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## Perspective Directions for Improving Acid Compositions and Methods of Influence on the Bottomhole Formation Zone

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### Перспективные направления совершенствования кислотных составов и методов воздействия на призабойную зону пласта

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bottomhole formation zone, acid treatment, acid compositions, technical lignosulfonates, polar nonelectrolytes, emulsion, limestones, dolomites, thermogenerating compounds.

The development of the acid treatment method of bottomhole formation zone (BFZ) has gone from understanding the physics and chemistry of the acid compositions (AC) reactions with rocks through the expansion of the acid components range, AC modification by foaming, emulsification, generation to modern acid treatment methods with a wide range of scientifically based ACs.

Through trial and error, we came to understanding the importance of maintaining high relative phase permeability of oil and gas in the BFZ with the negativity of its water saturation, imparting a hydrophilic state to the reservoir surface, preventing and eliminating the formation of clogging sedimentation as a result of corrosion during injection along the wellbore, neutralization rocks, mixing with oil, formation waters, hydrogen sulfide. As a result, the AC must additionally include ion stabilizers, steel corrosion inhibitors, demulsifying agents for the prevention and destruction of water-oil emulsions, hydrophilizers and a number of optional additives if necessary: nonionic surfactants, alcohols, polymers, antifiltrates, solvents for asphaltene-resin-paraffin deposits and a number of others. It is not always possible to combine them in one AC, which implies a complex effect on the BFZ with a number of compositions.

The article discusses the conditions for effective acid treatment, which presupposes its facilitated removal of solid impurities, water-oil emulsions, hydrophilization of the reservoir surface and minimal water saturation. Options for improving known acid compositions using nonionic surfactants, polar nonelectrolytes, technical lignosulfonates, including direct and reverse acid-containing emulsions were proposed. Technological approaches to heating the BFZ with heat-generating inorganic compositions were outlined to transfer the hydrochloric acid dissolution of dolomite into the diffusion region for the purpose of easy formation of acid dissolution channels.

#### Ключевые слова:

призабойная зона пласта, кислотная обработка, кислотные составы, лигносульфонаты технические, полярные неэлектролиты, эмульсия, известняки, доломиты, термогенерирующие составы.

Развитие технологического приёма кислотной обработки призабойной зоны пласта прошло путь от понимания физикохимии самих реакций кислотных составов (КС) с горными породами через расширение спектра кислотных составляющих, модификацию КС вспениванием, эмульгированием, генерированием до современных методов кислотного воздействия с широкой гаммой научно обоснованных КС.

Путем проб и ошибок пришло осознание важности сохранения в призабойной зоне пласта (ПЗП) высокой относительной фазовой проницаемости нефти и газа с негативностью её водонасыщения, придания гидрофильного состояния коллекторской поверхности, предупреждения и устранения процессов формирования коагулирующего осадкообразования в результате коррозии при нагнетании по стволу скважин, нейтрализации горными породами, смешивания с нефтью, пластовыми водами, сероводородом. Вследствие этого КС должны дополнительно включать стабилизаторы ионов ингибиторы коррозии стали, деэмульгирующие агенты для предупреждения и разрушения водонефтяных эмульсий гидрофиллизаторы и ряд факультативных добавок при их необходимости: неионные поверхностно активные вещества спирты, полимеры, антифильтраты, растворители асфальтеносмолопарафиновых отложений и ряд других. Далеко не всегда удаётся их совместить в одном КС, что предполагает комплексное воздействие на ПЗП рядом составов.

В статье рассмотрены условия эффективного проведения кислотной обработки ПЗП, предполагающие её облегчённую раскоагуляцию от мехпримесей, водонефтяных эмульсий, гидрофиллизацию коллекторской поверхности и минимальное водонасыщение. Предложены варианты усовершенствования известных кислотных составов с использованием неионных поверхностно активных веществ, полярных неэлектролитов, лигносульфонатов технических, в том числе, прямых и обратных кислотосодержащих эмульсий. Изложены технологические подходы к нагреву ПЗП теплогенерирующими неорганическими составами для перевода солянокислого растворения доломита в диффузионную область с целью незатрудненного формирования каналов кислотного растворения.

