Studying the formation of intermediate layers during the destruction of an oil-water emulsion on the example of the Priobskoye field

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Abstract. During oil production, as well as its transportation, the formation of persistent oil-water emulsions is inevitable. Their occurrence is associated with the ingress of water into the bottomhole zone, mixing of oil with water in the well, as well as the negative impact of water on electric submersible and sucker rod pumps. As a result, when rising to the surface, oil degassing occurs. The settling of an emulsion of water and oil leads to the formation of "intermediate layers". Within the framework of this study, it was considered what the intermediate layer is and methods of mitigating with it. The amount of sulfate-reducing and hydrocarbon-oxidizing bacteria in the samples was determined.

1. Introduction
The structure, composition and properties of the intermediate layer, the reasons and mechanism of its formation have not yet been fully understood. Their high stability and viscosity reduce the rate of separation of oil from water, which is a very big problem. It also affects economic performance. To separate well production, many different reservoirs and settling tanks have to be built. Among other things, the environment can also be affected, and in order to reduce this impact, it is necessary to dump the resulting intermediate layers into sludge storage pits, process and dispose of them.

Conventionally, the intermediate layers can be divided into several types.

Salimov M. in his research works conditionally divided the intermediate layers into lower, middle and upper ones. Solid particles settle in the lower layer, paraffin and resins are concentrated on the middle one, and paraffin accumulate in the upper layer.

In the book of Ibragimov N.G. and Ishemguzhina E.I., the formation of intermediate layers is described as follows. During separation, oil-water mixtures settle and cannot immediately go into the water zone. Drops of water are deposited on top. Then there is a gradual increase in the water layers until the amount of precipitated droplets equals the volume of droplets entering the water zone. This layer is called intermediate [1].

With an increase in the content of paraffins, iron and mechanical impurities in the layer, the layer thickness increases.
The calculation of the accumulation rate of an intermediate layer is regulated by STP–0147276–009–88 “Method of analysis of the intermediate layer during the inspection of an oil treatment unit” (an industrial standard). The calculation presented in this document is based on the correlation between the amount of impurities and the change in water content. It should be noted that this approach does not take into account all the factors that influence the formation of the intermediate layer.

The rate of formation of the intermediate layer depends on the composition and density of the oil, as well as technological parameters and droplet size.

The book also notes that the intermediate layer is formed due to the fact that the reinforcing shells on water droplets are not completely destroyed [2].

The main reasons for the formation of such a huge problem are as follows [3]:
1) Composition of reservoir products. The emulsion is more stable when a large amount of stabilizing components is included in the formation product;
2) Intensive hydrodynamic regime of fluid movement and dispersion at metering, pumping units and valves;
3) Injection of fresh water and, as a result, the formation of sparingly soluble salts (subject to the incompatibility of reservoir and injected waters);
4) Collection of spilled oil from the site of breakthrough of ground communications by the soil and return of this mixture to the collection system;
5) Mixing of fluids from different oil horizons;
6) Intensive modes of reservoir operation (for example, exceeding the normal speed modes of pumping fluid);
7) Return of poorly treated water;
8) Imperfection of technologies for limiting water inflow and hydraulic fracturing.

Currently, various technologies can be used to process layers. When choosing a processing scheme, it is necessary to take into account the properties of intermediate layers and ensure certain conditions [4]:
a) storage tanks are installed at oil treatment plants to collect intermediate layers;
b) in order to prevent hard impact on the emulsion, screw pumps are used. Severe impact can cause a shift in the liquid phase, so this problem cannot be neglected. As a result of hard action and fluid shear, droplets are dispersed, and the stability of the intermediate layer will increase even more. At a low velocity of the liquid phase, a soft effect is provided. This method helps to strengthen the drops;
c) thermochemical methods are used to separate oil and water;
d) washing of intermediate layers is carried out with mechanical impurities, surfactants, and technical detergents;
e) the strengthening of water droplets is carried out using ultrasonic methods. Due to this, a decrease in viscosity and centrifugation time is achieved;
f) by far the most effective separation method is centrifugation. A greater effect can be achieved through the use of two-stage centrifugation: the first stage is horizontal screw centrifuge; the second stage is disc centrifuge;
g) oil from the intermediate layers should be directed to the exit from the oil treatment units (OTU).

