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Hydrophobization of the Reservoir Surface in the Processes of Impact on the Bottomhole Formation Zone. Part 2. From Capillarity to Reality

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Гидрофобизация коллекторской поверхности в процессах воздействия на призабойную зону пласта. Часть 2. Сущность и реальность капиллярности

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bottomhole formation zone, oil and gas reservoirs, process fluids, filtration, wettability, hydrophobization, surfactants, capillary pressure.

The established opinion in the literature on the need for hydrophobization of the reservoir surface in the bottomhole formation zone (BFZ) when injecting aqueous process fluids into it, in particular, cationic surfactants (CS), to increase the relative phase permeability for oil and reduce it for water is refuted by the results of bench experiments on polymict cores. It was established that there was no additional washing of oil with a CS solution, a decrease in oil mobility with bound water under conditions of higher oil saturation than with ordinary water, and an increase in water mobility after exposure to a CS solution by more than two times. A conclusion was made about the potential applicability of CS in aqueous solutions at the stages of perforation and well killing with high oil saturation of the BFZ. The best option for increasing the relative phase permeability of oil over water should be recognized as its simple hydrocarbon saturation. The essence of capillary processes and the significance of capillary pressures actually occurring in reservoir conditions of heterogeneously wetted reservoir space for aqueous liquids with respect to well killing are briefly considered.
The inclusion of capillary forces in the consideration of this process against the background of hydraulic pressure actually acting in the BFZ indicates their insignificant role, which follows from the analytical calculations carried out in the work. The accepted methods of laboratory assessment of capillary impregnation of porous media at atmospheric pressure after their treatment with solutions of CS do not stand up to criticism. The obvious inconsistency of many theses of "hydrophobization" of the BFZ stems from incorrect assumptions about the fundamental provisions of reservoir fluids filtration through heterogeneously wetted reservoir space and adsorption processes of surfactants on rocks, which will be described in detail further in Part 3.

Ключевые слова:
призабойная зона пласта, коллекторы нефти и газа, технологические жидкости, фильтрация, смачиваемость, гидрофобизация, поверхностно-активные вещества, капиллярное давление.

Устоявшееся в литературе мнение о необходимости гидрофобизации коллекторской поверхности в призабойной зоне пласта (ПЗП) при внедрении в нее водных технологических жидкостей, в частности, катионных поверхностно-активных веществ (КПАВ), для повышения относительной фазовой проницаемости для нефти и снижения ее для воды опровергается результатами стендовых экспериментов на полимиктовых кернах. Установлено отсутствие дополнительного отмыва нефти раствором КПАВ, снижение подвижности нефти при связанной воде в условиях большей нефтенасыщенности, чем с обычной водой, и повышение подвижности воды после воздействия раствором КПАВ более чем в два раза. Сделан вывод о потенциальной применимости КПАВ в водных растворах на этапах перфорации и глушения скважин с высокой нефтенасыщенностью ПЗП. Лучшим же вариантом именно повышения относительной фазовой проницаемости нефти над водой следует признать ее простое углеводородонасыщение. Кратко рассмотрена сущность капиллярных процессов и значимость капиллярных давлений, реально имеющих место в пластовых условиях разносмачиваемого коллекторского пространства, для водных жидкостей применительно к глушению скважин.
Привлечение к рассмотрению этого процесса капиллярных сил на фоне реально действующего в ПЗП гидравлического давления свидетельствует о их незначительной роли, что следует из проведенных в работе аналитических расчетов. Подвергаются критике и принятые методики лабораторной оценки капиллярной пропитки пористых сред при атмосферном давлении после их обработки растворами КПАВ. Очевидная спорность многих тезисов «гидрофобизации» ПЗП исходит из дискуссионных предпосылок о фундаментальных положениях фильтрации пластовых флюидов по разносмоченному коллекторскому пространству и адсорбционных процессах ПАВ на горных породах, что будет детально изложено далее в части 3.

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Introduction

In scientific literature there is an established opinion about the need for hydrophobization of the collector surface in the bottomhole formation zone (BFZ) while introducing aqueous process fluids into it. One of the effective hydrophobizers of the sand and polymictic reservoirs surface are cationic surfactants (CS). It is believed that their use increases the relative phase permeability for oil and reduces it for water.

