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# Development of a demulsifier and technological process study for the preparation of highly viscous heavy oils for refinement

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## Abstract

One of the challenges in the petroleum industry is the production of highly viscous heavy oils, often accompanied by undesirable emulsion formation with very high aggregate stability. To prepare the crude oils for refinement, the oils must be destroyed. The destruction of aqueous emulsions containing highly viscous heavy oils is an intricate task owing to the comparatively small disparity in water and oil densities, as well as the high viscosity of the dispersive medium and its high content of mechanical impurities.

The problem of the destruction of petroleum emulsions arises desperately during the desalination and dehydration of crude oils with a high content of emulsifiers (resins, asphalts, paraffin, etc.) The creation of a highly efficient demulsifier and the development of an optimal technological process for the preparation of highly emulsifying oils that are distinguished by the composition and quantity of emulsifiers of West Siberian oils, which are widely refined in Russia, are the ways to resolve this challenging and timely issue. This study focuses on the viscous heavy oil of the Verbliouje deposit in the Astrakhan region. It also explains the creation of an effective demulsifier for the destruction of petroleum emulsions characterized by a very high emulsifying power and the fundamental principles of the development of deep dehydration technology and desalination of such high-viscosity heavy oils.

**Keywords:** Emulsions stability; Demulsifier; Heavy oils; Dehydration of crude oil; Desalination

## 1. Introduction

Oil production and transportation in the petroleum industry *via* pipelines results in the formation of water-oil emulsions owing to the presence of turbulent flow and pressure changes in choke valves[1-2]. During the steam treatment of crude oil and desalting process, water is also injected. Water droplets or brine are constantly mixed with crude oil to form water-in-oil emulsions. There are several impurity elements in the crude oil extracted from a reservoir. It may also contain hydrocarbons, such as asphaltenes, waxes, resins, solids from crude, and carboxylic acids, which serve as natural emulsifiers[3]. Some of these things can build up at the water-oil (w/o) interface, forming a solid film around the droplets. By hindering the coalescence of water droplets, this film promoted the formation of a stable w/o emulsion[4]. The co-production of water and crude oil can cause several problems. Many factors are involved, such as issues related to increased crude oil viscosity due to the presence of films. These issues may include corrosion in the production line, and industrial catalysts. Then the need to install extra equipment for the production of crude oil of export quality will be extra cost. From a financial and operational point of view, it's important to separate water from crude oil before moving

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it and making it better. There are four ways to reduce crude oil viscosity: mechanical, chemical, thermal, and electrical[5]. Among them, chemical demulsification are often employed in the dewatering of crude oil emulsions, but several parameters are involved in the efficiency of demulsification. The stability of the emulsion can be affected by the variation of each following parameters, such as salts concentration, temperature, concentrations of the emulsifier/demulsifier, time and rate of agitation, pH, oil/water content, size, and distribution of the droplets[6].

The study here was conducted incrementally in stages. Initially, the physicochemical characteristics of the camel field oil of the Astrakhan region were investigated. Subsequently, the selection of the demulsifier among the used demulsifiers in the industry was done. Then, the emulsifying power of petroleum and its mixtures with the diluent was studied. We carried out studies to develop an efficient composite of demulsifier and to determine the optimical parameters of the dehydration and desalination process on the crude-electric desalination pilot plant in the VNI-NP[7]: the specific performance of the electric dehydrator, temperature amount of the used wash water and demulsifier, the ratio of the oil-kerosene fraction. The actual process of deep dehydration and desalting of oil in a desalting unit was shown. The Mathematical processing, analysis of experimental data and choice of optimal parameters of the technological process were also demonstrated.

## 2. Material and methods

The chemicals and methods used in this study were selected based on their suitability and economic feasibility. The demusilfiers (oxyalkyl alkylphenolic-formol resins) used are listed in this study, including those with wetting agents. To determine the water content of the crude oil in the laboratory, we used the gasoline fraction, which has a boiling point interval of 80–150 °C. To develop an efficient demulsifier, we used a mixture of solvents: xylene (boiling point 144.4 °C) and isopropyl alcohol (boiling point 82 °C). To dilute the heavy viscous oil, the kerosene fraction, which has a boiling point in the 150–250 °C range, was used as the diluent. The solvent, gasoline, and kerosene fractions were provided by KINEF SARL.

KINEF is a crude oil refining company located in the city of Kirish in the Leningrad Region. KINEF is the leading supplier of petroleum products in northwestern Russia. It is a manufacturing company that produces a wide range of petroleum products, such as fuels of all types and raw materials, for chemical industries.

### 2.1. Method for determining the emulsifying power of crude oil

The emulsifying power characterizes the ability of an oil to form stable emulsions. Before determining the emulsifying power of crude oil, its water content in crude oil was determined using the Dean and Stark method. The artificial oil emulsion was prepared as follows:

In a 500 $cm^3$ glass volume, 140 $cm^3$ of dehydrated oil and 60 $cm^3$ of distilled water were transferred. The mixture was stirred for 10 min using an agitator at a frequency of 2000 revolutions/min. The prepared emulsion was poured into centrifuge tubes with a capacity of 100 $cm^3$ and a rotation frequency of 2000 revolutions/min was used for centrifugation for 20 min. The amount of water released was measured. The emulsifying power (EP) of the crude oil was calculated as the ratio of the volume of water released during centrifugation to the total volume of water in the oil.

$$EP = \frac{Vtotal\ water - Vreleased\ water}{Vtotal\ water} \text{ x } 100\%$$

### 2.2. Method to evaluate the effectiveness of a demulsifier

The effectiveness of the action of the demulsifier was evaluated according to the amount of water released during centrifugation (in %) compared to the total content in the emulsion. To determine the effectiveness of our studied oil, we prepared two samples of 30% emulsion with distilled water. The solution was mixed using a mixer at a rotation frequency of 500 rpm for 10 min. The resulting emulsion was poured into a centrifuge tube. Then, the calculated (desirable) amount of demulsifier was poured into a centrifuge tube and maintained for 10 min in a heated water bath at 80 °C. After heating, the tube was moved manually for two minutes and then placed in a centrifuge.

### 2.3. Method for experimental selection of a solvent when developing a commercial demulsifier.

We added a mixture of 50% demulsifier and 50% solvent at room temperature (20-25 °C) until a homogeneous solution was obtained (no disturbances, deposition, and suspended particles). We then placed 50 g of the demulsifier in a graduated flask of 100 mL. The volume of the solvent was then added. The flask was closed compactly with a cap and carefully stirred until the solvent was completely dissolved. The demulsifier solution became transparent without any

deposits. Hopefully, this was observed otherwise; when the solution of any demulsifier was cloudy or contained a deposit, it was necessary for this demulsifier to experimentally choose another solvent.

## 3. Results and Discussion

### 3.1. The physicochemical characteristics of the oil and its mixture with kerosene fraction

The oil studied was characterized by high viscosity and density, which predetermines the high kinetic and aggregative stability of its aqueous emulsions and presumes a high content of resins, paraffins, and mechanical impurities, as shown in Table 1.