At present, the intermediate layers have not been sufficiently studied. In particular, technologies for their high-quality processing have not been developed.

The most common reason for the disruption of the OTU technological mode of operation and a decrease in the quality of the oil produced is the accumulation of the intermediate layer.

2. Methods and materials
The stages of intermediate layer processing are as follows:
- output of the intermediate layer to a separate container;
- heating and settling;
- processing with high doses of demulsifier and other chemical reagents;
- flushing with fresh or formation water;
- centrifugation, filtration, disposal, processing.

At present, the processes of transportation and preparation of well products are complicated at the Priobskoye field. This is due to the receipt of highly viscous, aggregatively stable emulsions at the preparation facilities. When they enter the reservoirs, they contribute to the formation of an intermediate layer, the destruction of which requires a lot of labor and leads to economic losses [5].

At the moment, a reagent - demulsifier SNPKh-4460-8 with a specific consumption of 28 g/t is used at all preparation facilities. The reagent is fed through the dosing unit into the liquid flow from the direct well stock 70 meters before the first stage of separation. Based on the pilot tests carried out, the alternative demulsifier reagents are DecliveV-1323, SNPKh-4315-DL, DEM 0014.

In 2018-2019, two well pads were commissioned: K.P. 47а with 4 well formations AS12 (1) and K.P. 553 with 1 well formation AC12 (1), while new chemicals in the production process were not used.

Oils can be described and characterized as heavy, highly viscous, waxy and resinous. High asphaltene content increases the risk of formation of stable emulsions.

Modeling the main properties of water-oil mixtures confirmed the increase in viscosity and density as water in its composition increased. This fact indicates the inevitable aggravation of the problem of transportation and preparation of high-viscosity emulsions, since the water cut of the produced wells is steadily increasing, which confirms the need for an urgent solution of the tasks set [6].

To identify the reasons for the formation of stable and hard-to-break emulsions at the oil treatment facilities of the Priobskoye field, the Customer selected, provided and examined several samples.

For studies to determine the type of emulsion stabilizers, both qualitative and quantitative identification methods were used.

1. Qualitative reaction for boron ion \([\text{B}^{3+}]\) was carried out according to the express method. The technique is based on the fact that at low pH, boron is in the form of slightly dissociated boric acid; at high pH, it is in the form of a larger hydrated ion. Dissociation of boric acid begins at pH > 8.

\[
\begin{align*}
\text{H}_3\text{BO}_3 + \text{H}_2\text{O} & \leftrightarrow \text{B(OH)}_4^- + \text{H}^+ \\
\text{H}_3\text{BO}_3 + \text{OH}^- & \leftrightarrow \text{B(OH)}_4^-
\end{align*}
\]

The total boron concentration in waters was determined by the sum of the concentrations of boric acid \(\text{H}_3\text{BO}_3\) and \(\text{B(OH)}_4^-\) ions in solution. The ratio between these components was characterized by the pH of water. The higher the pH, the higher the equilibrium concentration of borate ions, respectively [7].

In order to enhance the acidic properties of boric acid, polyhydric alcohols or sugars are used to form complex compounds with stronger acidic properties. Therefore, the boron ion was qualitatively determined in water alkalized with a solution of soda and treated with glycerol (1:1) at room temperature. In the presence of phenolphthalein, a pink solution of strong glycerol boric acid becomes discolored, which indicates the presence of boron ions in the water.

2. Qualitative determination of biopolymers, for example, xanthan gum, based on its ability to be "salted out" (precipitated) with an 80% solution of ethyl or isopropyl alcohol, was carried out at room temperature by mixing a sample of produced water with isopropanol in a 1:1 ratio. The test was considered positive when a precipitate appeared after mixing the components.

3. Infrared spectra were recorded on a NicoletiS 10 Fourier spectrometer using an ATR attachment (diamond). The registration and processing of spectra was carried out using the OMNIC software in the frequency range 400–4000 cm\(^{-1}\).

4. Analysis of the material/elemental composition of mechanical impurities was carried out by X-ray fluorescence analysis.