Bench and field tests connected with the impact on the bottomhole formation zone

However, this opinion was not confirmed by bench experiments on polymictic cores. A.T. Gorbunov and his colleagues at the All-Russian Research Institute of Oil [1] in the late 1980s were the first to raise the topic of their use for hydrophobization of the reservoir space in the BFZ with the convicting the significant role of capillary forces and the reduction of water inflow into the wellbore. To this end they conducted bench experiments on a model of disintegrated cores of the Sutorminskoye field with gas permeability k_g = 0.5 μm^2, L = 25 cm, d = 2 cm at 85 °C with oil from this field diluted with octane, water p = 1020 kg/m^3 and a 2 % IVV-1 solution with an interfacial tension value at the boundary with oil σ1,2 = 0.2–0.25 mN/m at 20 °C. The rate of liquid injection into the model was 20 m/day. In the first series of experiments, the model was saturated with water and displaced with oil to determine the initial oil saturation S_0, and then again with water to the residual oil saturation S_{R0}.

In the second series oil was displaced with 2 PD of the cationic surfactant solution and then with water. In the third series, after saturation of the model with water, 2 PD of the cationic surfactant solution were filtered and successively displaced with water, oil and again with water. After each series the mobility of oil $P_0 = k_0/\eta_0$, water P_w and the final oil recovery factor β_0 were estimated (Table 1).

Table 1

Results of the influencing filtration of a 2 % aqueous solution of IVV-1 on the mobility of phases in a model porous medium

Parameter	Model № 1	Model № 2	Model № 3
After water is displaced by oil			
S_0, %	61.0	69.0	61.5
P_0, μm^2/mPa·s	0.50	0.41	0.49
After displacing oil with water			
S_{R0}, %	27.0	31.5	28.0
P_w, μm^2/mPa·s	0.25	0.59	0.60
β_0, %	55.7	54.3	54.5

Analysizing the tabular data indicates the absence of additional washing of oil with the cationic surfactant solution, a decrease in the mobility of oil with bound water under conditions of higher oil saturation than with ordinary water and an increase in the mobility of water after exposure to the cationic surfactant solution by more than two times. This is exactly the result that should be expected from the previously established facts of the influence of reservoir space hydrophobization on the relative phase permeability (RPP) of oil and water. As a result, the authors conclude that "... the use of cationic surfactants for treating the BFZ of flooded production wells can lead to an irreversible change in rock wettability and, as a consequence, to a progressive increase in the water cut of the product." It may be rational to use cationic surfactants while killing wells and BFZs in the initial period of operation in order to remove asphaltene deposits and destroy OWE. For example, killing 5 wells of the Sutorminskoye field with 1 % IVV-1 solutions in 1989–1990 was not accompanied by an increase in their water cut and a decrease in oil flow rates. Field tests of the BHT technology 48 low-water-cut wells of the Noyabrskneftegaz PD fields with 1–3 m^3/m 1.5 % aqueous solutions of IVV-1 in 1989–1990 showed their success rate to be only 56–70 % with insignificant additional oil production.

V.N. Glushchenko who took part in the work of the national research and development centre of Oil on the hydrophobization of the BFZ and the development of a technology for the efficient use of surfactants, in his work [2] assigned a subordinate role to capillary processes compared to the hydrodynamic pressure from the wellbore, and agreed with the opinion of V.T. Gorbunov on the potential applicability of surfactants in aqueous solutions at the stages of perforation and killing of wells with high oil saturation of the BFZ. The best option for increasing the relative permeability of oil above water should be recognized as its simple hydrocarbon saturation. In 1991–1992 the BFZ treatment of more than 30 production wells of the Samotlor field was already carried out with 1–2 m^3/m of hydrocarbon solutions of surfactants with oil squeezing with a success rate of 75–85 % [3]. As a rule, these were wells after the initial opening or complicated by frequent killing. The BFZ of a number of wells was carried out with aqueous solutions of 12 % HCl with cationic surfactants at a rate of 0.2–2 m^3/m which no longer allows grading their efficiency due to the use of cationic surfactants.

I.I. Minakov [4] in his approach to the hydrophobization of the BFZ proceeded from the following assumptions: “In a hydrophilic rock, $\Theta < 90°$ and the pressure arising at the phase boundary in the pores retains water in them. If the surface of the reservoir rock is treated with hydrophobizing substances, its wettability will change and it will acquire water-repellent properties. In this case $\Theta > 90°$ and can increase to 180°, the capillary pressure will change its sign to the opposite, i.e. will now facilitate the displacement of water from the capillary. Thus, in the formation water will be displaced by oil from small pores to large ones where it can be easily removed later during well operation.” The question arises: will it not flow back into these channels from the reservoir?