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## Introduction

The development of the technological process of acid treatment in bottomhole formation zone (AT BFZ) in the oil and gas industry (OGI) started from the first applications in 1895 in the USA and in 1934 in the USSR. It has progressed from understanding the physicochemical nature of the acid reactions with the rock formations under the geological conditions of productive deposits, through the expansion of acid components range, modification of acid compositions (AC) by foaming, emulsifying, and generating, to modern methods of acid treatment with scientifically justified acid compositions [1–8].

An understanding came of the importance of maintaining high relative phase permeability (RPP) of oil and gas in the BFZ with negative water saturation, imparting a hydrophilic state to the reservoir surface, preventing and eliminating the processes of colmatating sedimentation formation as a result of corrosion during injection along the wellbore, neutralization by rocks, mixing with oil, formation waters, and hydrogen sulfide ( $H_2S$ ). As a result, the acid compositions should additionally include  $Fe^{3+}$  ion stabilizers, corrosion inhibitors (CI) of steel, demulsifying agents for the prevention and destruction of water-oil emulsions (WOE), hydrophilizers and a number of optional additives if necessary: non-ionic surfactants (NIS), alcohols, polymers, anti-filtration agents, asphaltene-resin-paraffin deposit solvents (ARP),  $H_2S$  neutralizers, scale inhibitors (SI), complexing agents of F ions and a number of others.

It is not always possible to combine them in one acid composition, which implies a comprehensive impact on BFZ by a number of compositions. However, developers of new acid compositions should be guided by this combination and goals achieved thereby, constantly improving them.

It is also necessary to calibrate the feasibility of choosing a AC according to the temperatures of productive formations, lithological and morphological structure, the degree of water cut of well production (W), and the sequence of AT application at the same site. Thus, among the recommendations for the BFZ acid treatment process, particularly for carbonate reservoirs, Russian specialists hold the opinion of a consistent change from simple hydrochloric acid treatments (HAT) with water-based solutions of HCl up to  $W \approx 30\%$  to the use of inverse acid emulsions (IAE) up to  $W \approx 50\%$  and directional acid treatments (DAE) with prior plugging of highly conductive channels up to  $W \approx 80\%$  [1, 3, 9–11].

Qualified specialists of petroleum chemistry should supervise these issues, the training of which is practically insufficient, although the relevant textbooks are regularly published, and annual conferences are held [12]. Often, the implementation of a justified acid treatment technique of the bottomhole formation zone is held back by the economy of oil and gas companies.

At present, the low level of technical solutions for the acid treatment technique of the bottomhole formation zone, misconceptions about the mechanism of AC action, the increasing number of reports on testing AC under conditional numbers and trademarks, are alarming. At the same time, the acid treatment technique of dolomitized reservoirs of large oil and gas

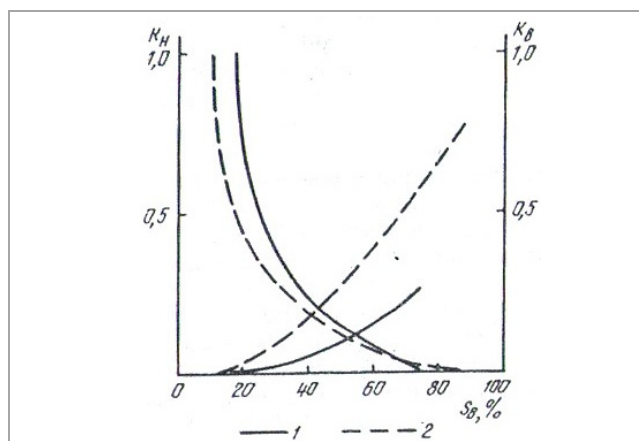


Fig. 1. The influence of wettability on the patterns of the relative phase permeability curves.  
Rocks: 1 – hydrophilic; 2 – hydrophobic

condensate fields in Eastern Siberia, the Bazhenov formation, Achimov deposits, the Turonian gas-bearing formation, Jurassic formation and a number of others urgently requires the solutions.

In this regard, we will consider the main groups of AC, the most acceptable mining and geological conditions for their use and progressive chemical and technological methods for improving the main functions of AC or giving them positive properties.