**Table 1** Physicochemical characteristics of the studied oils

| **Parameters** | **Heavy oil from the Verbliouje deposit** | **Heavy oil mixture and kerosene fraction*(75:25)** |
|---|---|---|
| Density, g/cm$^3$ | | |
| at 20 °C | 0.952 | 0.921 |
| at 50 °C | 0.930 | 0.900 |
| Kinematic viscosity (cSt) | | |
| at 50 °C | 64.35 | 32 |
| at 80 °C | 41.18 | 6.2 |
| Sulfur content, (Mass %) | 0.55 | |
| Resins content, (Mass %) | 28.82 | |
| Content of paraffin (Mass %) | 4.49 | |
| Flow point (°C) | +15 | |
| Water content (% vol.) | 1.3 | 0.98 |
| Chlorides content (mg/dm$^3$) | 1513 | 1100 |

The kerosene fraction used had a density of 0.830 g/cm$^3$ at 20 °C, an initial crystallization temperature of – 60 °C, and a boiling thermal interval of 150–250 °C.

The values in the table show that the studied oil is characterized by high viscosity and density, which predetermines the high kinetic and aggregative stability of its aqueous emulsions and a high content of resins, paraffins, and mechanical impurities. The high content of these substances in oil causes the formation of petroleum emulsions that are difficult to destroy during the desalination of heavy oils. By diluting our oil with the kerosene fraction in 25% proportion, we decreased the density and significantly reduced the different emulsifier contents.

### 3.2. Study of the emulsifying power of oil

The emulsifying power characterizes the ability of the oil to form stable emulsions and is determined, in particular, according to the method[8] by the amount of water settled in 5% of petroleum emulsion prepared under special conditions after centrifugation (2000 rpm). The results of studies have shown that the oil of the Verbliouje deposit of the Astrakhan region, under the standard conditions of preparation, forms very stable emulsions and comparatively considerably exceeds the stability of the emulsions of the oil «WEST SIBERIAN» as seen in table 2.

**Table 2** Emulsifying power of 6.3% oil and water emulsions

| Samples | Density at 20 °C g/cm³ | Emulsifying power (%) |
|---|---|---|
| Astrakhan oil | 0.952 | 100 |
| Heavy oil mixture and kerosene fraction in ratio | | |
| 75:25 | 0.921 | 42 |
| 50:50 | 0.891 | 28 |
| 25:75 | 0.860 | 24 |
| « West Siberian » Oil | 0.855 | 25 |

The dilution of this oil with the kerosene fraction great reduce the abilities of the oil to form very stable petroleum emulsion to values quite close to the low stability of the oil "WEST SIBERIAN."

### 3.3. The development of a new effective de-emulsifier for the destruction of petroleum emulsions formed by high-viscosity heavy oils

According to the adopted classification[9], heavy oils are oils of density.

$$\rho_4^{20} = 0{,}871\text{-}0{,}8950 \text{ g/см}^3$$

Crude oils with densities greater than 0.8950 are called bitumen oils.

Many years of experience have shown us that, among a wide range of demulsifiers used in petroleum refineries, the most effective are oxyalkyl alkylphenolic-formol (OAFR) resins[10], which were used in this study as the basic active component in the composition of the demulsifier. Previously, studies have been carried out to optimize each step of the synthesis of the basic components (condensation and oxyethylation). The optimal composition obtained from the base component was alkylphenolic-formol oxyalkyl resins (OAFR) with medium degrees of condensation (m = 4) and oxyalkylation (n = 9)[11].

On the basis of the representation of the mechanism of the rupture of petroleum emulsions and the methodology of selection of the components of the demulsifier and their functional objective, we have included in the composition of the new de-emulsifier a wetting agent — butanedioic acids, and octaglycerides (wetting agent SV-104P).

Model emulsions were used to optimize the proposed demulsifier composition. For their preparation, mechanical and emulsifying impurities were extracted from the oil emulsion samples from the Verbliouje deposit (Astrakhan region). For studies on the optimization of the proposed demulsifier composition, model emulsions were used.

Experimental studies were carried out on model emulsions with constant emulsifier content (0.7% by mass), variable water content (3.0, 16.5%, and 30% by volume), and mechanical impurities (0.1%, 1.5%, and 3.0% by mass). To organize the experiments, we used the methods of mathematical planning of experiments.

Based on preliminary studies[12], it was found that the factors influencing the breaking efficiency of petroleum emulsions are (for a constant emulsifier content):

- X1: initial water content in the emulsions (vol.%);
- X2: initial content of mechanical impurities in emulsions (% by mass).
- X3: amount of OAFR in the demulsifier composition (g/t emulsion).
- X4: amount of wetting agent in the demulsifier composition (g/t emulsion).

Emulsions (the main response functions) were used as the criteria for breaking efficiency:

- Y1: amount of water released from the emulsion (% of the initial content)
- Y2: amount of mechanical impurities released from the emulsion (% of the initial content).

As oxy-alkyl phenolic-formol (OAFR) resins, we used the basic active component of the demulsifier "Hercule 1603"[13], and as the wetting agent — octaglycerides of butanedioic acids (wetting agent SV-104P).

We determined the effectiveness of emulsion destruction by centrifugation of the emulsion samples. Table 3 presents the experimental design and results.

**Table 3** Design and results of experiments to determine the destruction efficiency of petroleum emulsion models with different OAFR and wetting agent relationships

| **Experience Levels** | **Initial content in the multiple emulsion** | | **Consumption (g/т)** | | **Ratio$X_3/X_4$ (%)** | **Amount of emulsion released (% of initial content)** | |
|---|---|---|---|---|---|---|---|
| | **Water (vol %) $X_1$** | **Mechanical Impurities (mass %) $X_2$** | **OAFR $X_3$** | **Wetting Agent $X_4$** | | **Water $y_1$** | **Mechanical Impurities $y_2$** |
| Base (0) | 16.5 | 1.5 | 525 | 350 | | - | - |
| Lower (-1) | 3.0 | 0.1 | 50 | 0 | | - | - |
| Higher (+1) | 30.0 | 3.0 | 1000 | 700 | | - | - |
| Experiences | | | | | | | |
| 1 | 3 | 0.1 | 50 | 0 | 100 : 0 | 50 | 0 |
| 2 | 16.5 | 0.1 | 525 | 350 | 60 : 40 | 90 | 95 |
| 3 | 30 | 0.1 | 1000 | 700 | 60 : 40 | 92 | 95 |
| 4 | 3 | 1.5 | 525 | 700 | 43 : 57 | 70 | 0 |
| 5 | 16.5 | 1.5 | 1000 | 0 | 100 : 0 | 73 | 50 |
| 6 | 30 | 1,5 | 50 | 350 | 12.5 : 87.5 | 77 | 55 |
| 7 | 3 | 3.0 | 1000 | 350 | 75 : 25 | 77 | 0 |
| 8 | 16.5 | 3.0 | 50 | 700 | 7 : 93 | 89 | 90 |
| 9 | 30 | 3.0 | 525 | 0 | 100 : 0 | 83 | 50 |
| 10 | 3 | 0.1 | 50 | 700 | 7 : 93 | 60 | 0 |
| 11 | 30 | 0. | 50 | 0 | 100 : 0 | 80 | 70 |
| 12 | 3 | 3.0 | 50 | 0 | 100 : 0 | 33 | 0 |
| 13 | 30 | 3.0 | 50 | 700 | 7 : 93 | 92 | 90 |
| 14 | 3 | 0.1 | 1000 | 700 | 60 : 40 | 70 | 0 |
| 15 | 30 | 0.1 | 1000 | 0 | 100 : 0 | 80 | 50 |
| 16 | 3 | 3.0 | 1000 | 0 | 100 : 0 | 33 | 0 |
| 17 | 30 | 3.0 | 1000 | 700 | 60 : 40 | 95 | 85 |

