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# Research of Temperature Conditions of Organic Sediments Formation in the Productive Formation at Paraffinic Oil Well Production

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# Исследование температурных условий образования органических отложений в продуктивном пласте при скважинной добыче парафинистой нефти

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*Keywords:*
organic deposits, computed tomography, temperature of oil saturation with paraffin, filtration studies, phase transitions in the reservoir, clogging of the pore space, thermobaric conditions for the formation of deposits.

The paper presents the results of the studies of temperature conditions for the formation of organic (asphalt-resin-paraffinic) deposits in the productive formation during the downhole production of paraffinic oil, including the results of experimental studies to assess the temperature of oil saturation with paraffin in the pore space of reservoir rocks. The studies were carried out in order to substantiate and develop a technology for preventing such deposits in the "reservoir – well" system. The results of filtration and rheological studies showed that for the same oil, the wax saturation temperature in the pore space of the reservoir rock could exceed the value of this parameter in the free volume. It was found that for the investigated solutions (models of highly paraffinic oils), the phase transition of paraffin from liquid to solid state, the formation of wax crystals in the pore space occurred at a temperature 3-4°C higher than in the free volume. The results of tomographic studies of the core material performed before and after filtration of a paraffin-containing solution through it with a decrease in temperature, showed that open porosity of rock samples decreased on average four times due to the clogging of their pore space with paraffin. Based on the results of the filtration experiment and computed tomography, a digital core model was created, which allowed modeling the fluid flow in the pore space of the rock before and after the formation of paraffin deposits in it. The results of calculation of the changes dynamics in the thermal field around the injection well confirmed the probability of cooling the bottomhole zone of the well to a temperature equal to the temperature of the onset of wax crystallization, as well as the probability of the cold water front advancing to neighboring production wells, which could cause a significant decrease in the productivity due to the formation of paraffin deposits in pore space of reservoir rocks. The research results are recommended to be taken into account when developing oil fields in conditions of possible formation of organic (asphalt-resin-paraffinic) deposits in the productive formation. This will make it possible to more reliably predict and effectively prevent its formation in the "reservoir – well" system.

*Ключевые слова:*
органические отложения, компьютерная томография, температура насыщения нефти парафином, фильтрационные исследования, фазовые переходы в пласте, кольматация порового пространства, термобарические условия образования отложений.

Представлены результаты исследований температурных условий образования органических (асфальтосмолопарафиновых) отложений в продуктивном пласте при скважинной добыче парафинистой нефти, в том числе результаты экспериментальных исследований по оценке температуры насыщения нефти парафином в поровом пространстве пород-коллекторов. Исследования проведены с целью обоснования и разработки технологии предотвращения таких отложений в системе «пласт – скважина». Результаты фильтрационных и реологических исследований показали, что для одной и той же нефти температура насыщения парафином в поровом пространстве породы-коллектора может превышать величину этого параметра в свободном объеме. Установлено, что для исследованных растворов (моделей высокопарафинистых нефтей) фазовый переход парафина из жидкого в твердое состояние, то есть образование кристаллов парафина в поровом пространстве, происходит при температуре на 3–4 °С выше, чем в свободном объеме. Результаты томографических исследований кернового материала, выполненных до и после фильтрации через него парафинсодержащего раствора при снижении температуры, показали, что открытая пористость образцов горной породы уменьшается в среднем в четыре раза из-за кольматации их порового пространства парафином. На основе результатов фильтрационного эксперимента и компьютерной томографии создана цифровая модель керна, которая позволяет моделировать течение флюида в поровом пространстве горной породы до и после формирования в нем парафиновых отложений. Результаты расчетов динамики изменения теплового поля вокруг нагнетательной скважины подтвердили вероятность охлаждения призабойной зоны скважины до температуры, равной температуре начала кристаллизации парафина, а также вероятность продвижения фронта холодной воды до соседних добывающих скважин, что способно вызвать значительное снижение продуктивности последних из-за образования парафиновых отложений в поровом пространстве пород-коллекторов. Результаты исследований рекомендуется учитывать при разработке нефтяных месторождений в условиях возможного образования органических (асфальтосмолопарафиновых) отложений в продуктивном пласте. Это позволит более надежно прогнозировать и эффективно предотвращать их образование в системе «пласт – скважина».

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## Introduction

Well production of paraffinic oil can be significantly impaired by the formation of organic (asphaltene-resin-paraffinic) deposits not only in the production wells but also in the productive formation. Though the subject of combating deposits of asphaltene-resin-paraffinic substances (ARPD) has been studied in multiple works, the mechanism of such deposits formation in pore space of reservoir rocks remains understudied. Some works use rheological, filtration and optical research methods as well as pulsed nuclear magnetic resonance to study the mechanism of this phenomenon [1–8].

It is known that the main factors influencing the formation of organic deposits in formation pore space are pressure and temperature. Use of formation pressure maintenance system in the course of deposits development ensures that the formation energy state remains at the specified level. But in most cases, the temperature of the injected water is not regulated. Thus, when big volume of cold water is injected, the formation temperature decreases [9–12]. The issue of pore space clogging in the bottomhole zone due to paraffin depositing caused by temperature decrease is studied in works by Borisov G.K., Yusupova T.N. et al. [13–21]. These authors undertook filtration studies that revealed that with a temperature decrease core permeability decreases, too, due to the formation of wax crystals. This being said, some scientists state that organic depositing in pore space of the productive formation may start even during the initial formation penetration as a result of cold process fluid loss [22, 23].

One of the key parameters determining the choice of the technology to prevent paraffin depositing in the formation bottomhole zone [24] is wax saturation temperature of oil within the formation. Oil is a multicomponent disperse system and a change in its composition in the course of an oil field development entails significant impact on the wax saturation temperature of oil and on other properties of the system. Even considering all currently available research methods and laboratory equipment, the researcher is not able to fully describe all possible combinations of disperse system composition or define the impact of each separate component on changing of the properties of the entire system. As multifactor analysis of the impact imposed by different oil components on the paraffin depositing is a complex process, this work analyses research methods and modeling results related to maximum simplified systems, that is of paraffin-containing solutions.