In 1993–1996 at the Samotlor field the technology of bottomhole treatment acquired a complex nature, including pumping an HCl solution into the BFZ removing part of the water from the BFZ with acetone or methanol with cationic surfactants injecting 0.1–1 % solutions of cationic surfactants in hydrocarbon liquid or oil stopping for 24 hours to react and starting up the wells. It remains unclear what share should be attributed to the hydrophobization of the BFZ.

A.V. Starkovsky and T.S. Rogova [5] exaggerated the importance of capillary processes in the BFZ during its hydrophobization with the claim to increase oil recovery from the reservoirs: “The technology of hydrophobization ... increases oil saturation in the BFZ, improves the conditions for the flow of oil or gas into the well. Reduction of oil filtration resistance due to hydrophobization of the porous medium surface in a small formation zone restores the potential of wells and helps to increase oil production." Are such simplicity and efficiency of the method possible? Further: "... for a hydrophobic porous medium filled with oil, the capillary pressure for water is directed towards water, it prevents its penetration. Therefore a hydrophobic porous medium has significantly lower phase permeability for water not only horizontally but also vertically."

Finally, the authors believe that it is the influx of oil from the formation into the network of the least permeable reservoir space that will displace the water. There is the question if oil will be filtered here if there is hydraulic pressure and macro-open channels with a certain oil saturation. Let us turn to M. Masket who writes on p. 163 of their book [6]: “With favorable geometry of the pore space, capillary pressure causes water to move from permeable rock to dense rock and oil in the opposite direction”.

The technical solution they proposed according to the patent [7] includes the following successive stages: replacing the aqueous KF with anhydrous oil pumping a clay-acid composition (CC) with 0.5 % CS at a rate of 0.5–11 m^3/m which for some reason is called a microemulsion, 0.1–5 % hydrocarbon CS solution at a ratio of 1:1-3 to CS and anhydrous oil in a volume equal to the CS solution holding for 6 hours and starting the well into operation. According to the results of the BHT of 11 low-flow or idle wells of JSC Noyabrskneftegaz in 1995, an influx of oil was obtained from all of them with both high and low water cut of the product with an effect duration of 1–5 months.

Research by D.Yu. Kryanev et al. [8] on bulk models of quartz sand and disintegrated cores of the Sutorminskoye field without specifying their characteristics and the methodology for conducting experiments confirmed a virtually linear increase in the water filtration rate with an increase in the concentration of IVV-1 in the displacing water from 0.2 to 6 %, which the authors called the stimulation coefficient.

They conditionally assume unimpeded removal of the introduced water from the BFZ and the fact of the same intensified movement of water coming from the formation in the post-repair period is hushed up.

However, the phrase: "... the use of surfactants in a hydrophilic reservoir can be effective if their use does not change its hydrophobization very much, since in this case the phase permeability can increase significantly", does not reveal how exactly to regulate "not very much"? But the BFZ at the fields of the Noyabrsk region were carried out with acidic compositions, including additionally hydrophilizing NS-AP9-12 or alkyl dimethyl amine oxide (Sinol KAM) for the purpose of washing out asphalten deposits and destroying OWE. There is the question why the CS are needed if its adsorption will be suppressed by NS? Again, there is uncertainty and avoidance of the topic of hydrophobization efficiency.

After a series of works [1, 3, 4] and an article [2] R.N. Fakhretdinov et al. [9] addressed this topic focusing on the importance of complex decolmatation of the BFZ in wells operating low-permeability polymictic reservoirs of West Siberian fields associated with its saturation with a finely dispersed solid phase and water filtrate at the stages of opening killing wells (KW) as well as water coming from the formation. We also started Part 1 of this article with this question. When considering the technological methods of increasing the relative permeability of oil in the bottomhole zone and reducing it for water using surfactants, the authors drew attention to the unfounded advertising of their effectiveness for the relative permeability of both production and injection facilities. Moreover, for 51 relative permeability of production wells in 1996 at the fields of Western Siberia the success rate was 69 % with an effect duration of 140 days and for 241 relative permeability of injection wells is 82 % and 248 days, respectively, which may be due to the hydrophobization of the collector surface in the latter case. They believed that: "The mechanism of action of surfactants is the result of various complex physical and chemical processes, therefore, most often, choosing the type of surfactants, their concentration and objects of action is carried out empirically." In this regard, its in-depth studies are important for oilfield practice.