The relationships obtained during the processing of these data are presented graphically by a range of zones that characterize the state of the system with different water contents and mechanical impurities in the emulsion **(Figures 1-5**).

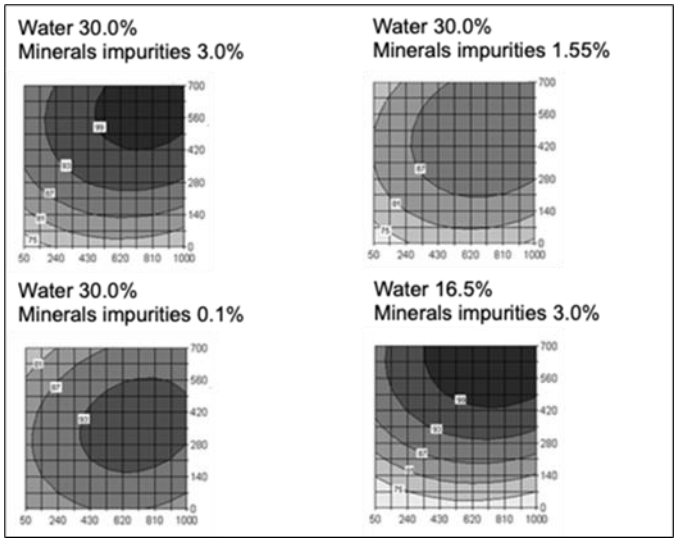


**Figure 1** Quantity of precipitated water from emulsion at different parameter values in % of the initial content. Abscissa: demulsifier OAFR (oxyalkyl alkylphenolic-formol resins), g/t; Ordinate: wetting agent, g/t

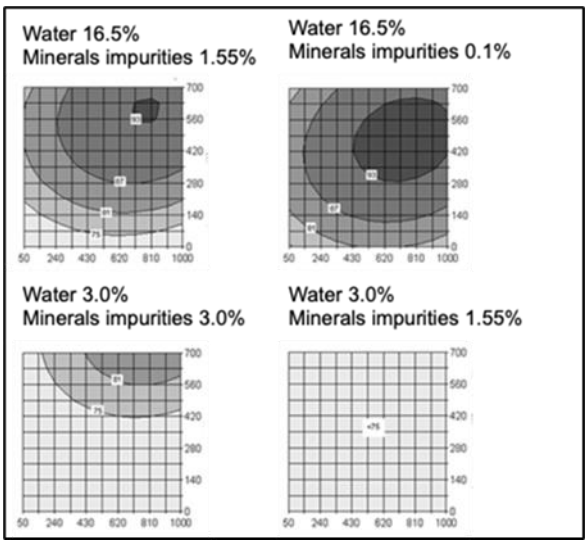


**Figure 2** Quantity of precipated water from emulsion at differents parameters values, in % of the initial content), Abscissa: OAFR (oxyalkyl alkylphenolic- formol resins) , g/t; Ordinate: wetting agent, g/t

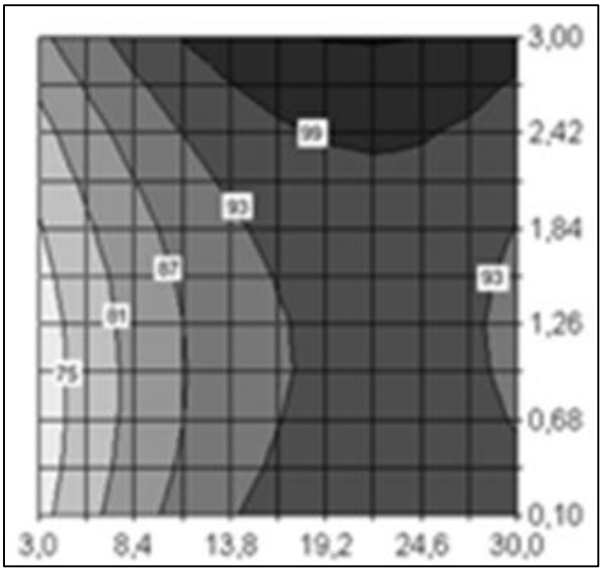


**Figure 3** Quantity of precipated water from emulsion, in % of the initial content, for the optimal composition of OAFR (oxyalkyl alkylphenolic- formol resins) and wetting agent. Abscissa: Water content, % vol. Ordinate: Minerals impurities, % mass

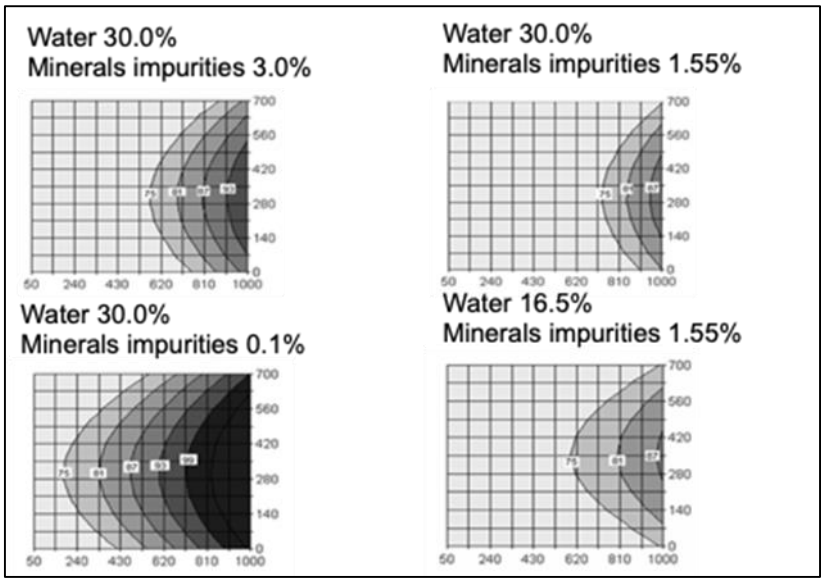


**Figure 4** Quantity of precipitated mineral impurities at different parameter values in % of the initial content. Abscissa: OAFR (oxyalkyl alkylphenolic- formol resins), g/t ; Ordinate: wetting agent, g/t