The novelty of the undertaken research manifests itself in proving by three independent methods (filtration, rheological and tomographic) that for one and the same oil its wax saturation temperature in pore space of reservoir rock may be significantly higher than the same parameter of this oil in free volume.

## Information on the Subject of the Study

The Romashkinskoye field is taken as an example of the issue of paraffin formation in the well bottomhole zone and possible solutions of the issue are proposed. The field was discovered in 1984 and represents the largest field in the Volga-Ural Petroleum Province. The average depth of productive formations is 1750 m. The initial formation temperature varies around 37 °C. The oil of the Romashkinskoye field is paraffin (about 5 %) and low resin (16.5 %), with the density of 820 kg/m$^3$. The development of the field commenced in 1952. As the size of the field is large, both peripheral and marginal artificial flooding patterns proved poorly efficient and did not ensure the formation pressure maintenance at the specified level. Therefore the field became the first in Russia to try and use a contour water flooding system. Thus, rows of injection wells were drilled to section the field into more than 20 blocks. But several interlayers stopped absorbing water over time. It is commonly believed that one of the main complicating factors for oil production at this particular field is the paraffin formation. In the 1950–60s, during the period of peak oil production level, the well cleaning interval at some wells was about 3–4 hours [25, 26]. This field is one of the few in this country, for which a long-term comprehensive study was undertaken, dedicated to temperature variations in the productive formations in the course of production, as big volumes of cold water were being injected in them. Inspection wells were used to study the impact of cold water injection on the temperature front variation in the formation during 6–7 years of operation [10, 11].

The first significant temperature drop down to 23 °C was registered in 1966 in a well located 250 m away from the injection well. The well production rate amounted to 70–110 t/day. Water injection started in 1960. The well injectivity varied from 700–1800 m$^3$/day, the formation thickness was about 10 m. The temperature of water in front of the absorbing stratum varied in the range from 7 to 12 °C in winter and from 18 to 25 °C in summer. Five months after the water injection started, the pore space was washed with water in the four-fold volume, and the production well with a water cut of 50 % was converted into an inspection well. Two other production wells can also be taken as an example: they were drilled at the distances of 390 m and 600 m from a row of injection wells, respectively. Over 6 years, the temperature in the first well dropped from 37° down to 26–27 °C. The formation in the area of the second well was washed with 1–2 of pore space of water volume, and the bottomhole temperature decreased only by 1–2 °C. The production rate in the first well was three times less as compared with the production rate of the second well (23 t/day vs. 60–80 t/day, respectively). Authors point out that the decrease of the production rate in the wells of the cooled down formations could have been caused both by the decrease in oil mobility and by the formation of paraffin crystals. Another possible factor complicating the production process could be the cooling-down of non-developed strata above and below the water injected strata [10, 11].

## Laboratory Test Method

Determination of the temperature of saturation of the model oil solution with paraffin using the rheological method. The temperature of saturation of the modelled oil solution with paraffin was estimated by preparing the 20 % wt. paraffin-containing solution. The calculated amount of kerosene was poured into a quartz glass vial. Then the calculated amount of solid paraffin was added. The bowl was sealed and heated using water bath up to 52–58 °C (until the paraffin dissolved completely). The solution was prepared immediately before the experiment.

This study used grade 1-K kerosene as per the ASTM D-3699-78 (less than 0.04 % sulfur by weight). Kerosene is obtained by oil fractional distillation at 150 to 290 °C and atmospheric pressure, producing a hydrocarbon mixture with carbon number value from $C_9$ to $C_{16}$. Kerosene density is 780–810 kg/m$^3$, its setting point standardized at –47 °C and clouding point around –40 °C. Paraffin is obtained from oil and is a hydrocarbon mixture with carbon number value from 20 to 40. Paraffin melting temperature is around 52 °C, so in ambient temperature conditions it is solid. Paraffin density is around 900 kg/m$^3$ [28].

Rheological survey was undertaken to determine the setting point of kerosene-containing solution using the automated viscosity analyser (a rheometer) at ambient pressure in a plate-plate measurement system (open measurement system). The following conditions were maintained during the test of the model solution: no slipping, laminar steady flow, no chemical change of the sample. A Peltier element was used to cool down and heat up the solution in the course of the experiment.

After the solution was prepared it was placed in a measurement system and was held there for several minutes at 60 °C. Then the experiment was performed with 5.1 s$^{-1}$ shear rate and 1 °C/min temperature decrease rate. The solution was cooled down from 60 °C to 10 °C, with the measurement system recording the solution temperatures and viscosity values. The temperature of paraffin crystals formation in the solution was determined by a break in the viscosity curve (on the viscosity vs. temperature graph).

Determination of the saturation of the model oil solution with paraffin in pore space of the rock. Filtration method was used to determine the temperature of saturation of the model oil solution with paraffin in pore space of the rock. This method is based on obtaining a dependence between the pressure gradient during solution filtration and the temperature. In this case, the temperature of solution saturation with paraffin is determined by a break in the obtained curve.

A filtration unit is composed of two mechanical duplex pumps, two piston accumulators (for the fluids under study) and a core holder. Fluid pressure is monitored and controlled using pressure sensors at the input and output of the core holder. All the assembly elements are located inside an oven. The filtration unit can generate conditions of overburden pressure and pore pressure up to 70 MPa, and temperature up to 150 °C with the accuracy ± 0.5 °C.

A core sample of 3 cm in diameter and 5 cm long was first extracted with 1:2 alcohol-benzene mixture. Then the core was placed in the oven and dried at the temperature of 105 °C until constant weight settled.

Two fluids were prepared for the filtration experiment: paraffin-containing solution with 20 % wt. concentration of paraffin, and a model of reservoir water.