The role of capillary forces in comparison with hydrodynamic forces for porous media

The role of capillary forces and capillary imbibition in oil displacement processes has been the subject of many studies, including [10–34].

Let us briefly consider the essence of capillary processes and the significance of capillary pressures that actually occur in reservoir conditions of heterogeneously wetted reservoir space for aqueous liquids as applied to well killing.

In practice well killing requires creating a repression in the wellbore with a KW column ≈ 10 % higher than the reservoir pressure which can be ΔP_h = 2–3 MPa or more. This assumes KW filtration into the BFZ along the most open reservoir space in accordance with the Hagen–Poiseuille equation [35]:

$$Q = \frac{n\pi r^4 S \Delta P_{\text{h}}}{8\eta L}, \tag{1}$$

where Q – volumetric flow rate of liquid, m^3/s; n – number of filtration channels on area S, m^2; r – channel radius, m; ΔP_{h} – hydraulic pressure difference, Pa; η – dynamic viscosity of the filtered liquid, Pa·s; L – length of filtration path, m.

Based on modern concepts the process of recoverying formation fluids is controlled by the values of a number of reservoir space key parameters:

- permeability;
- wettability;
- structure of the porous medium (ratio of the proportions of flow-through and non-filtering pores and channels);
- ratio of hydrodynamic and capillary forces;
- oil and water saturation.

Flow channels r_k < 0.1 μm do not participate in hydrodynamic movement, and at r_k > 150 μm the fluid moves under the influence of hydrodynamic

Table 2

The magnitude of the applied pressure to displace the oil and the counteracting capillary pressure

Type of saturating fluid	Displacement pressure, MPa	Pressure gradient, MPa/m	Pore channel radius, μm	Capillary pressure, MPa
Free-flowing oil	< 0.05	< 1.7	3–100	$< 8.5\cdot10^{-3}$
Film oil	0.05	1.7	0.3–3.0	$8.5\cdot10^{-2}$
Adsorbed oil	0.52	17.3	0.2–0.3	0.09
Residual water	0.7	23.3	< 0.2	0.12

Table 3

Bench experiments

Fluid	Θ = 76–83°		Θ = 93°	
	Δ*P*, MPa	$k\cdot10^3$, μm²	Δ*P*, МПа	$k\cdot10^3$, μm²
Nitrogen	0.03	40.6	0.03	12.2
	0.06	38.5	0.06	11.3
	0.09	35.6	0.09	10.5
Reservoir gas	0.03	36.4	0.03	8.3
	0.06	32.0	0.06	8.2
	0.09	23.1	0.09	7.6
Water	0.03	0.57	0.06	2.04
	0.06	0.54	0.09	2.01
	0.09	0.54	0.12	2.01
Kerosine	0.03	1.95	0.06	1.59
	0.06	1.95	0.09	1.57
	0.09	1.95	0.12	1.57

Table 4

Capillary pressure during water absorption in hydrophilic oil-saturated sand cores

k, μm²	S_w				
	100	80	60	40	30
0,5	1.4	2.8	5.5	9.7	16.6
0,2	4.1	9.0	16.6	34.5	51.7
0,005	11.7	16.2	49.7	93.2	132.5

pressure only. Pores of size r < 0.2 μm are filled with residual water and do not participate in filtration, pores r = 0.2–3 μm contain adsorbed and film forms of oil and freely moving oil is concentrated in pores r = 3–100 μm. In the work [36] using the example of a hydrophilic terrigenous core sample with gas permeability values of k_g = 0.09·10–3 μm², m = 6.4 %, with S_w = 50 %, the following ratio of N channels of different radii was established:

r_k, μm	0.01–0.1	0.1–1.0	1–10	10–100
N, %	40	30	20	10

Bench studies on oil displacement by water from this sample have established the extraction of almost only its free-moving form and only 2–5 % of the film form with increasing pressure until water breakthrough. The values of the applied pressure for oil displacement and the counteracting capillary pressure from the oil are presented below (Table 2).

Bench experiments on the predominantly hydrophilic terrigenous core of the Urengoy field and the predominantly hydrophobic core of the Rudovskoye field (Ukraine) have established the following permeability for gases, water and kerosene [37] (Table 3).