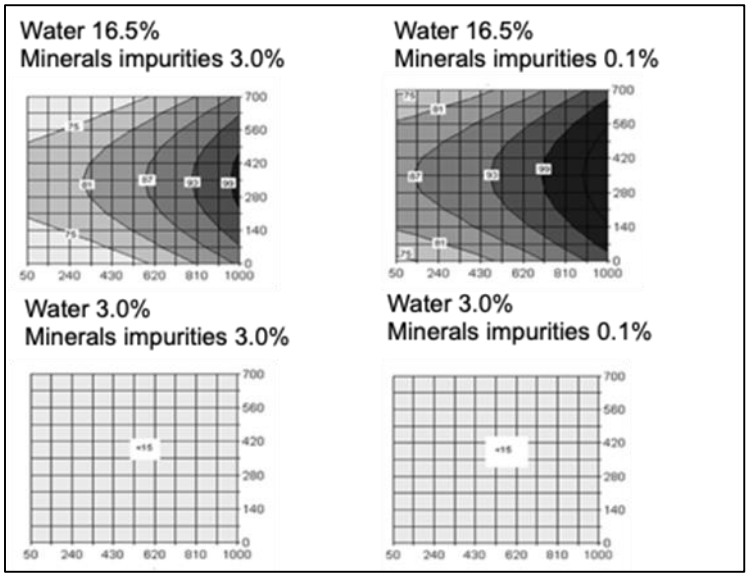


**Figure 5** Quantity of precipitated mineral impurities at different parameter values in % of the initial content. Abscissa: OAFR (oxyalkyl alkylphenolic- formol resins), g/t; Ordinate: wetting agent, g/t

In each figure, the hatched zones correspond to the greatest synergy of the simultaneous action of the OAFR and wetting agent. The figures in the figures indicate the maximum amount of water (see Figures 1-3) and mechanical impurities (see Figures 4-5) released from emulsions with reagent relationships, whose consumption is in the hatched area. The data in the figures show that the relationship between OAFR and wetting agent in the composition of the demulsifier can be predicted according to the content of water and mechanical impurities in the initial multiple emulsion.

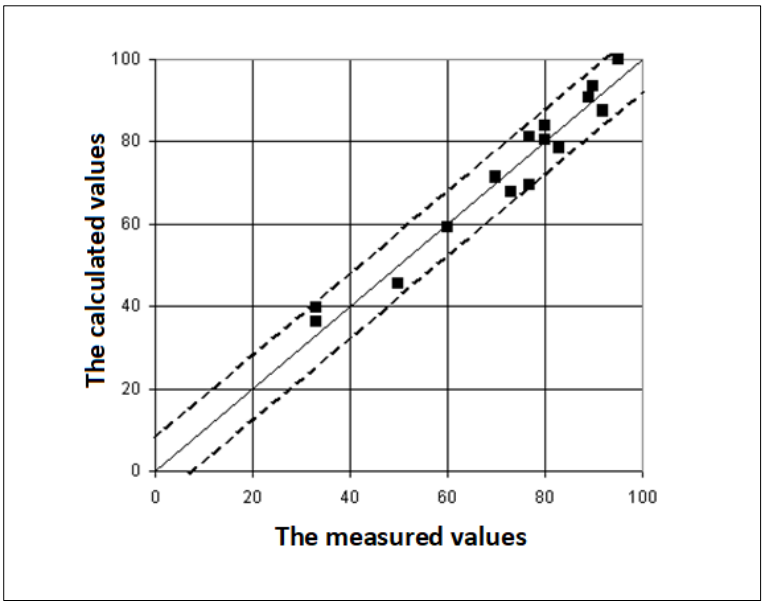


**Figure 6** Comparison of calculated and experimental data for precipitated water quantity (%) in relation to the initial content.

As the results of the experimental data processing show, the amount of water released from emulsion Y1, according to the adopted model with sufficient precision (fig. 6), can be calculated by the regression equation:

$$Y_1 \cong 88{,}78 + 12{,}83x_1 + 0{,}74x_2 + 3{,}92x_3 + 9{,}71x_4 - 4{,}72x_1x_4 + 5{,}28x_2x_4 + 2{,}28x_3x_4 - 11{,}41x_1^2 + 5{,}44x_2^2 - 5{,}20x_3^2 - 7{,}78x_4^2. \quad (1)$$

With $x_1, x_2, x_3, x_4$ — dimensional variables expressed by the initial physical parameters $X_1, X_2, X_3, X_4$ (see Table 1):

$$x_1 = \frac{X_1 - 16,5}{13,5}, x_2 = \frac{X_2 - 1,55}{1,45}, x_3 = \frac{X_3 - 525}{475}, x_4 = \frac{X_4 - 350}{350} \text{ .....(2)}$$

The dependence of the amount of water released from the emulsion as a function of the relationship between the OAFR and the wetting agent is shown graphically in Figures 1 and 2. In the next step, we used the calculation model built for the selection of the optimal composition «OAFR: wetting agent».

$$X_3^{optim} = 600 + 0,297X_4 \text{ ..... (3).}$$

The required amount of OAFR can be determined from the condition of the maximum of the entire function. It follows from the model that this quantity is entirely determined by the content of the wetting agent and explicitly does not depend on the characteristics of the emulsion (Figure 7):

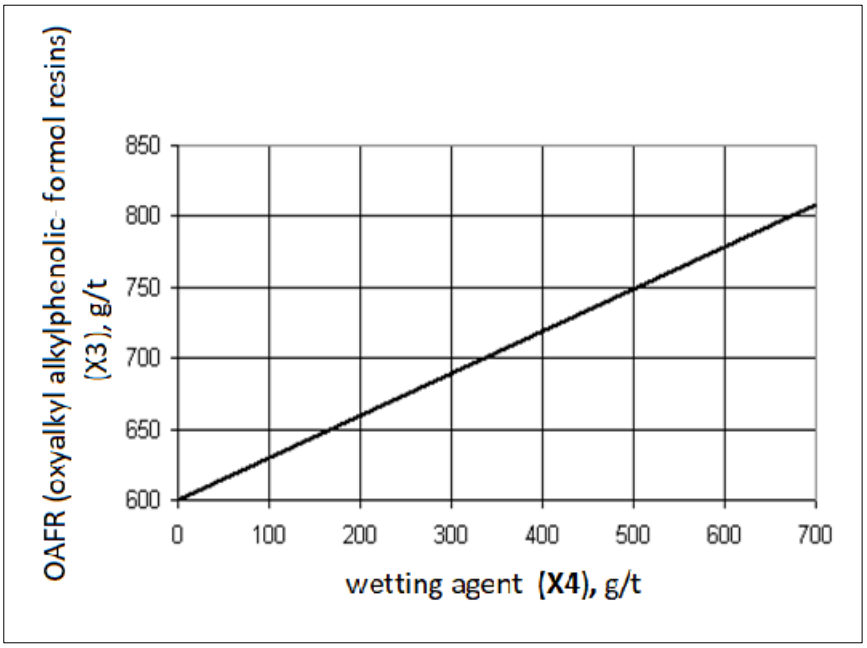


**Figure 7** Optimal ratio of OAFR and wetting agent; Abscissa: wetting agent (X4), g/t; Ordinate: OAFR (oxyalkyl alkylphenolic- formol resins) (X3), g/t

It is important to note that the required amount of OAFR indicated above varies within the limits of 600 to 800 g/t, i.e it is in the field of the experimental study (see Table 1). Thus, the results presented in Figures 1 and 2 were correct.