V.N. Glushchenko and O.V. Pozdeev [7] defined the main task of the AT BFZ as "... restoration of reservoir properties in the BFZ by destroying, dissolving and removing into the wellbore colmatating solid particles of natural and man-made origin, improving the filtration characteristics of the BFZ by expanding existing and creating new fluid-conducting channels, preferably by throughout the perforated thickness of the layer."

The decolmatation of the BFZ, starting from the stages of opening up productive layers and developing wells, should be carried out with compositions that minimize its water saturation, giving the collector surface predominantly hydrophilic wettability. This conclusion follows from the course of typical RPP curves shown in Fig. 1, when the maximum "vulnerability" of oil inflow is in  $S_w \geq 30\%$ . Besides the water saturation, oil flow is hampered by fine hydrophobized particles, stable WOE, and at many fields additionally formed ARP, poorly soluble salts, gas phase release and other factors [13].

Unfortunately, unlike foreign specialists many Russian researchers since the early 1990s to the present day, have misunderstood the necessity of the reservoir surface hydrophobization in enhanced oil recovery under any form of treatment.

M.A. Kelland [6] considers corrosion inhibitors,  $Fe^{3+}$  ion stabilizers, and hydrophilic surfactants as essential additives to acidizing fluids. He notes: "Hydrophilic agents are necessary... to remove the oil film from the rock or deposits to ensure good contact with water-based acids and to hydrophilize the formation, which increases oil production." It is also evident from the relative permeability curves, where oil mobility is maintained at higher water saturation in a hydrophilic porous medium compared to a hydrophobic one.

Table 1

Solubility of alcohols

Alcohol	$C_w$ , wt. %	$C_{inv}$ , g/dm <sup>3</sup>	Alcohol	$C_w$ , wt. %	$C_{inv}$ , g/dm <sup>3</sup>
Methanol	Unlimited	159	Isobutanol	9.0	14
Ethanol	Same	127	Butanol	7.9	8
Isopropanol	Same	50	Isopentanol	2.8	5
Propanol	Same	20	Hexanol	0.6	-

Table 2

Contact angle value of hydrophobic surface wetting by drops of water-based solution of ethanol

Parameter	Value					
$C_w$ , g/dm <sup>3</sup>	0	35	87	299	537	754
$\theta$ , deg.	108	101	95	77	66	44

Among the hydrophilizing agents used in AC, there are ethoxylated nonionic surfactants (ENS) of the AF<sub>9</sub>-12 type and polar nonelectrolytes (PN) as alcohols, ethers, ketones, dioxane [2-4]. For terrigenous reservoirs, cationic surfactants serve as hydrophobizing agents. All oil-soluble surfactants have this function, including those for carbonate reservoirs, in particular, emulsifiers of reverse emulsions, asphaltene-resinous substances (ARS) from oil, as well as oil with their high content.

In real reservoir conditions, the reservoir surface wettability varies widely from mostly hydrophilic to hydrophobic. Under such conditions, the adsorption of nonionic surfactants or alcohols gives a hydrophilic state to hydrophobic surfaces, nonionic surfactants have a weak hydrophobizing effect on hydrophilic surfaces, and polyols do not change it at all. Cationic surfactants can have an inverting character of hydrophobic surface wettability depending on the concentration and hydrophilize a hydrophobic surface. However, foreign specialists keep from using them due to the unpredictability of such action in reservoir conditions.

In this regard, PNs are more preferable, which are referred to a group of mutual solvents (MS) in domestic practice, and to universal solvents (US) in foreign practice due to their unlimited individual solubility both in water and hydrocarbons. These include aliphatic alcohols C<sub>1</sub>-C<sub>3</sub>, acetone, dioxane, aliphatic acids as formic, acetic, and propionic. Ethylene glycol monobutyl ether (EGMBE) is used as a mutual solvents widely. As the molecular weight of aliphatic alcohols increases, the required concentration in water-based solution for converting a hydrophobic surface to a hydrophilic state ( $C_{inv}$ ) decreases. However, starting from C<sub>4</sub> and higher, solubility in water is limited, as shown below [4] (Table 1).

The contact angle ( $\theta$ ) values of the hydrophobic surface with drops of a water-based ethanol solution are presented in Table 2.

