken emulsion.

2. Results and discussion

The study of the mixture of water-oil emulsions of wells that were treated and non-treated by ASP showed that:

- mixture of emulsions breaks down better at 70 °C;
- favorable ratio is 9:1 - between emulsions that were treated and non-treated by ASP;
- residual water content in broken emulsion comprises up to 10%;
- with any emulsion ratios separated water contains a lot of oil products 560 mg/l at emulsions ratio of 20:1;
- application of flocculant IronGuard-2495 has not achieved satisfactory results;

The photos of emulsion sample under the microscope with 100 g/ m³ of IronGuard-2495 and 50 g/t of Emulsotron R2601A are represented in figure 2.

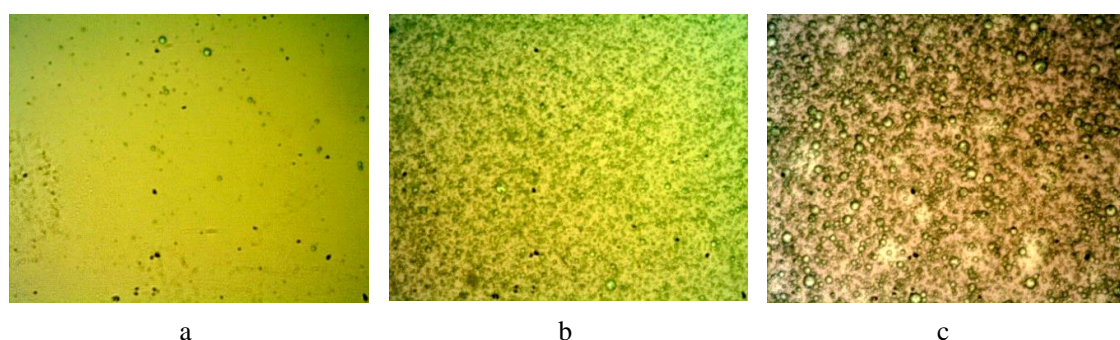


Figure 2. Emulsion sample under the microscope (600x).
Oil layer (a), interlayer (b), water phase (c)

Examining of emulsion treated by Emulsotron R2601A under the microscope DINO AM-451 (600x) showed that oil layer contains small amount of water, interlayer is a complex emulsion, and water phase is characterized by high oil products content.

Table 1. The results of laboratory researches of breaking of water-oil emulsions in Zapadno-Salymskoye oilfield

Sample no.	Agent, g/t	Water-cut, %	Amount of separated water in % over the time, min.						Residual water content in % over the time, min.						Note
			5	10	15	20	30	40	5	10	15	20	30	40	
1	Intex-720, 50 g/t	40	63	95	99	99	99	99	20	3.2	0.8	0.8	0.8	0.8	Sharply defined interface, visually clean
2	Emulsotron R2601A, 50 g/t	40	88	95	99	99	99	99	8	3.2	0.8	0.8	0.8	0.8	Sharply defined interface, dirty water
3	Without agent	40	0	0	0	0	0	0	40	40	40	40	40	40	No boundary interface, emulsion was not broken

Water-oil emulsion of the wells that were not ASP treated breaks by 99% over 15 minutes, having sharply defined interface and clean water. In case of thorough mixing emulsion is kneaded.

3. Conclusions

On the basis of laboratory research and results of pilot tests on Emulsion Breaking Unit (EBU) the following results were obtained:

1. Water-oil emulsion of the flowing wells that were not ASP treated breaks over 10-15 minutes at 70°C with specific flow of demulsifier of 50-70 g/t of oil. Residual water content in oil is less than 5 percent. Refinery water is visually clean with sharply defined interface.

2. Microemulsion (multiple emulsion) formed after ASP application has low boundary tension, high pH. It contributes to transfer of oil phase into a water one, forming oil-in-water emulsion. Residual water is characterized by high oil products content.

3. According to the data obtained in the course of the laboratory research on dilution of ASP-treated emulsion it is found that favorable ratio is 9:1. Residual water content in oil phase is less than 10 percent.

Dosing of demulsifiers at EBU input has not achieved satisfactory results. In liquid arriving for treatment on EBU boundary tension has the value close to zero. Additional dosing of the agent decreasing boundary tension has an adverse effect both on oil and residual water quality.

Oil-in-water emulsion is stable. Classic method are not suitable for residual water treatment:

- sediment gravity flow;
- filtration (filtration through Blue ribbon paper filter with pore size 3-5 microns).
- centrifuge test. (The test was performed at 170° revolutions, temperature – 70°C during 40 minutes).