In turn, the required amount of the wetting agent and therefore the corresponding amount of OAFR $X3^{optim}$ depend on the water content X1 and mechanical impurities X2:

$$X_4^{optim} = 598,5 - 8,12X_1 + 84,7X_2 \text{ ..... (4)}$$

$$X_3^{optim} = 777,7 - 2,41X_1 + 25,2X_2 \text{..... (5)}$$

The optimal ratio «OAFR: wetting agent» in the studied field varies within narrow limits: from 0.5 (3% water + 3% mechanical impurities) to 0.65 (30% water + 0.1% mechanical impurities). Therefore, the ratio "OAFR: wetting agent" in the composition of the demulsifier, which ensures the maximum release of water and mechanical impurities distinguishable from the composition of emulsions, can be taken as 60:40.

With such an addition of OAFR and the wetting agent, the amount of water released depends on the composition of the emulsion (see Fig. 8). Interestingly, the best results were obtained with an initial water content of 20-23%.

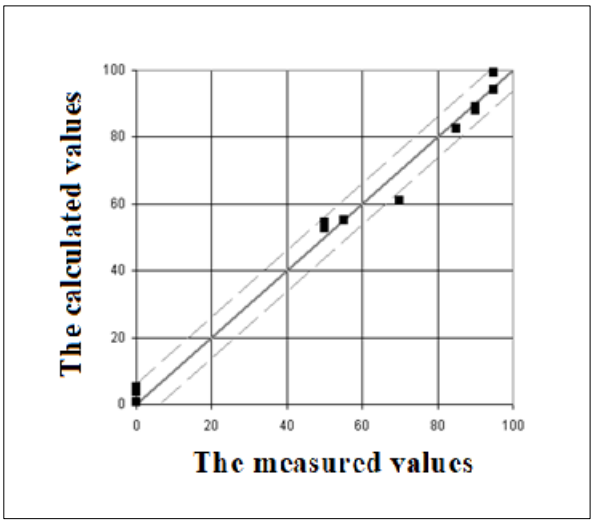


**Figure 8** Comparison of calculated and experimental data for precipitated mineral impurity quantity (%) in the fraction of the initial content. Abscissa: measured values; Ordinate: calculated values

The amount of mechanical impurities released Y2 (in % of the initial content), with satisfactory accuracy (fig. 9), can be calculated by the equation of regression:

$$Y_2 \cong 73{,}26 + 35{,}36x_1 - 4{,}27x_2 + 11{,}45x_4 - 4{,}07x_1x_2 - 3{,}27x_1x_3 + 11{,}01x_1x_4 - 44{,}43x_1^2 + 16{,}71x_2^2 - 12{,}47x_3^2 + 3{,}38x_4^2 \quad \text{.....(6)}$$

with $x_1, x_2, x_3, x_4$ — dimensional variables expressed by initial physical parameters $\mathbf{X_1, X_2, X_3, X_4}$:

$$x_1 = \frac{X_1 - 16{,}5}{13{,}5},\ x_2 = \frac{X_2 - 1{,}55}{1{,}45},\ x_3 = \frac{X_3 - 525}{475},\ x_4 = \frac{X_4 - 350}{350} \quad \text{.....(7)}$$

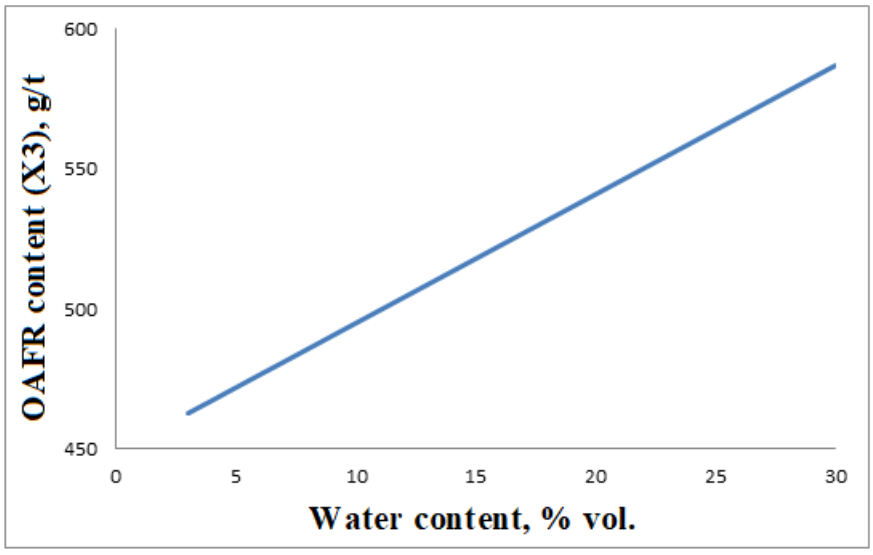


**Figure 9** Relation of OAFR, optimal for the separation of mineral impurities in the the water content fraction in the emulsion. Abscissa: water content, % vol. Ordinate: OAFR (oxyalkyl alkylphenolic- formol resins) (X3), g/t

$$X_3^{optim} = 448{,}9 + 4{,}6\,X_1 \quad \text{.....(8)}$$

To put our new demulsifier in a commercial form, we conducted studies on the choice of a solvent that can ensure the stability of the solution of the active components of the demulsifier. Because of the different solubility of the components "OAFR" and "wetting agent" in aromatic solvents and alcohols, we chose a mixture of solvents xylene + isopropyl alcohol in a ratio of 60:40, so an analogy of the ratio "OAFR" and "wetting agent" in the active part of the demulsifier.

In Table 4, we show the results of the studies on the stability of samples of commercial demulsifiers when using different solvents.