Important features of alcohols behavior in hydrochloric acid and clay-acid compositions (CAC) are

the complete solubility of butanol and the increased solubility of homologues C > 4 at a concentration of HCl > 20 %, as well as mixtures of low and higher alcohols to octanol. The "alcohol - hydrocarbon" mixtures are stratified with the additional introduction of a water or water-acid phase above a certain amount, the more intensely, the lower the concentration of water-soluble alcohol with redistribution between the water and hydrocarbon phases. However, the transition of alcohol to the hydrocarbon phase also gives it hydrophilizing functions. Below are the values of interfacial tension  $\sigma_{12}$  at the boundary of a water-based solution of isopropanol (IPS) and toluene as well as the mixture a mixture of a wide hydrocarbon fraction (WHF) with a density of 662 kg / m<sup>3</sup> with IPS at the boundary with the Cenomanian water model (Table 3).

It is also worth noting that the main negative properties in MS are:

1. Chlorination in HCl solutions, which intensifies to a dangerous level of chlorohydrocarbons in the contacting oil phase at  $t > 90$  °C [5, 14, 15]. To eliminate it at high-temperature facilities, it is recommended to replace HCl with CH<sub>3</sub>COOH or aminopolycarboxylates [5].

2. Initiation of asphaltene precipitation from the composition of the contacting oil happen at their high initial content in the oil followed by adsorption onto the surface of a fine dispersed solid phase and the formation of sludge. Their prevention is ensured by preliminary testing of the AC, adding aromatic hydrocarbons, as well as preliminary and subsequent injection into the BFZ. For this purpose, EGMBE, which does not cause precipitation of asphaltene, or its mixtures with hydrocarbons can be used [4].

3. Increase in the corrosion rate of the composite material, which requires careful selection of appropriate CI [4].

The reservoir hydrophilic state of the surface and finely dispersed colmatants facilitates their removal from the pore space into the wellbore due to the lower free energy of contact interaction  $\sigma_c$ , and in the

Table 3

Research data

IPS, wt. %	$\sigma_{12}$ , mN/m	WHF + IPS, vol. %	$\sigma_{12}$ , mN/m
7.8	19.2	100	37.0
14.4	12.1	80	10.2
26.3	5.8	60	1.4
53.9	1.9	50	0.14
71.6	0.9		
98.4	0.5		

presence of nonionic surfactants and/or MS – a decrease in  $\sigma_{12}$  between hydrophobized particles and the AC [13]:

$$\sigma_r \approx 2\sigma_{12}(1 - \cos\Theta), \text{ N/m.} \quad (1)$$

Thus, at  $\sigma_{12} = 30 \text{ mN/m}$  and  $\Theta = 20^\circ$  ( $\cos\Theta = 0.94$ ) we obtain  $\sigma_r \approx 3.6 \text{ mN/m}$  for hydrophilic particles in a water medium, and  $\Theta = 100^\circ$  ( $\cos\Theta = -0.17$ ) –  $\sigma_r \approx 70 \text{ mN/m}$  in their hydrophobic state, i.e. ~20 times more. Additional reduction of  $\sigma_{12}$  to 1 mN/m further reduces this value by 30 times.

Demulsifying action of ENS and/or high-molecular alcohols in the AC of non-ionic surfactants eliminates the problem of the WOE occurrence, which are easily formed in hydrophobic channels during the movement of the water phase through their globular constrictions [13]. The destruction of WOE is also facilitated in environments with such additives, as is the movement of globules with a diameter  $d_{gl}$  through a network of constricted channels of a smaller diameter  $d_c$ , with the hysteresis elimination of the contact angles of wetting:

$$\frac{P_c}{L} = \frac{4\sigma_{12}}{d_{gr}} \left( \frac{1}{d_c} - \frac{1}{d_{gl}} \right), \text{ Pa/m,} \quad (2)$$

where  $P_c$  is the capillary pressure that prevents the movement of globules at a distance  $L$ ;  $d_{gr}$  is the diameter of the rock grains.