Alkaline condition (pH=10-11) has adverse effect on demulsifying ability of agents, flocculation and boundary tension.

For breaking of water-oil emulsion at EBU before interchanger water or water-oil emulsion from the well that were not APS-treated in ratio of 1:9 shall be delivered.

Residual water after EBU must be prepared in water tanks by dilution in great volume.

There is no necessity in demulsifier dosing at EBU input.

All produced water shall be completely discharged at EBU.

References

- [1] Konoryshkina I.Y., Tsutskareva N.V. Development of effective separation of compositions based on surfactants of domestic production for oil treatment light type. // Perm: Publishing house of the Perm state technical university. 2000. P.78-82.
- [2] Galyautdinov A.A., Basimova R.A., Rahimov H.H. и др. The new demulsifiers for dehydration and desalting of crude oil. // Refining and petrochemicals. 2003. No. 10. P.73-75.
- [3] Tronov V.P. The destruction of water-oil emulsion under the influence of the surfactant. // Chemistry and technology of fuels and oils. 1982. No 12. P.24-26.
- [4] Usheva N.V., Moyzes O.E., Kuzmenko E.A., Kim S.F., Khlebnikova E.S., Gizatullina S.N., Filippova T.V. Analysis of technological conditions influence on efficiency of oilfield treatment (Article number 012047) // IOP Conference Series: Earth and Environmental Science. – 2015 – Vol. 27. – P. 1-5
- [5] Mikula R.J.; Munoz V.A. Characterization of Demulsifiers in Surfactants, Fundamentals and Applications in the Petroleum Industry, Schramm, L.L. (Ed.), Cambridge University Press: Cambridge, UK, 2000, pp. 51–78.
- [6] Smith V.H.; Arnold K.E. Crude Oil Emulsions in Petroleum Engineering Handbook, Bradley H.B. (Ed.), Society of Petroleum Engineers: Richardson, TX, 1992
- [7] Pozdnyshev G.N., Stabilization and destruction of the oil emulsion. -M.: Nedra, 1982, 221 p.
- [8] Buhidma A. and Pal R. Flow Measurement of Two-phase Oil-in-water Emulsions using Wedge Meters and Segmental Orifice Meters // Chem. Eng. J., 1996 v N 63., P. 59-64.

- [9] Pal R. Techniques for Measuring Composition (Oil and Water Content) of Emulsions // Colloids & Surfaces, 1994. - N 84. v P. 141-193.
- [10] Sokolov A. G., Shabaev E. F., Vladimirov Yu. D. current status and ways to improve dewater oil // VNIOENG, Oilfield business.1984. - 12 (84). 56 p.
- [11] Sergienko N. D. the Research, development and implementation of process preparation of oil for processing oil-water resistant vysokoporodnyh emulsions with a high content of mechanical impurities. // Diss. M.: VNII NP. 2005. 154 p.
- [12] R. Z. Sakhabutdinov, F. R. Gubaidulin and others. Features the formation and breaking of water-oil emulsion at a later stage the development of oil fields. - .M: VNIOENG publ., 2005. - 324 p.
- [13] Surface phenomena and surfactants: a Handbook. Ed. by A. A. Abramson and E. D. Shchukin, L.: Chemistry, 1984. 392 p.
- [14] Khutoryanskaya F. M., Somov, V. E., V. P. Gaskin etc. Develop and the introduction of oil-soluble demulsifier "Hercules 1017". // SB. scientific. "Kirishinefteorgsintez" LLC NIF "Inzhener-SERVIS, VNII NP ". Moscow: Tsniiteneftekhimi, 2005. Pp. 116-145.
- [15] Khutoryanskaya, F. M., Antonov, T. A., Potapochkina N. N. etc. New oil-soluble demulsifier domestic production - "Hercules 1603". Development, laboratory and pilot testing. // SB. scientific. "Kirishinefteorgsintez" LLC NIF "Inzhener-SERVIS, VNII NP ". Moscow: Tsniiteneftekhimi, 2005. Pp. 146-151.
- [16] James G. Speight, Baki Oum. Petroleum refining processes. New York: Marcel Dekker inch. 2002. 695 pages.
- [17] Jean Pierre Wauquier. Le raffinage du petrole.Tome 2,Procedes de separation.Paris: Technip, 1998, 627 pages.
- [18] GOST R 51858-2002 Crude petroleum. General specifications Standards publishing house, 2002. Standards publishing house, 2002.