The water separated from the samples was also analyzed for the content of sulfate-reducing (SRB) and hydrocarbon-oxidizing bacteria (HOB). SRBs and HOBs were cultivated using special media (Postgate B and Raymond, respectively) [8].
An enrichment culture with a volume of 1 ml was isolated from the samples with a sterile syringe and introduced into a penicillin vial containing a nutrient medium. The film was wiped with an alcohol solution before the sample was added. Then the contents of the vial were mixed.

Then the filled vials were transferred to a thermostat at a temperature of 30–35 °C. The observations were carried out for 15 days.

At the same time, vials with the medium without adding samples were placed in the thermostat to control the sterility of the culture medium. The presence of SRBs was established by the development of the sulfate reduction process in the contaminated environment. Sulfate reduction was recorded by increasing the content of hydrogen sulfide in the contaminated environment. The presence of hydrogen sulfide was determined by the presence of a black precipitate (iron sulfide), quantitatively it was determined by iodometric titration [9].

The presence of HOBS in the studied samples was determined by the following indicators:
- turbidity of the nutrient medium;
- changing the color of the culture medium from red to yellow;
- accumulation of volatile fatty acids;
- availability of live forms of HOBS.

If during the entire observation period these signs did not appear, then this was a confirmation that the corresponding groups of bacteria were absent in the studied sample [10].

3. Results
The samples revealed a significant amount of sulfate-reducing and hydrocarbon-oxidizing bacteria, the waste products of which significantly increase the risks of the formation of highly stable emulsions and give them aggregate stability [11].

According to the analysis of solubility and fractional composition, IR spectra and XRD spectroscopy data, mechanical impurities isolated from intermediate emulsion layers were solid compounds with different solubility in acid agents (hydrochloric acid, clay acid, alkali solution).

A high content of mechanical impurities in the samples can be observed as a result of the removal of rock, corrosion products, etc., or, for example, when discharging wells after hydraulic fracturing and carrying out hydrochloric acid treatments of the bottomhole formation zone. All of these reasons have a tangible impact.

The results of the determination of sulfate-reducing and hydrocarbon-oxidizing bacteria in the samples are presented in Table 1.

| Sample | Bacteria type | SRB [c/ml] | HOB [c/ml] |
|--------|---------------|------------|------------|
| Interm. layer DNS-3 as of 07.19.2019, 21:30, demulsifier SNPKh-4315D | 10<sup>4</sup> | 10 |
| Interm. layer RVS-1, BPS-3 as of 21.07.2019, 03:30 | 10<sup>3</sup> | - |
| Interm. layer UPN as of 20.07.2019 | 10<sup>4</sup> | 10 |
| RVS-1 438 cm, DNS-5 as of 21.07.2019, 04:40, demulsifier SNPKh-4460 | No water in sample |
| USLB input sample as of, 22.07.2019 | 10<sup>4</sup> | 10 |
| 10452GS/147TSDNG-1, 22.07.2019 | 10<sup>3</sup> | 10 |
| 42550GS/615CDNG-1, 22.07.2019 | No water in sample |
| Produced water BPS-3 | 10<sup>3</sup> | - |
| Bottom water BPS-5 | 10<sup>4</sup> | 10 |
| Produced water of the UPN | 10<sup>3</sup> | 10 |
4. Conclusion
The following approaches were used to destroy the initial anomalously stable emulsion [11]:

1. Temperature exposure: the intermediate emulsion layer separated from the samples was heated to 70 °C and thermostated for 4 hours.

2. The effect of the acid composition MKhK-715-C: the intermediate emulsion layer was mixed with the acid composition MKhK-715-C in a volume ratio of 1:3, heated to 60 °C and thermostated for 4 hours.

3. The use of demulsifiers: the intermediate emulsion layer separated from the samples was mixed with one of the provided demulsifiers (basic SNPKh-4315D, SNPKh-4460, DWP-931, WNE-135) in a volume ratio of 3:1, heated to 60 °C and thermostated within 4 hours.

4. Application of destructors: the intermediate emulsion layer was mixed with a destructor (50% citric acid solution) in a volume ratio of 3:1, heated to 40 °C and thermostated for 4 hours.