For example, under the conditions  $\sigma_{12} = 0.1 \text{ mN/m}$ ,  $d_{gr} = 100 \text{ }\mu\text{m}$ ,  $d_c = 10 \text{ }\mu\text{m}$  and  $d_{gl} = 15 \text{ }\mu\text{m}$  we obtain  $\Delta P_c \approx 1.3 \text{ MPa/m}$ , which promotes the movement of globules at a distance ~3 m from the wellbore with depression of 5 MPa in it.

Additional positive functions of MS in AC are the increased solubility of the released gaseous  $\text{CO}_2$  with the minimization of the difficult globule filtration by analogy with the equation (2), the binding of water phase part with its transfer to a more mobile state for removal from the BFZ, an increase in the thermal stability of nonionic surfactants, an antihydrate effect [4], and also a decrease in the degree of silicic acid gelation  $\text{Si}(\text{OH}_4)$  in AC [5].

Review of works by M.I. Maksimova (1945) and B.G. Loginova (1951) demonstrates that the formation of extended acid dissolution channels in limestone cores with general patterns, established by these authors, was not supported and substantiated by

Russian researchers, and the initiative passed to American specialists, starting with the study by B. B. Williams and O. E. Nierode (1972) [3, 5].

The initiation and development of a channel into the reservoir is caused by the following factors [3, 5]:

- diffusion mode of heterogeneous reaction during rock dissolution of the AC;
- A wide range of pore sizes in the reservoirs, from filtration pores up to 100 micrometers, cracks up to 1 mm and caverns of several mm in size with channel formation occurring in the most opened ones exhibiting higher reactivity;
- approximate equal volumes of the AC entering the top of the channel and the leakage rates along its perimeter into the porous matrix;
- exceeding the true AC filtration rate of porous medium ( $V_{tr} = V/m$ ) over the rate of its chemical reaction by approximately three times as indicated by the Damköhler number to minimize the required pore volume (PV) of the AC to facilitate the formation of extended channels. This factor is the main research task in core experiments aimed to find the optimal ratio between injection rate of the AC and the minimum injection of pore volume required for successful breakthrough through the core.

### Lignosulfonate acidic compositions (LAC)

First, using LAC for acid fracturing, described in the book by B.G. Loginov and V.A. Blazhevich (1958), dates back to the early 1950s [4]. In 1971, I.V. Krivosov and G.A. Makeev published results on the formation of deep channels (up to 30 cm) in carbonate cores using HCl solutions through a cyclical injection of water-based solutions of technical lignosulfonates (TLS) and HCl solutions. The role of TLS was to reduce the flow rate losses of HCl solutions from the channels into the porous matrix.

In the work of V.N. Glushchenko and O.V. Pozdeev [7], experimental data were presented for in-depth study of the properties of various LACs, including TLS and mono spent sulfite liquor (MSSL). The efficiency of the passivating action on the dissolution rate of limestone was up to 50 times, the complexation of  $\text{Fe}^{3+}$  ions in a ratio of 1 g: 20  $\text{cm}^3$ , and the anti-filtration capacity were evaluated. Alcohol forms of TLS and MSSL with a freezing point of  $\leq -30 \text{ }^\circ\text{C}$  were obtained, and their emulsifying capacity in relation to hydrocarbons and as a dispersing phase in the

composition of oil emulsions was established. The research [4, 16] presented the results of laboratory experiments on the formation of dissolution channels in LAC on porous, poro-fractured, and fractured limestone cores.

The research data served as the basis for the widespread use of LAC since the late 1990s in the fields of Tatarstan, Bashkortostan, Udmurtia and Perm Krai for deep AT BFZ of carbonate reservoirs in various versions [4, 10, 17]. Since 2008 on the deposits of the Perm Krai, LAC have been successfully used for combined hydraulic fracturing of carbonate formations with cross-linked polymer gels and subsequent injection of the "FLEC KS-401" composition, which was later replaced by similar DN-9010 [4, 18].

In foreign practice, to reduce high-speed leaks, finely dispersed silicon oxide or oil-soluble polymeric materials are introduced into the compressor station [3, 6, 19].

A number of Russian researchers [20] instead of improving AC and searching for the optimal injection rate introduce 2.5 % LAC into a 15 % HCl solution to form acid dissolution channels in carbonate cores at the same rate and concentration.