Based on the results of bench experiments, the permeability for kerosene in the hydrophilic reservoir exceeds the permeability for water by 3.6 times, while in the hydrophobic reservoir, on the contrary, it is 1.27 times lower. For the core sample of the Rudovskoye field with neutral wettability Θ = 90°, the permeabilities of water and kerosene were equal. The magnitude and sign of the capillary pressure P_k (Pa) for a liquid penetrating into a cylindrical capillary with an internal radius r_k or located in it, upon contact with an antipolar liquid, is determined by the resulting contact angle of wetting Θ of its capillary surface and the interfacial tension σ12 between the liquids in accordance with the Young-Laplace equation [39]:

$$P_k = \frac{2\sigma_{12}\cos\Theta}{r_k}. \qquad (2)$$

In particular, when water is absorbed into a hydrophilic capillary Θ < 90° filled with oil, the value of P_k is the driving force of such a process proportional to the growth of the values of σ12, cosΘ and the decrease in the radius of the capillary. For example, a decrease in σ12 by dissolving the surfactant in water restrains the intensity of capillary impregnation and the force of water retention in the capillary. For the case of a hydrophobic capillary Θ > 90° it is already necessary to apply some hydraulic pressure P_h for water absorption, when $P_h > P_k$, i.e. the sign of P_k changes to the opposite.

In the case of oil absorption into a hydrophilic capillary filled with water, the vector P_k is directed towards the oil and everything will depend on its wetting properties, the thickness and resistance of the water film on the capillary surface. While containing surfactant-hydrophilizers, the film thickens and can serve as a hydraulic substrate for oil accelerating its movement along the hydrophobic surface. Water containing surfactant-hydrophilizers can change the wettability of the hydrophilic surface to hydrophobic and then the oil will begin to be absorbed. And finally in the case of unimpeded adsorption of polar components from oil (resins, asphaltenes, naphthenic acids, metal porphyrin complexes, etc.) on the hydrophilic surface, it will begin to be wetted by oil and impregnate the capillary.

In order to bring model experiments closer to oil field practice or to predict capillary pressures arising in porous media without setting them up, r_k is replaced in (2) by the filtration-capacity characteristics of collectors through the term $r_k = 2\sqrt{2k/m}$ additional input of the Leverett function depending on their water saturation. Without damage to the calculations it is possible to accept:

$$P_k = \frac{\sigma_{12}\cos\Theta}{\sqrt{2k/m}}\left(1 - S_w\right), \text{ Pa}. \qquad (3)$$

Below there are the values of P_k (kPa) for water absorption in hydrophilic oil-saturated sand cores with different water contents according to *N.* Mangan [38] (Table 4). From the Darcy and Poiseuille equalities for horizontal capillaries, Ushborn obtained an equation for the depth of capillary imbibition L (m) in time τ during the displacement of an antipolar liquid with viscosity η:

$$L = \sqrt{\frac{r_k \sigma_{12} \cos\Theta}{2\eta}\tau}, \quad (4)$$

from which it follows that the rate of impregnation decreases over time proportionally $V \approx L/\sqrt{\tau}$. Similarly (3) it can be replaced by r_k term $2\sqrt{2k/m}$.

With the applied hydraulic pressure P_g, equality (4) is transformed to the form:

$$L = \sqrt{\frac{r_k^2}{4\eta}\left(P_h + P_k\right)\tau}. \quad (5)$$

For a system of two immiscible liquids, when one of them with viscosity η_1, introduced into the capillary to a depth of l_1, displaces another liquid with viscosity η_2 located at a depth of l_2 the Washburn equation for the capillary imbibition rate (V, m/s) is used

$$V = \frac{r_k \sigma_{12} \cos\Theta}{4\left(\eta_1 l_1 + \eta_2 l_2\right)}, \quad (6)$$

and accordingly with the applied hydraulic pressure difference:

$$V = \sqrt{\frac{r_k^2\left(P_h + P_k\right)}{8\left(\eta_1 l_1 + \eta_2 l_2\right)}}. \quad (7)$$

Under conditions of $\Delta P_h >> P_k$ it obeys the usual Poiseuille flow. Analysis of these equations indicates a positive effect on the removal of the aqueous phase from the BFZ in the area of combined action of capillary and hydrodynamic pressure of the following factors:

• low value of σ12 and η of the liquids contained in them;

• poor wettability of the surface by them;

• increased permeability of the reservoir space;

• increased hydraulic pressure in the direction opposite to impregnation.