**Table 4** Study of the commercial* demulsifier samples stability when using the different solvents. N.B __ no results, * Ratio active component and solvent 50/50, ** at 20 °C, *** at -18 °C

| **Actif component (proportion)** | **Solvent (proportion)** | **Time** | **Time** | **Time** |
|---|---|---|---|---|
| | | **24 h**** | **48 h**** | **120 h***** |
| OAFR + SV-104P (60:40) | Petroleum solvent 130/150 + methyl alcohol (60:40) | Differentiation | __ | __ |
| SV-104P (60:40) | Isopropyl alcohol | Stable | Stable | Stable |
| OAFR + SV-104P (60:40) | Isopropyl alcohol | Differentiation | __ | __ |
| OAFR + SV-104P (60:40) | Petroleum solvent 130/150 | Differentiation | __ | __ |
| SV-104P (60:40) | Toluene | Differentiation | __ | __ |
| OAFR + SV-104P (60:40) | Toluene | Differentiation | __ | __ |
| OAFR + SV-104P (60:40) | Toluene + Isopropyl alcohol | Deposits | Stable | Stable |
| OAFR + SV-104P (60:40) | Xylene + Isopropyl alcohol | Stable | Stable | Stable |

The efficiency of the demulsifier composition, with an optimal proportion of components, was verified during the destruction of the oil emulsion samples from the Verbliouje deposit (Astrakhan region). Simultaneously for comparison under identical conditions, we tested the demulsifiers «Hercule 1603S» (SARL Koltec-EcoHim) and «M-109» (TOHO KEMIKL).

The tests were conducted under laboratory conditions using the "Bottle test" method (thermal settling at 80°C and centrifugation). We evaluated the effectiveness of the demulsifiers, based on the residual content of water and mechanical impurities in the upper layer of emulsions.

The results of Table 5 show that the application of the composition developed by the demulsifier OAFR + SV-104P (60:40) led to the destruction of the petroleum emulsion. It should also be noted that the effective composition developed from the composition of the demulsifier, as shown in the data in Table 5, can be used both at the stage of oil preparation at the place of exploitation, and in the desalination unit, during desalination and deep oil dehydration.

**Table 5** Results of comparative laboratory tests* of the destruction efficiency of the oil emulsion sample from the Verbliouje deposit (Astrakhan region), when applying different demulsifiers. * Conditions of the experiment: original content in the sample of the emulsion (ρ=0.942 g/cm$^3$): water — 36% vol.; mechanical impurities — 1.2% of the mass.

| **Demulsifiers** | **Residual content in the top layer of emulsion (50 % vol.)** | |
|---|---|---|
| | **Water, % vol.** | **Minerals impurities, % mass.** |
| **Control | 29 | 0.96 |
| «Hercule 1603» | 3.6 | 0.48 |

| | | |
|---|---|---|
| M-109 | 1.7 | 0.14 |
| OAFR+wetting agent (60:40) | 1.8 | 0.08 |

**Control is without demulsifiers

Therefore, for emulsions with a high-water content and mechanical impurities, we otimized the composition of the designed demulsifier (OAFR + a wetting agent). Using the mathematical analysis method, we defined the optimal ratio of OAFR and wetting agent SV-104P in the composition of the demulsifier as 60:40.

The effectiveness of the optimal composition of the demulsifier was verified during the destruction of a real sample of stable emulsion of the heavy oil deposit Verbliouje (Astrakhan region) in comparison with an ordinary demulsifier and a better sample of demulsifier of foreign origin. We demonstrated the high efficiency of our developed demulsifier.

### 3.4. Studies in the desalination unit

Studies have been conducted to determine the optimal process parameters and the amount of desalination require to ensure deep oil preparation. The optimal parameters (specific desalination productivity, temperature, washing water consumption, and oil ratio: kerosene fraction) and the technological regime of deep desalination and oil dehydration were carried out in the desalination unit of the laboratory of the Russian State Research Institute for Crude Oil Refining (VNI-NP) for desalting the oil and mixing it with the kerosene fraction at an electrical level under the following conditions:

The specific productivity of the desalter, 0.5-1.5 towers/towers.h.

- Temperature, 80-130 ºC.
- Wash water consumption, 0-10% vol
- Consumption of demulsifier (OAFR + SV-104P), 0-50g/t.
- Pressure, 0.8-1.0 MPa.
- The oil ratio: kerosene, 100:0%, 75:25%, 50:50%.
- Chloride and water contents were 1513 mg/dm$^3$ and 1.3% vol. respectively.

The selected factor variation intervals based on preliminary experiments in the desalination pilot unit, are listed in Table 6.

**Table 6** Levels of variation in the parameters of the experiments for the dehydration and desalination of very viscous heavy oil from the Verbliouje deposit (Astrakhan region)

| **levels of experience** | **Lower -1** | **medium 0** | **higher +1** |
|---|---|---|---|
| $X_1$ | 50 | 75 | 100 |
| $X_2$ | 0.5 | 1 | 1.5 |
| $X_3$ | 80 | 105 | 130 |
| $X_4$ | 0 | 25 | 50 |
| $X_5$ | 0 | 5 | 10 |

The experimental planning matrix and results of the dehydration and desalination processes are listed in Table 7.

**Table 7** The plan and results of the experiments

| № | $x_1$ | $x_2$ | $x_3$ | $x_4$ | $x_5$ | Y1 | Y2 |
|---|---|---|---|---|---|---|---|
| 1 | -1 | 1 | 1 | 1 | 1 | 0.49 | 63.1 |
| 2 | 1 | -1 | 1 | 1 | 1 | 0.5 | 90.2 |
| 3 | 1 | 1 | -1 | 1 | 1 | 1.1 | 426 |
| 4 | -1 | -1 | -1 | 1 | 1 | 0.27 | 17.5 |
| 5 | 1 | 1 | 1 | 1 | -1 | 0.63 | 483.1 |
| 6 | -1 | -1 | 1 | 1 | -1 | 0.9 | 491.8 |
| 7 | -1 | 1 | -1 | 1 | -1 | 0.7 | 518 |
| 8 | 1 | -1 | -1 | 1 | -1 | 0.46 | 807.1 |
| 9 | 1 | 1 | 1 | -1 | 1 | 1.6 | 512.2 |
| 10 | -1 | -1 | 1 | -1 | 1 | 0.24 | 43.6 |
| 11 | -1 | 1 | 1 | -1 | -1 | 0.23 | 177.5 |
| 12 | 1 | -1 | 1 | -1 | -1 | 0.45 | 118.9 |
| 13 | 1 | 1 | -1 | -1 | -1 | 1.6 | 318.3 |
| 14 | -1 | -1 | -1 | -1 | -1 | 0.3 | 93.1 |
| 15 | 0 | -1 | 0 | 0 | 0 | 0.2 | 69.8 |
| 16 | 0 | 0 | 1 | 0 | 0 | 0.19 | 45.2 |
| 17 | 0 | 0 | -1 | 0 | 0 | 0.3 | 113.5 |
| 18 | 0 | 0 | 0 | 0 | 1 | 0.33 | 61.1 |
| 19 | 0 | 0 | 0 | 0 | -1 | 0.35 | 122.1 |
| 20 | 0 | 0 | 0 | 1 | 0 | 0.21 | 58.2 |
| 21 | 0 | 0 | 0 | -1 | 0 | 0.65 | 100.5 |
| 22 | -1 | 0 | 0 | 0 | 0 | 0.1 | 49.5 |
| 23 | 1 | 0 | 0 | 0 | 0 | 0.65 | 197.5 |

In this study, we used a the third-order polynomial mathematical model.

$$y_k = a_0 + \sum_{i=1}^{5} a_i x_i + \sum_{ij=1}^{5} a_{ij} x_i x_j + \sum_{ij=1}^{5} b_{ij} x_i^n x_j^m \, , m + n = 3 \ldots\ldots\ldots\ldots (9)$$

Where $y_k$ the optimization parameters

K=1.2;

$y_1$ - residual water content in the oil after desalination plant (not more than 0.2%);

$y_2$ - residual chloride content in oil after desalination plant (not more than 50 mg/dm$^3$).