The experiment procedure included four stages:

1) the core was saturated with reservoir water in vacuum conditions;

2) centrifuge method was used to create residual water saturation in the core;

3) the core sample was placed in a filtration unit. Initial temperature in the oven was set to 40 °C (which is 10 °C higher than the saturation temperature of the solution), overburden pressure was set to 4.1 MPa. The paraffin-containing solution was filtered at the constant flow rate (0.5 cm$^3$/min) and temperature decrease rate of 1 °C/h. The temperature decreased from 40 °C to 33 °C. Pressure gradient, temperature, and the amount of the pumped solution were measured;

4) filtration of reservoir water model was done at constant flow rate (0.5 cm$^3$/min) at the temperature of 33 °C until kerosene stopped coming out, in order to remove from the core all the excessive kerosene with paraffin that was not participating in the process of deposition in the pore space.

Tomographic studies of the core. Computer-aided tomography is a non-destructive method analysing rock volumetric properties. It is based on the difference in X-ray radiation absorption properties of minerals composing the rock. Rock sample was placed in the sample holder inside the tomograph chamber. After the scanning process commenced, the sample holder started its 360° revolution about vertical axis at a specified rate to obtain a set of X-ray images. X-ray radiation passes through the sample losing its intensity proportionally to the rock density and is then registered at the receiving end. The recorded data were used to create 2D shadow projections of the sample – half-tone (gray-scale) images. In such images, brightness represent the value of X-ray beams attenuation (Hounsfield scale) by the rock matrix as a result of photoelectric effect and Compton scatter. The differencies between the densities of rock, water, and paraffin allow filtering off of each phase in such images. Afterwards, a 3D sample is modeled using these images.

X-Ray computed tomography SkyScan 1173 was used for the study. This scanner is equipped with a 40–130 kW radiation source and produces resolution up to 7–8 μm.

The study was performed in three stages. The first step was to calibrate the tomograph scanner for paraffin. For this purpose a lump of hard paraffin was scanned and –600 Hounsfield measurement unit (HU) was obtained.

The next stage was to assess the ability to identify paraffin within the rock pore volume. The core was prepared by drilling a Ø 3.5 mm hole along the entire length. This sample was scanned and the volume of the hole was assessed by tomography. Then the hole was filled with melted paraffin and, as it hardened, the sample was scanned again. A mismatch between the drilled hole volume measured during the first scanning and the volume of paraffin measured during the second scanning was 3–4 %. The results are shown in Fig. 1.

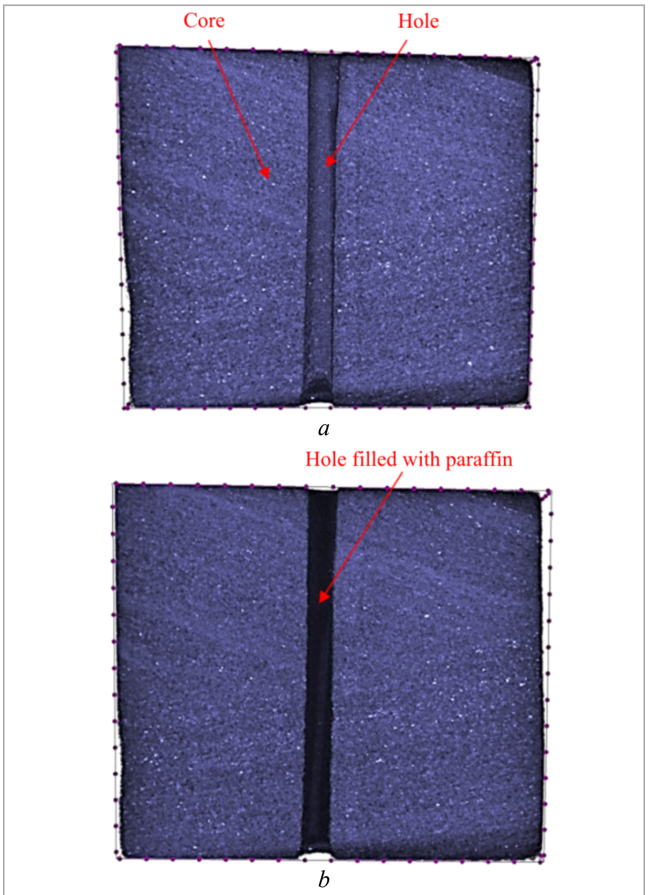


Fig. 1. Tomography study outcomes for the core with the drilled hole: *a* – core with the hollow hole; *b* – core with the hole filled with paraffin

When the digital model data were processed, the previously obtained calibration Hounsfield values for paraffin were considered. After that, the main stages of the tomographic study began.

The study was performed in two stages:

1) the extracted and dried core sample was scanned to define the initial pore volume and connected porosity;

2) then the core was scanned after the filtration of paraffin-containing solution under the temperature decreasing conditions to define the volume of the pores clogged by paraffin.

The Hounsfield unit for paraffin was taken into account when reconstructing the images. As the HU for paraffin (–600 HU), water (0 HU) and rock (≈600 HU) are very different, each phase can be distinguished in the images as well as the volume of clogging.

### Laboratory test results

The outcomes of the rheological studies are shown in Fig. 2. The paraffin-containing solution vs. temperature relation was used to determine its paraffin saturation temperature: it amounted to 30 °C. It should be noted that for the same solution this parameter measurement results may vary between the open measurement system and reservoir rock pore space.

Fig. 3 shows the results of the filtration experiment.

The data in Fig. 3 indicate that pressure gradient increases when temperature decreases. A minor pressure gradient increase in the range of 40–35 °C is due to the increase of the solution viscosity. A sharp pressure gradient increase in the range of 35–33 °C indicates that core permeability decreased, which can be explained by the formation of paraffin crystals in the pore space.