Thus, both in the forward direction of filtrating water KF from the wellbore to the BZP, and in the reverse direction – from the BZP to the wellbore, the most favorable picture is for liquids with the minimum created capillary pressure. In real conditions it is possible to reduce the σ12 values of water at the boundary with oil by 20–300 times from 20–30 to 0.1–0.2 mN/m by dissolving the surfactant, and change the wettability of the predominantly hydrophilic reservoir surface from cosΘ ≈ 0.6 for Θ ≈ 50° to cosΘ ≈ 0.1–0.02 for Θ ≈ 84–89°.

Let us consider the factors of hypothetical control of capillary forces for filtrate penetration into the BFZ from the position of BFZ hydrophobization apologists.

In the case of a predominantly hydrophilic and intermediate-wetted reservoir, the P_k vector is directed deep into the formation with an advanced growth into a network of low-permeability channels predominantly filled with residual and relatively mobile water. However, since in such zones the water saturation can approach 100 %, then $P_k \to 0$. Consequently, a significant part, and perhaps even more, of the water filtrate will be redistributed into the oil-saturated space with residual water where the value of P_k and the rate of water impregnation will melt.

The presence of surfactants in the filtrate also intensifies the rate of its impregnation into the oil-saturated zone with residual water to a greater extent than into the water-saturated zone. This circumstance is favorable for oil washing but in the case of BFZ water saturation it is negative. Only taking into account the onset of more complete hydrophilization of the reservoir surface and an increase in the proportion of washed oil we can assume local acceleration of subsequent oil filtration.

The penetration of the filtrate into a hydrophobic oil-saturated reservoir should be restrained by the opposite direction of the P_k vector, although, taking into account heterogeneous wettability, capillary absorption may also take place. Impregnation will be weakened in the water-saturated zone. However, no matter how hypertrophied the role of capillary pressures may be, they constitute a small fraction of the hydrodynamic pressure applied to productive formations by injection and production facilities which follows from the experimental data on cores and the calculated equations for P_k and the imbibition rate given above.

Otherwise, it would be impossible to develop deposits with a predominantly hydrophobic type of wettability of the reservoir surface.

The process of removing water filtrate from the BZP into the wellbore will also be carried out under control of the hydrodynamic pressure created in the BZP by depression on the formation. The role of P_k can be significant only in porous media with values of $k < 1 \cdot 10^{-3}$ μm². Let us conditionally accept the processes of displacement of discrete oil and water phases. In any oil-saturated reservoir with penetrated filtrate its displacement will be significantly facilitated due to the advanced flow of oil through more open channels in accordance with (1) up to the point of intersection of the RPP curves (see Fig. 1 in Part 1).

Exceeding these S_w values initiates independent movement of the filtrate with acceleration along the hydrophobic space. Due to the inaccessibility of the most low-permeability channels for oil filtration where the filtrate will partially concentrate, it will be relatively motionless, i.e. capillary-pinched, the residual water saturation increases. In this case, the maximum decrease in the P_k values for it by dissolving in the surfactant liquid gas will have a favorable effect.

The displacement of the filtrate from the oil-saturated space by the aqueous phase together with oil is subject to the well-known laws of two-phase filtration: piston – for the hydrophilic space, and globular – for the hydrophobic.

In any of them, with the onset of mixing of water and filtrate, supersaturation of the intersection point of the RPP with such an aqueous phase and an advanced flow into the wellbore with its share determined by formula (1) of Part 1 of the article can occur. In the water-saturated zone, the penetrated filtrate will also mix with the residual water, increase its content to a mobile state and initiate independent filtration with additional water coming from the formation. Again, with a hydrophobic state of the reservoir surface, such movement is intensified compared to a hydrophilic one.

Table 5

P_k value in low-permeability shale formations

Parameter	Data							
$k \cdot 10^3$, μm²	1		0.1		0.01		0.001	
S_w, %	20	40	20	40	20	40	20	40
~P_k, MPa	0.4	0.15	1.4	0.4	2.9	1.3	4.1	3.4