5. Use of fracturing gel breakers;
6. Use of acidic compounds;
7. Physical methods.

Electric field
Samples of intermediate emulsion layers were exposed to a uniform electric field, under the influence of which the composition of the mixture was destroyed when dipole water clusters were pulled out of it. Reorientation with rotation along the lines of force of electromagnetic fields leads to the structuring of water molecules. As a result, the surface tension of the globules decreases, and coalescence occurs with the expulsion of non-polar hydrocarbon molecules beyond the lines of electromagnetic induction. The liquid processed by the electric field was settled, the volume of released water was recorded.

Ultrasonic exposure
Ultrasonic treatment of the intermediate emulsion layer was carried out for 15 min at a temperature of 20 °C, at a frequency of 50 Hz, an external voltage of ~100 V, and a field intensity of 18 W/cm². Then, the emulsions were settled at 20 °C for 1 hour. The volume of released water was recorded.

Ultrasonic action leads to the aggregation of particles of the dispersed phase, which is accompanied by the release of the aqueous phase. The decrease in the water content in the emulsion after ultrasonic exposure is due to the prevalence of the process of aggregation of water particles over the process of dispersion.

Exposure to magnetic field
The main mechanism of destruction of water-oil emulsions in a magnetic field is the impact on the reinforcing shells of oil globules in water. This effect consists in loosening the reinforcing shells at the oil-water interface, as a result of the movement of iron compounds in them towards the sources of the magnetic field. A set of neodymium magnets with a magnetic induction of 0.6 T was used as a source of a constant magnetic field. After 5 minutes of exposure, the volume of released water was recorded with each type of physical field. Heating stable intermediate layers to a temperature of 70 °C is ineffective and does not lead to the destruction of the emulsion. During the treatment of intermediate layer with demulsifiers, partial destruction of the emulsion was observed for samples No. 5 "USLB input sample as of 22.07.2019, No. 6 "10452GS/147 TsDNG-1 as of 22.07.2019" and No. 7 "42550GS/615 TsDNG-1 as of 22.07.2019".

Partial destruction of stable intermediate layers was observed when using a destructor (50%-citric acid) to destroy stable emulsions of samples No. 3 "Interm. layer UPN as of 20.07.2019" and No. 4 "RVS-1438 cm, DNS-5 as of 21.07.2019, 04:40, demulsifier SNPKh-4460". The use of 50%-citric acid for the destruction of other studied stable emulsions is ineffective. It was found that fracturing gel breakers have no effect on the studied intermediate layers: there is no separation of the aqueous phase from the emulsion treated with a breaker after holding it for 4 hours both at room temperature 20 °C and when heated to 40 °C. For the destruction of stable emulsion No. 3 "Interm. layer UPN as of
20.07.2019” acid compositions "Inhibited mixture of acids, batch No. 258", "Inhibited hydrochloric acid, batch No. 256" and "SKS 22-24%, batch No. 258" can be used. The use of the studied acid compositions for the destruction of stable emulsion No. 4 "RVS-1 438 cm, DNS-5 as of July 21, 2019. 04:40, demulsifier SNPKh-4460" is ineffective [12]. Taking into account the results of laboratory studies, there are three main reasons for the formation of highly viscous hard-to-break intermediate layers: removal of hydraulic fracturing reagents into the collecting reservoir, biocontamination of the collection and preparation system, and the presence of fine mechanical impurities. All problems are interconnected and it is worth taking a comprehensive approach to their solution, in compliance with the following recommendations:
- After hydraulic fracturing, the well should be developed into a separate container, the liquid should be disposed of at the landfill, and not returned to the reservoir;
- To increase the volume of the fracturing gel breaker and the time of its exposure, as well as to control the supply of effective bactericides in sufficient quantities;
- To identify the causes and localization of bioinfection, select effective bactericides;
- To consider the possibility of mechanical impact on the intermediate layer (screw installations) in order to destroy it;
- To carry out pilot testing of acid compositions and citric acid for the destruction of the intermediate layer;
- To conduct pilot testing on the impact of an electric field on the intermediate layer with the aim of destroying it.

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