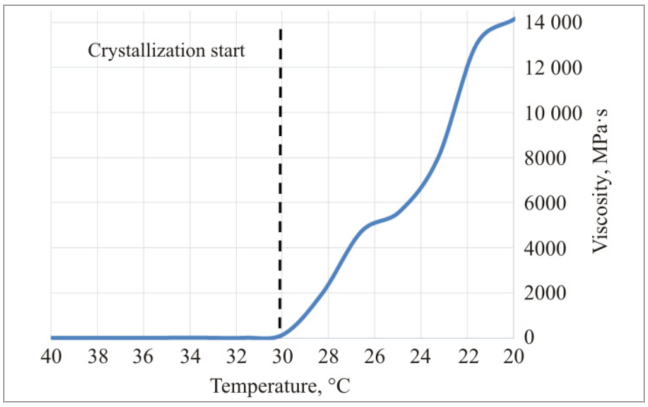


Fig. 2. Viscosity vs temperature relation of paraffin-containing solution under temperature decreasing conditions

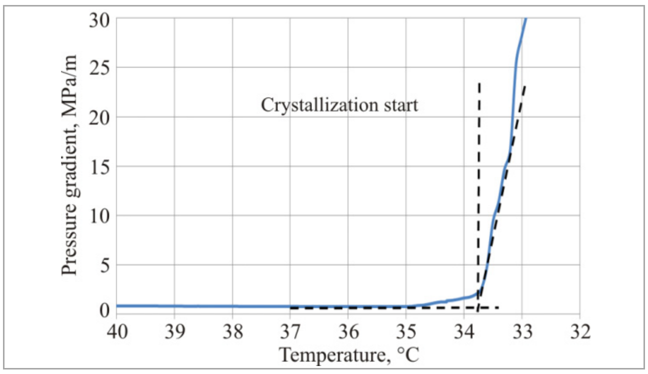


Fig. 3. Pressure gradient vs temperature relation during paraffin-containing solution filtration under temperature decreasing conditions

The comparison of the above rheological and filtration studies results indicates that for paraffin-containing solution the formation of paraffin crystals in pore space of rock was registered at 3–4 °C warmer conditions as compared with the open measurement system. The authors explain this phenomenon by the fact that the filtration method is more sensitive as compared with the rheological (viscosimetric) method. The bend of the viscosity vs. temperature curve appears at the temperature, at which the solution under study starts to form paraffin space lattice. The process of paraffin formation, from crystal nuclei appearance to space lattice creation, can last for a long time depending on the tangential stress and temperature gradient. The core pore space consists of pores and channels of various diameters, comparable to paraffin crystal nuclei in size. Therefore, even stable paraffin crystal nuclei may become obstacles for fluid mobility in the pore space. Consequently, the beginning of paraffin crystallisation in the solution is registered by the filtration method at higher temperature.

A computer-aided tomography method was used to estimate the change of core pore size due to paraffin crystallisation. 3D models of the core before and after filtration of the paraffin-containing solution were created, and the sample connected porosity was determined. The test results are shown in Fig. 4.

Micro tomography measurements of connected porosity of the rock sample were as follows:

– extracted rock sample – 9.0 %;

– rock sample after filtration under decreasing temperature conditions – 2.1 %.

Thus, the above data indicate that after filtration of the paraffin-containing solution under the decreasing temperature conditions the connected porosity of the rock sample decreased from 9.0 down to 2.1 % which is indicative of a significant clogging of core space by paraffin.

For the purpose of a more detailed analysis of changing pore space in the rock sample due to clogging by solid particles, a detailed pore channels distribution over the diameter before and after filtration was built. The results are shown in Fig.5 and indicate that 76.7 % of pore space (in the pore diameter range from 20 to 70 μm) is affected by the paraffin clogging process. Pores over 70 μm are not considered, as they do not participate in the clogging process. Presumably, the pores with the diameter comparable with (and less than) the size of the paraffin particles appearing in kerosene get clogged. Pores with the diameter slightly bigger than the size of paraffin particles adsorb paraffin. The survey results have shown that pores of bigger size are not involved in the process of clogging, which is in line with several other studies [29, 30].

Modeling of rock pore space clogging. Generalized Navier–Stokes equations and Darcy's law were used to describe the flows of incompressible fluid within the pore space. Normal and tangential velocity components at outer borders and solid surfaces were assumed to be zero. The dynamic model represents the pore space by two continuously permeable and impermeable paths. Fluid flow in the pore medium can be described by specifying a total porosity model. Those model areas where geometry of pore channels is too complex, flow resistivity factors may be specified. In this case, the model contains a diffusion factor.

Inertial resistance factor, obtained from the generalized Darcy's law can be written down by the following equation:

$$k_{IRF} = -\frac{2\Delta PA^2}{\rho LQ^2}, \qquad (1)$$

where $\Delta P$ – pressure drop along the sample of $L$ length, Pa; $A$ – filtration surface, m$^2$; $Q$ – volumetric fluid flow rate, m$^3$/s.