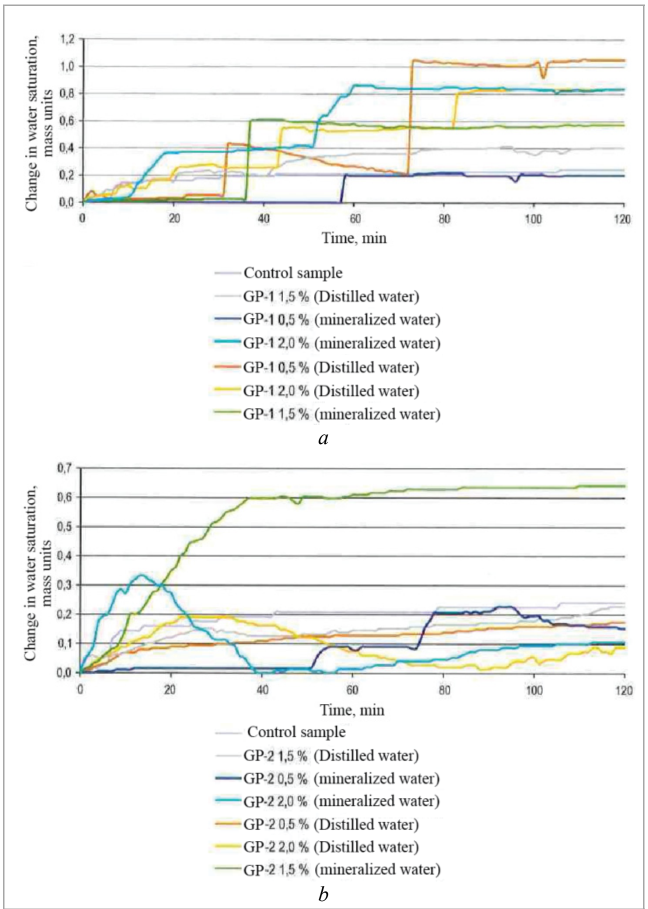

Fig. 1. Effect of concentrating and mineralizing solutions of hydrophobizing agents GP-1 (*a*) and GP-2 (*b*) on the kinetics of water saturation [49]

Thus, the maximum vulnerability of the BFZ to the penetration of water filtrate occurs at the stage of its high oil saturation when the P_k values are high, and the oil RPP curve can be sharply shifted to the right along the axis of increasing water saturation. This stimulates the hydraulic mobility of the aqueous phase from the depth of the formation, although the hydrophilic state of the surface will provide it with a certain resistance.

M. Masket [6] on p. 164 notes that "capillary forces are a secondary factor in the dynamics of oil production", and their role can be significant in "... equalizing the rate of oil displacement between dense and permeable areas of the productive zone" [6, p. 163].

Well-known specialists N.A. Cheremisin, V.P. Sonich, Yu.E. Baturin and N.Ya. Medvedev [40] believe that "... capillary impregnation cannot be the driving force of phase redistribution", but "... can block movement both in a separate pore and in entire blocks and layers". At the same time, the role of capillary processes is extremely significant in overcoming by liquids of communicating channels of different macro-openness and the movement of globules along channels of smaller radius which we will cover in the third part of the article.

The values of P_k for water are significant in low-permeability shale formations, especially with a low residual amount [40, p. 265] (Table 5).

In terms of BFZ hydrophobization the point of view of A.M. Svalov from the Institute of Oil and Gas Geology of the Russian Academy of Sciences [16] deserves attention. He rejects the thesis accepted by many specialists that the hydrophobization of BFZ rocks reduces the relative permeability for water. He correctly emphasizes the impossibility of reducing the volume of formation fluids entering the wellbore due to hydrophobization and the spread of such an effect only on the intensity of their filtration.

The determining factor in BFZ hydrophobization is the relative permeability of formation fluids [41]. In the case of low water cut of well production, the well productivity factor (K_{pr}) may even decrease due to the increase in the resistance of oil filtration in the hydrophobic capillary space. High water cut requires water restriction works in wells with selective agents, hydrophobization of the bottomhole zone of such objects increases their K_{pr} only due to an increase in the proportion of water in the product. Water-repellent properties of hydrophobized porous media are valid only in the area of action of capillary pressures which are insignificant when hydraulic pressures dominate.

On the contrary, with high oil saturation K_{pr} decreases for the total inflow which is directly opposite to the goals of hydrophobizing the bottomhole zone.

In layered heterogeneous formations flooded interlayers due to hydrophobization can increase the proportion of water in well production and reduce the oil inflow from oil-saturated interlayers.