$x_{ij}$ – 1,2,,.. ,5 independent variables.

$X_1$ – the ratio: petroleum-diluent, % vol.

$X_2$ – specific desalinator production (volume 1 L), L/h;

$X_3$ – temperature, °C;

$X_4$ –amount of demulsifier Hercule 1017g/t of oil;

$X_5$ – wash water consumption, % vol.

Based on a quadratic polynomial model for residual water and chloride content, we obtained regression equations that allowed for the determination of the optimal parameters of the technological regime to achieve minimum amounts of chloride in oil.

For the response functions, the following regression equations were obtained:

$$Y_1 \cong 0{,}4020 + 0{,}0912\,x_1^2 - 0{,}0601\,x_2^2 + 0{,}0449\,x_3^2 - 0{,}1683\,x_4^2 - 0{,}0831\,x_5^2 - 0{,}0093\,x_1^3 + 0{,}0024\,x_2^3 - 0{,}0351\,x_3^3 + 0{,}1076\,x_4^3 + 0{,}0579\,x_5^3 + 0{,}0193\,x_1.x_2^2 - 0{,}0164\,x_1.x_3^2 - 0{,}0473\,x_1.x_4^2 + 0{,}0261\,x_5.x_1^2 - 0{,}0161\,x_2.x_3^2 - 0{,}0183\,x_2.x_4^2 - 0{,}1059\,x_2.x_5^2 + 0{,}1161\,x_5.x_2^2 - 0{,}0679\,x_3.x_4^2 + 0{,}0983\,x_4.x_3^2 - 0{,}0042\,x_5.x_3^2 - 0{,}0339\,x_5.x_4^2 ; \quad \text{……..(10)}$$

$$Y_2 \cong 139{,}9927 - 34{,}5237\,x_1^2 - 61{,}4709\,x_2^2 - 18{,}9054\,x_3^2 + 48{,}9787\,x_4^2 - 6{,}0913\,x_5^2 + 17{,}0893\,x_1^3 + 24{,}4165\,x_2^3 - 5{,}5112\,x_3^3 + 30{,}0206\,x_4^3 + 9{,}1691\,x_5^3 - 6{,}5417\,x_1.x_2^2 - 3{,}8493\,x_1.x_3^2 + 5{,}1382\,x_1.x_4^2 + 1{,}3931\,x_5.x_1^2 - 3{,}4569\,x_2.x_3^2 - 16{,}2007\,x_2.x_4^2 - 5{,}1125\,x_2.x_5^2 + 22{,}4882\,x_5.x_2^2 - 50{,}0667\,x_3.x_4^2 + 51{,}1333\,x_4.x_3^2 - 4{,}6667\,x_5.x_3^2 - 40{,}3229\,x_5.x_4^2 ; \quad \text{……(11)}$$

### 3.5. Discussion of the results and conclusions of the statistical analysis

- **I**n the ratio “petroleum –kerosene” 100:0 (without dilution) neither the rise in temperature nor the increase in the consumption of washing water and demulsifier. The reduction in the specific load of the desalinator has not ensured the reduction of the residual content of chlorides and water up to minimum values and required because of the high density and viscosity of the oil.
- The higher the amount of wash water injected into the oil (up to 5-7%), the less water that remains in the oil at the outlet of the desalinator. This is explained by the fact that when the input of wash water is high, the concentration of its droplets increases, and the wash water droplets take over the formed droplets. A high concentration of water droplets improves their coalescence. This mechanism implies that a sharp drop in the water content of the oil leads to a sharp drop in the chloride content. A wash water intake of 5-7% causes the opposite phenomenon (Figure 10).

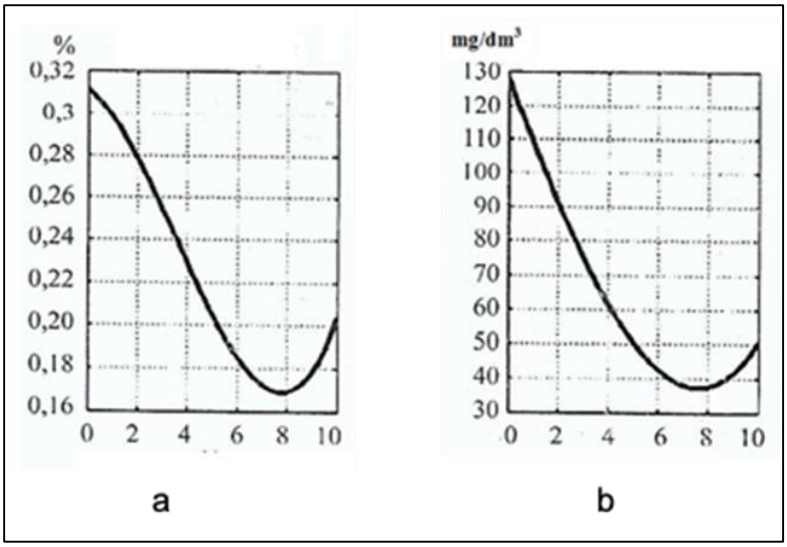


**Figure 10** Dependence of residual water content (a) and chloride (b) on the amount of wash water (petroleum: kerosene,75:25). Conditions: 105 ºC, 1 L/h, 32.5 g /t.

- When the productivity is reduced to 1 L/h (i.e., the residence time in the desalinator is increased), the residual water and chloride content decrease. A subsequent decrease does not change the results. An increase in the consumption of demulsifiers leads to a decrease in residual water and chlorides content. The optimal consumption of demulsifiers for ratios (petroleum: kerosene) 75:25 and 50:50 were 32.5 and 25 g/t, respectively (Figure 11).