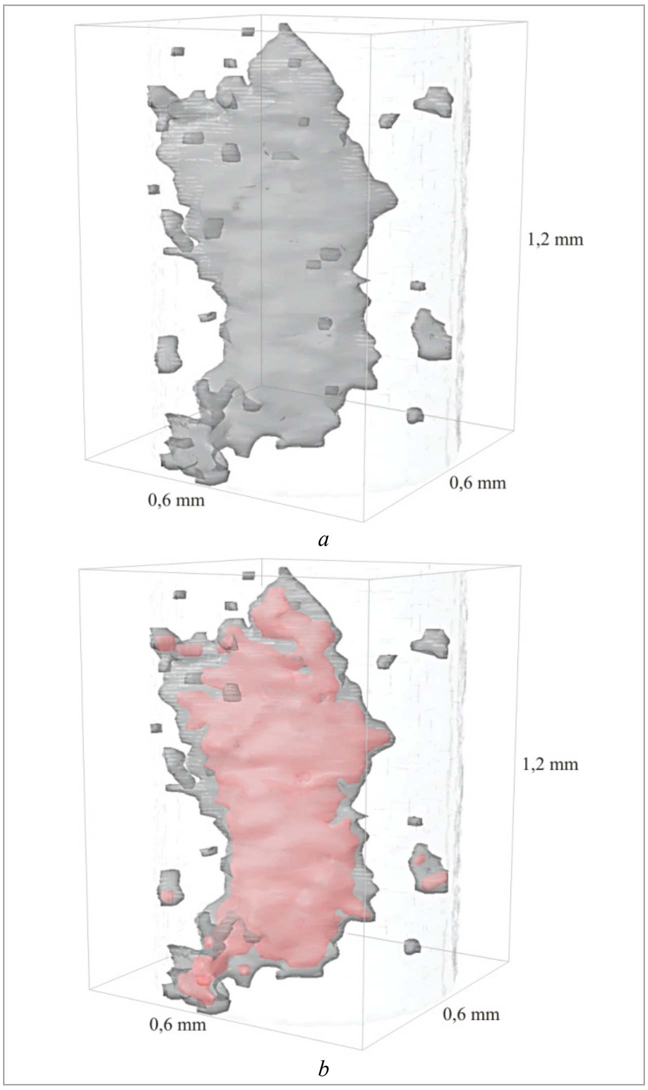


Fig. 4. Models of core pore space: *a* – extracted and dried sample; pore of 0.6×0.6×1.2 mm core sample, light gray – rock, dark gray – pore space; *b* – sample after filtration of the paraffin-containing solution under decreasing temperature conditions; light gray – rock, dark gray – pore space, red – paraffin

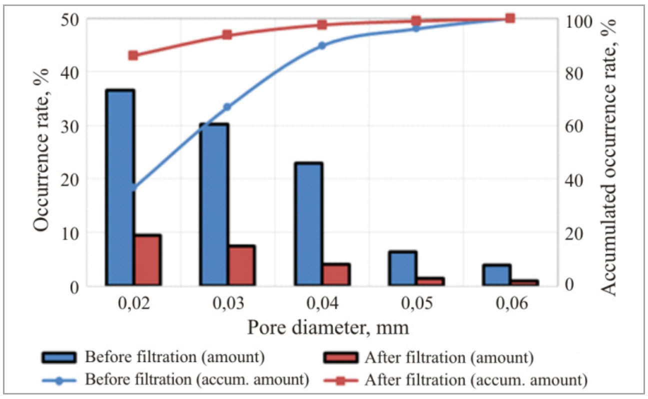


Fig. 5. Distribution of the core pore volume over the diameter before and after paraffin-containing solution was filtered though it

In laminar flows passing through the pore medium, the pressure drop is usually proportional to the rate, and the inertial resistance factor may be considered equal to zero. The filtration model therefore comes down to the linear Darcy's law.

Two dynamic models (pore domains with filtration properties) were simulated based on the data obtained by computer-aided tomography and adjusted for the results of filtration experiments before and after paraffin deposition in the pore space. Fig. 6 shows rate profiles in three sections of the core sample for two dynamic models, as well as flow lines. Fluid filtration direction coincides with the direction of $Y$ axis.

Paraffin sedimentation reduces pore hydraulic diameter and therefore the porosity and permeability decrease. Paraffin particles that get adsorbed on the pore channels surface occupy the space needed for filtration, thus the areas with high filtration rates diminish, while the areas with minimum filtration rates grew as compared with the initial sample (see Fig. 6, *a*).

3D modelling using digital core allows for quick determination of permeability and porosity properties of a sample without costly and time-consuming filtration experiments. Quite often, there is not enough core material to duly justify a technology of formation stimulation, and traditional laboratory methods provide no opportunity for repeated modeling of filtration processes after core sample is subjected to chemical or physical impact (such as after acid treatment), as the initial core structure gets destroyed. In this case, a core digital model comes to aid; it can also be used in cases when core the filtration survey method is infeasible (for example, for poorly cemented rocks).

Calculation of temperature field when cold water is injected. When cold water injection is used in the course of oil fields development, the temperature field of a productive formation may vary and cause phase transitions of paraffin contained in oil during filtration. To assess the probability of paraffin crystallization in pore space of the formation, the authors calculated variation of the temperature field in the vicinity of the cold water injection well of the Romashkinskoye field. Lauwerier's concept was the basis of the calculations [43]. The concept is to calculate heat transfer within a formation of constant thickness, porosity, and permeability. The main assumptions and simplifications were as follows: vertical temperature gradient in the formation is disregarded; the formation bottom limit is impermeable to water and heat, while the top limit is impermeable to water only. Lauwerier proposed the equations to calculate temperature distribution over formation depending on time and location when hot water is fed into the injection well. Later Barends [31] proposed to use the Lauwerier's concept as the basis for calculation of temperature field of hot formation when cold water is fed into the injection well.

The calculation results are shown in Fig. 7. The graph was created taking into account the geological properties of the rocks of the field and the information about the development process.

The figure shows that one year after cold water injection started, the formation temperature in the area 280 m from the bottomhole of the injection well started to decrease. After 7 years of the injection well operation the temperature front would move by 600 m. Thus, there is evidence that formation temperature can decrease and, consequently, paraffin crystallization in the pore space and clogging of the pore volume between wells can occur. It should be noted that accuracy of the calculations is limited by vertical heterogeneity of the formation, which leads to washing the highly permeable formation areas with bigger amount of water, which promotes their faster cooldown.