A critical approach should be taken to the use of laboratory methods for spontaneous impregnation of model porous media accepted in the circle of oil specialists for assessing the effectiveness of hydrophobizing agents. They are based on experimental work with differently wetted capillaries from the field of colloid chemistry and porous media under atmospheric conditions. Such materials are useful in relation to the mathematical apparatus for describing capillary impregnation, the effect of various surfactants on the inversion of contact angles of wetting surfaces and other effects, some of which we have considered above. Other materials summarized in [38] were studied from the point of view of the influence of P_k in capillaries on the movement of gas and liquid globules, fine particles and the role of surfactants in these processes which we will address in Part 3 of the article.

The express method for assessing the rate of spontaneous capillary impregnation of water or its absorbed volume in bulk sand models at atmospheric pressure after their treatment with hydrophobic compounds currently accepted by many researchers is described in [42]. The porous medium is formed from ground hydrophilic quartz sand with a fraction of 0.1–0.2 mm or disintegrated extracted cores of a specific deposit L = 14–15 cm, d = 6–7 cm. After filling it under vacuum with one pore volume (1 PD) of the studied surfactant solution or a solution of organosilicon liquid in kerosene, the model is kept for 12–24 hours, successively washed with 10 PD of water and kerosene, vacuum dried and the mass of water absorbed by the end surface is estimated for 2 minutes. A number of researchers keep the tested surfactant solutions in porous media for 24 hours. It should be noted that dry porous media are subject to hydrophobization, and the fact that disintegrated cores can be used after their extraction does not add anything in terms of research, as does the very short time of impregnation with water. How realistic is it to transfer the surfactant concentrations selected in this way to reservoir conditions? However, they do tolerate it, recommend 0.05–0.1 % in PD, prove that their surfactants are better than others, since 0.05 cm^3 less water is absorbed, in other cases water is not absorbed at all, etc. Perhaps it is worth trying to create hydraulic pressure, oil-water saturation, increase the temperature in such models? Most likely, it will be absorbed even faster than without water repellents. They will object that this is already filtration. But in reality, we just “have” a combination of these two pressures.

A positive factor of such express methods is the possibility of observing the non-monotonicity of impregnation of porous media with surfactant solutions, when one can conclude about their adsorption and, as a consequence, a change in the wettability of the filtration surface.

I.A. Guskova et al. [43] studied the kinetics of capillary impregnation of oil-saturated sand-siltstone cores of the Bobrikov horizon of the Chernoozerskoye field in Tatarstan with aqueous solutions of various concentrations of the composition of CS-HP-1 and NS-HP-2. Unfortunately, all the data necessary for commenting on the experiments are missing. However, in this case, the course of the curves in Figure 1 from [43] is interesting indicating the non-monotonicity of such impregnation and the complex effect of the surfactant concentration on kinetics. This picture is more realistic, as discussed above. Unfortunately, Professor I.A. Guskova of the Almetyevsk Oil Institute starts from the following thesis: "The expected effect consists in an increase in oil production due to hydrophobization of the near-wellbore part of the formation and, accordingly, an increase in the relative permeability of oil in this zone." That is the reason for the discussion.

In the work [44] on samples of oil-saturated oil model η = 1.2 mPa·s hydrophilic sand cores of the Novo-Dmitrovskoye field (Krasnodar Territory) with the values of k = 0.113 μm^2, m = 27.2 % with controlled water saturation with formation water p = 1020 kg/m^3 and σ12 = 20.4 mN/m, the capillary absorption of this water was studied at t = 108 ºC and P = 23 MPa for 10 min.

During this time, ~50 % of the oil was displaced. The rate of capillary imbibition linearly decreased with increasing water saturation of the cores from $V \approx$ 80 cm/day (S_w = 0) to $V \approx$ 10 cm/day (S_w = 60 %).

On the hydrophobic model k = 2.1 μm^2, m = 29.3 % at σ12 = 16.7 mN/m, t = 65 °C and P = 16 MPa, the impregnation rate increased from $V \approx$ 0.8 cm/day (S_w = 0) to a maximum of $V \approx$ 2.5 cm/day (S_w = 30 %) over 60 minutes, and then decreased to $V \approx$ 0.8 cm/day (S_w = 60 %). Under atmospheric conditions, impregnation was absent at S_w = 0, began with values S_w = 10 % ($V \approx$ 0.1 cm/day), reached an extreme

$V \approx$ 1.3 cm/day (S_w = 20 %) and then decreased to $V \approx$ 0.1 cm/day for S_w = 60 %. In these experiments everything is in accordance with equation (2).

General conclusions will be made at the end of the third part of the article.

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