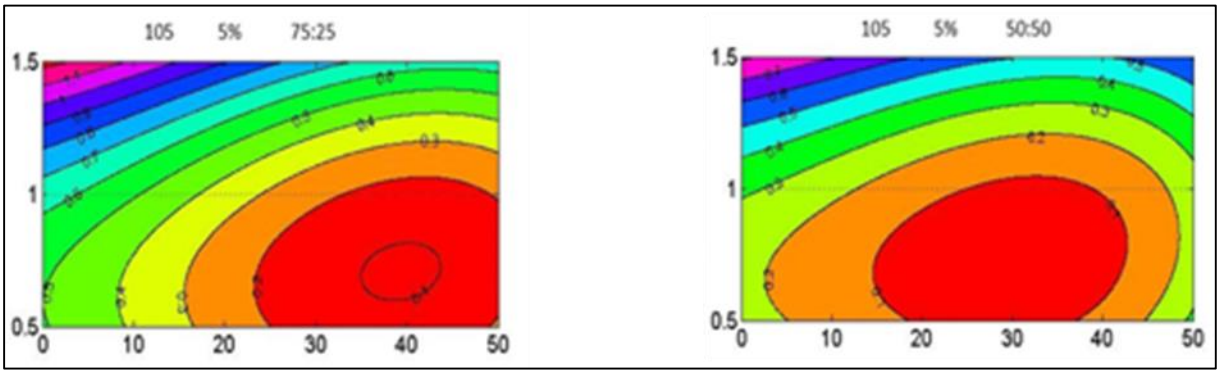


**Figure 11** Residual water and chloride content in oil as a function of desalinator productivity and demulsifier consumption. Abscissa: consommation of demulsifier, g/t; Ordinate: specific load of desaler, liter per hour (L/h)

$X_3 = 110$ °C , $X_2 = \frac{1\,L}{h}$, $X_5 = 5\%$ vol. , $X_4 = 32.5$g/t for the ratio «petrol :kerosene» – 75:25;

$X_3 = 105$ °C , $X_2 = \frac{1\,L}{h}$, $X_5 = 5\%$ vol. , $X_4 = 25$g/t for the ratio «petrol : kerosene» – 50:50;

- In desalination plants, the heating applied to oil reduces its viscosity, which increases the mobility of water droplets in the oil medium and accelerates their melting and sedimentation (Figure 12). By increasing the temperature by 25 ºC (from 80 to 105-110 °C) there is a considerable drop in chloride content (50 and 60 g/t for the petroleum ratio: kerosene 70:25 and 50:50, respectively), but a subsequent increase in temperature is insignificant.

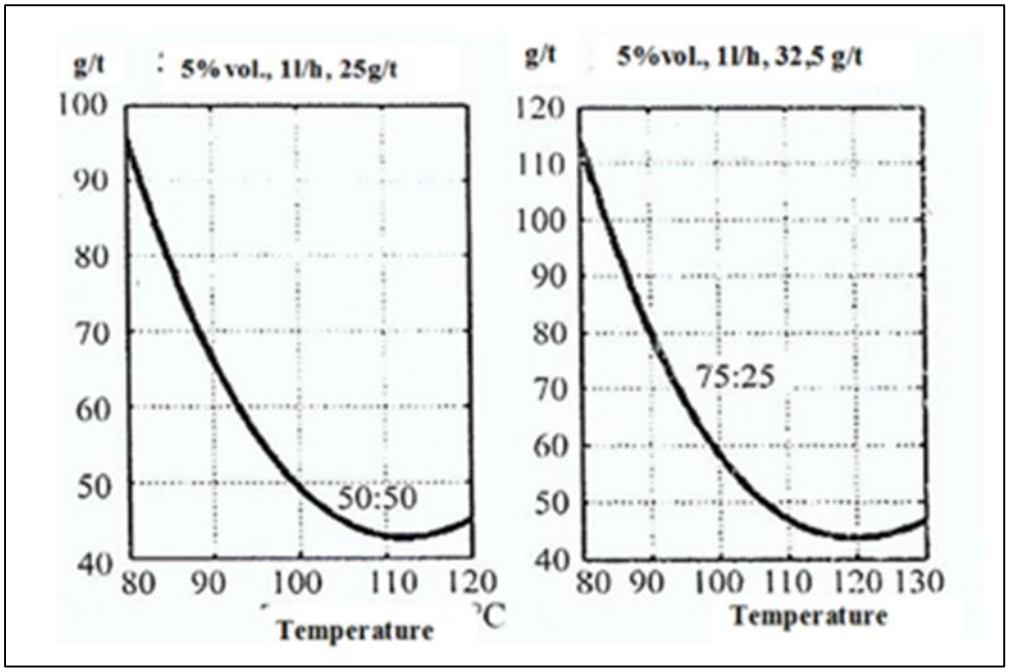


**Figure 12** Residual chloride content with respect to temperature

Based on the experiments carried out and the results of their mathematical treatment of the oil treatment in a single step, to achieve a residual water content (Y1 < 0.2% vol.) and minimum chloride levels (Y2 < 50 mg/dm$^3$) in oil, we recommend two desalination technology regimes in the oil desalination unit (Table 8).

**Table 8** Recommended technology regimes for desalination and oil dewatering

| **Parameters** | **Technology Regime** | |
|---|---|---|
| | **1** | **2** |
| Ratio oil:diluent | 75:25 | 50:50 |
| Temperature (°C) | 105 -110 | 105 -110 |
| Specific production of desalinator (L/h) | 1 | 1 |
| consumption of demulsifier (g/t) | 30-35 | 20-25 |
| consumption of washing water (% vol) | 5-7 | 4-6 |

As can be seen from the data in Table 7, in the second regime (ratio oil: kerosene 50:50) a large amount of kerosene input is required for oil dilution, which causes an increase in the specific heat consumption for heating and evaporation of oil volume unit, an increase in the heat loads of the atmospheric columns, and also an increase in pumping costs. We chose the first diet. Thus, following studies carried out using mathematical planning methods and statistical analysis of the results obtained, it was found that the required thorough preparation of the oil in the desalination unit can be ensured at two levels with the following parameters of the technological regime:

- 75:25 dilution of crude oil with kerosene cutting;
- Specific load of desalinators :1 L/h;
- 105 °C temperature;
- Washing water consumption at 5% vol.;
- Consumption of demulsifier (OAFR + SV-104P) – 32.5 g/t.

## 4. Conclusion

The instability of conventional oil prices in the international market, increase in overall fuel consumption, and rapid and gradual depletion of conventional oil deposits are pushing the industry to direct its research towards the exploitation of highly viscous heavy oils that were not perceived earlier as energy sources competitive with the chemical industry. The world has huge reserves of very viscous heavy oils, and the current energy context pushes us to consider very viscous heavy oils as an alternative energy source in the coming years. The reason for the very viscous heavy oils was the focus that aims to optimize their conversion into high-demand products and significantly reduce their impact on the environment. The data obtained from the research in the pilot desalination unit were used by Russian specialists from the laboratory of OAO VNI NP for the development of the basic data for the design of a desalination unit block for the preparation of petroleum refining very viscous heavy oil from the Verbliouje deposit in the primary oil refining desalination plant with a capacity of five hundred thousand (500,000) t/year.

## Compliance with ethical standards

*Disclosure of conflict of interest*

No conflict of interest to be disclosed.

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