Estimation of volume of paraffin deposits in formation. At the temperature lower than its saturation temperature paraffin can be partly dissolved, suspended in oil and partly adsorbed at on the surface of pore walls. Paraffin dissolvability and deposition can be described using the ideal solution theory [33]:

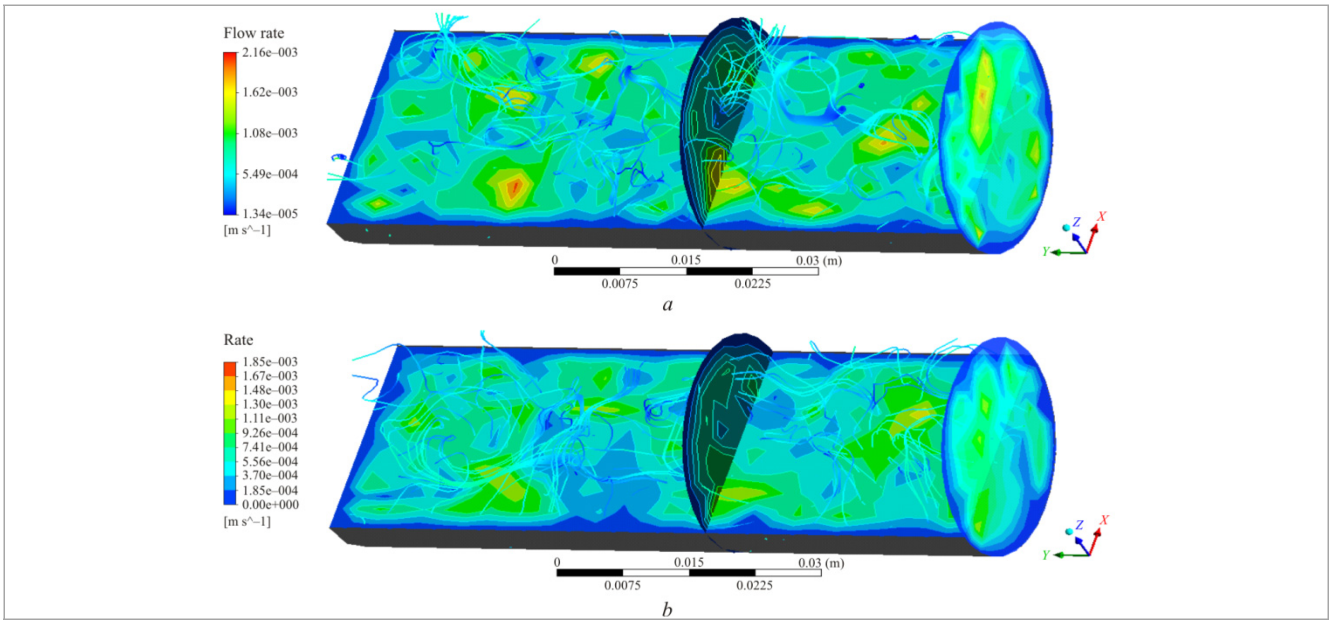


Fig. 6. Flow rate profile through the core sample: *a* – before paraffin deposition; *b* – after paraffin deposition

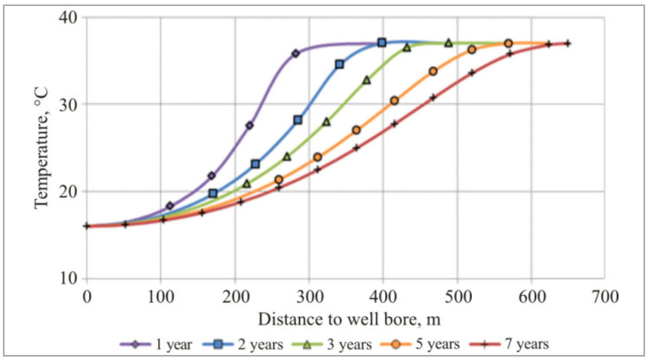


Fig. 7. Calculated field of formation temperatures in the vicinity of injection well

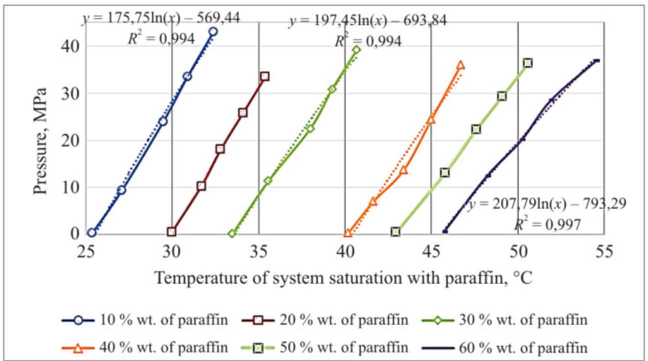


Fig. 8. Temperature of saturation of the solution by paraffin vs. pressure for different paraffin concentrations in the solution [33, 34]

$$x_{ws} = x_{wl} \exp\left[\frac{\Delta H}{RT}\left(1 - \frac{T}{WAT}\right)\right], \tag{2}$$

where $x_{ws}$ – mole fraction of sedimented paraffin, unit fraction; $x_{wl}$ – mole fraction of paraffin dissolved in oil, unit fraction; $\Delta H$ – enthalpy of paraffin crystallization, kJ/mol; $R$ – general gas constant, kJ/mol·K; $T$ – absolute temperature, K; $WAT$ is temperature of oil saturation with paraffin, K.

In the course of temperature decrease the equilibrium in equation (2) shifts towards paraffin crystallization. Equation (2) can be used to estimate the amount of paraffin that deposits from oil depending on temperature. To find the relation of the amount of suspended paraffin vs. the amount of dissolved paraffin in oil at various temperatures, paraffin crystallization enthalpy needs to be found. To do this, I.A. Struchkov and M.K. Rogachev [33, 34] obtained experimental relations of pressure values of model solutions saturation with paraffin vs. concentration of paraffin in said solutions. The results are shown in Fig. 8.

The authors showed that the dependence of the paraffin crystallization start on pressure for all paraffin concentrations in kerosene is logarithmic and can be expressed as follows:

$$P = P^* + k\ln\left(\frac{WAT}{WAT^*}\right), \tag{3}$$

where $P^*$ – ambient pressure, MPa; $WAT^*$ – saturation temperature under ambient pressure , °C; $WAT$ – saturation temperature under pressure $P$, °C; $k$ – phase transition constant in Clausius-Clapeyron equation.

The obtained data fully match the Clausius-Clapeyron thermodynamic equation describing transition of substances from one phase to another when environmental conditions change [31]. Such phase transitions are called first order transitions and are characterized by constant temperature and varying entropy and volume. During paraffin crystallization, the removed heat is used to form paraffin crystal lattice. As a result the system's state becomes more ordered, which, according to the second law of thermodynamics, is accompanied by the system's entropy decrease.

Based on the obtained results (see Fig.8), authors of the work [34] created Van't Hoff dependence of pressures in the range from 0.1 to 35 Mpa on paraffin concentrations in kerosene in the range from 10 to 60 % (Fig. 9).

By conversion of Van't Hoff and Gibbs' equation [35], the following equation was obtained [36]:

$$In\left(\frac{1}{x}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}, \tag{4}$$

where $x$ – mole fraction of paraffin in kerosene, unit fraction; $\Delta S$ – entropy of paraffin crystallization, kJ/mol·K.

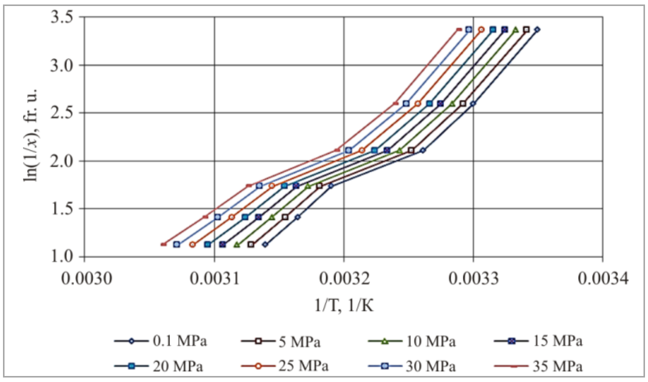


Fig. 9. Van't Hoff's dependence for different pressures [34]

Thermodynamic parameters of paraffin crystallization in kerosene can be obtained by processing the data shown in Fig. 7 using equation (4). This way enthalpy of paraffin crystallization in kerosene under ambient pressure is 81.7 kJ/mol, which is consistent with the results obtained in work [37]. The deviations of the calculated parameters may be explained by an error in paraffin and kerosene molecular weight determination as well as by high mole concentration of paraffin in kerosene, as the Van't Hoff's equation describes highly diluted solutions. For the calculations, molar weight of paraffin ($C_{36}$) and kerosene equal to 506 and 163 g/mol, respectively, were used.

The paraffin mass balance can be described by the following equation:

$$\frac{\partial}{\partial t}\left(\varphi S_o C_w \rho_w + \varphi S_o \rho_o w_{wl}\right) + \frac{\partial}{\partial x}\left(\rho_o u_o w_{ws} + \rho_o u_o w_{wl}\right) = -\rho_w \frac{\partial E_w}{\partial t}, \qquad (5)$$

where suffixes $w$ and $o$ stand for wax and oil, respectively, $S_o$ – oil saturation, unit fraction, $C_w$ – volume fraction of paraffin crystals suspended in oil, unit fraction, $\rho_o$ and $\rho_w$ – density of oil and paraffin, respectively, kg/m$^3$, $w_{ws}$ and $w_{wl}$ – mass fraction for paraffin suspended and dissolved in oil, respectively, unit fraction, $E_w$ – volume fraction of paraffin deposited on pore walls, unit fraction, $u_o$ – oil flow velocity, m/s.

Flow velocity can be found using the Darcy's law:

$$u_o = -\frac{k k_{ro}}{\mu_o}\frac{\partial P}{\partial x}, \qquad (6)$$

where $k$ – absolute permeability of porous medium, m$^2$, $k_{ro}$ – relative oil permeability, decimal quantity, $\mu_o$ – oil viscosity, Pa•s, $P$ – pressure, Pa, $x$ – linear coordinate, m.

The rate of solid paraffin sedimentation in the pore volume can be assessed using a sedimentation model. The calculations used the sedimentation model described in work [38], that is representative of fine particles sedimentation in porous media:

$$\frac{\partial E_w}{\partial t} = \overbrace{\alpha_w S_o C_w \varphi}^{adsorption} - \overbrace{\beta_w E_w \left(v_o - v_{cr,o}\right)}^{desorption} + \overbrace{\gamma_w u_o S_o C_w}^{clogging}, \qquad (7)$$

where $\frac{\partial E_w}{\partial t}$ – paraffin sedimentation rate, $\alpha_w$ – adsorption factor, $\beta_w$ – desorption factor, $v_o$ – interstitial velocity, m/s, $v_{cro}$ – critical interstitial velocity, m/s, $\gamma_w$ – clogging factor.

$$v_o = \frac{u_o}{\varphi}. \qquad (8)$$

The first addend of equation (7) describes the rate of paraffin adsorption on pore surface. The second addend represents the rate of paraffin desorption from pore surface when interstitial velocity is higher than critical interstitial velocity. The third addend stands for pore channels clogging with paraffin.

The calculation method is to estimate the amount of pore volume of oil with suspended paraffin transported through the porous medium. Concentration of suspended in oil paraffin from rock sample input to output is described by the power law. The amount of paraffin deposited in the core increases with the increase of the pore volume through which product is pumped. The calculation provides estimated variation of the formation filtration properties when paraffin deposits in the pore space, as well as a prediction of well operation parameters.

Adsorption and desorption factors can be estimated using the results of filtration experiments. At first stage, a model solution is injected in the rock sample with interstitial velocity lower than critical interstitial velocity determined empirically. The concentration of suspended paraffin in the solution at core output is measured by any available method (nucleic magnetic resonance method [39], paraffin freezing out from saturated hydrocarbons by SARA fractionating [40], etc.), while the concentration at core input remains constant. Paraffin concentration in solution at core output is lower than at core input until paraffin is adsorbed on the surface of pore walls. The experiment produced the following results: the amount of pumped pore volumes of the solution, the concentration of suspended paraffin at core output over time, initial core porosity, and experiment duration. To calculate the amount of paraffin deposited in the rock sample the following equations were used. Duration of core contact with the solution:

$$t = \frac{\pi m D^2 L}{4Q} n. \qquad (9)$$

where $m$– core porosity, unit fraction; $D$ – core diameter, cm; $L$ – core length, cm; $Q$ – flow rate, cm$^3$/min; $n$ – amount of pore volumes of the pumped solution.

The weight of paraffin deposited in the pore space is a time function and can be calculated using the terms of paraffin mass balance with the help of the following equation:

$$m_w(t) = \frac{1}{4}\pi m D^2 L \rho \left(\omega_i - \int_0^{t_{end}} \omega(t)\, dt\right), \qquad (10)$$

where $\rho$ – oil density at core input, g/cm$^3$.

During the next stage, the interstitial velocity is set higher than the critical interstitial velocity, and the experiment is repeated. The paraffin concentration in the solution at core output becomes higher than at the input. The data obtained during the first and the second stages are substituted in equation (7), the clogging rate factor is zero. The needed adsorption and desorption factors are calculated by solving a set of equations. The more stages the experiment comprises, the more accurate the retrieved factors are.

Instant porosity is calculated as the difference between initial porosity and volume fraction of paraffin that was adsorbed on the pore wall surface:

$$\varphi = \varphi_i - E_w, \qquad (11)$$

where $\varphi$ and $\varphi_i$ – instant and initial porosity, respectively, unit fraction.

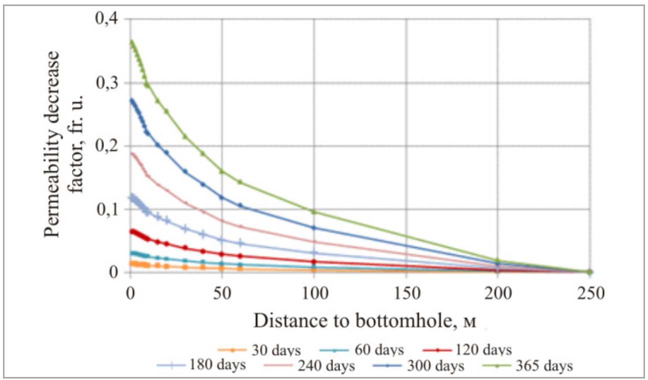


Fig. 10. Formation permeability decrease vs distance from injection well bottomhole

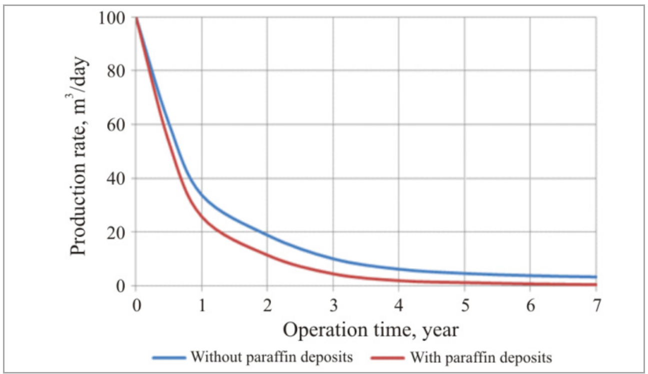


Fig. 11. Production rate dynamics in a production well with and without paraffin deposits in productive formation

Permeability can be expressed the following way:

$$k = k_i \left(\frac{\varphi}{\varphi_i}\right)^3 \left(\frac{1-\varphi_i}{1-\varphi}\right)^2, \qquad (12)$$

where $k$ and $k_i$ – instant and initial permeability, respectively, μm².

To assess the relative variation of the formation permeability, a permeability decrease factor was introduced (*Kdf*):

$$Kdf = 1 - \frac{k}{k_i}. \qquad (13)$$

We took into account the variation of the temperature field caused by cold water injection and, using the paraffin deposition model, obtained the dependence of the productive formation permeability decrease factor *Kdf* on the distance to the injection well bottomhole and the duration of cold water injection. We also assessed production rate dynamics of the production well with and without paraffin deposition in the formation. The calculation results are shown in Fig. 10 and Fig. 11.

The data shown in Fig. 10 indicate that, after one year of operation, the average permeability of the injection well bottomhole area will decrease by 28 % due to the impact of paraffin deposition on the formation.

## Conclusion

A series of experiments were undertaken to assess temperature conditions under which organic (asphaltene-resin-paraffin) depositions are formed in a productive formation in the course of well production of paraffinic oil. The experiments were aimed, inter alia, on the determination of the temperature of oil saturation with paraffin in the pore space of reservoir rock.

The outcomes of filtration and rheological studies revealed that for the same oil the temperature of saturation with paraffin in the pore space of reservoir rock may be higher than the same value in free volume. It was found that in the studied solutions (models of high-paraffin oil) the phase transition of paraffin from liquid to solid state occurs at a temperature that is 3–4 °C higher than in free volume.

The results of tomographic surveys of the core material undertaken before and after filtering of the paraffin-containing solution through it, showed that connected porosity of rock samples decreases on average four-fold due to clogging of the pore space with paraffin.

A digital core model was created using filtration and computer-aided tomography survey results; this model is able to simulate fluid flow through the pore space of rock before and after paraffin deposition in it. The results of thermal field dynamics calculation around the injection well confirmed the probability of bottomhole area cooling down to temperature at which paraffin starts to crystallize, as well as the probability that the cold water front may travel to neighboring production wells and cause significant decrease of productivity of the latter as a result of paraffin deposition in the pore space of reservoir rocks.

The obtained experimental data shall be considered for oil fields development under the conditions of organic (asphaltene-resin-paraffin) depositions in the productive formation, especially in the bottomhole areas of injection and production wells. This can ensure more reliable predictions and prevention of their occurrence.

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