**Group of alcohol-containing acidic compositions (ACAC)**

The properties of the ACAC are well covered in papers [2, 4]. To a large extent, they correspond to the AT conditions of gas wells to reduce water saturation and the bottomhole zone decolmation, as well as influence the low-permeability clayey polymictic reservoirs [8]. They can obviously be recommended for the AT of the Bazhenov Formation reservoirs and Domanik deposits with low residual water saturation, Turonian and Achimov formations. Alcohols in AC and HAC, can act as effective interfacial tension reducers in high-temperature applications, where the surface-active agents may become inactive. So, introducing higher alcohols with greater interfacial activity and hydrophilizing capacity is more rational. It is known that the alcohol-containing acidic compositions (ACAC) of isopropanol with octanol in a volumetric ratio of 5:1 (AC) are added in amounts of 30–70 vol.% to 15 % HCl [14]. In [21], such a composition of 30 wt.% isopropanol and 20 wt.% octanol additionally includes 50 wt.% of a 60 % water-based solution of non-ionic surfactant (NAS) with subsequent addition of 0.1–10 vol.% to 15 % HCl. Below are the values of  $\sigma_{12}$  for the 15 % HCl solutions with these alcohol additives (AD) at the interface with kerosene (Table 4)."

Table 4

Values of HCl solutions with alcohol additives on the border with kerosene

Parameter	Value				
AD, vol. %	-	AC-35	EGMBE -10	EGMBE-35	surfactant
$\sigma_{12}$ , mN/m	18.8	3.2	8.0	4.6	2.6

A significant source of alcohols is the secondary products of butanol production. To create channels for acid dissolution in low-permeability reservoirs, 1-2 % TLS polyvinyl alcohol, benzoic acid, or compatible polymers of the acrylic series may be introduced into them.

Formation of such channels in terrigenous reservoirs deserves the closest research attention.

V.A. Sidorovsky in his monograph (1978) formulated the main conditions for their emergence and development:

- values of the absolute permeability coefficient  $k_g \geq 0.05 \mu\text{m}^2$ ;
- the content of film carbonate cement, including kaolinite, is more than 30 %;
- presence of natural cracks;
- an increase in the volumetric filtration rate of the HAC in core tests is from 1 to 12 cm<sup>3</sup>/min, which corresponds to an injection rate in the wellbore zone from 5 to 30 m<sup>3</sup>/m<sup>2</sup> h) along the open surface of the wellbore.

They can be supplemented by the temperature > 90°, when clay-acid reactions transfer to the diffusion mode [5]. For example, by filtering HAC based on 14 % HCl + 4 % HF through formation cores BS<sub>10</sub><sup>2+3</sup> Tevliny-Russkinskoye deposit ( $k_g = 0.0015\text{--}0.148 \mu\text{m}^2$ ) at 60 °C channels with a diameter of  $w_d = 0.3\text{--}3$  mm were observed on their inlet surface, which did not develop through the entire length [5].

In core samples from the EK<sub>1</sub> and SK<sub>2-5</sub> reservoirs of the Rogozhnikovskoye field, with values of  $k_g = (1\text{--}15) \times 10^{-3} \mu\text{m}^2$ , channels were observed along the entire length of the samples during the filtration of 2-3 pore volumes of clay-acid composition with isopropanol at 105–115°C.

In the study [22] on low-permeability core samples from the Bazhenov suite in the Palyanovskaya area, which are penetrated by a network of cemented calcite fractures with openings up to 35  $\mu\text{m}$ , filtration of 40 pore volumes of clay-acid composition containing 25-30 vol.% isopropanol and iron stabilizers at 105 °C and an average flow rate of  $1 \cdot 10^{-6}$  m/s established a network of through dissolution channels. It can be assumed that by increasing the filtration rate and modifying such clay-acid compositions, the required pore volumes can be reduced. According to foreign data, preliminary filtration of 10 % acetic acid (CH<sub>3</sub>COOH) and reducing the concentration of HF to approximately 1 % is recommended for this purpose [5]. Due to the presence of high-permeability layers in the Bazhenov suite with  $k_g$  values of approximately  $0.06 \mu\text{m}^2$  and fractures sealed by kerogen soluble in aromatic hydrocarbons, it is reasonable to include them in such an acid treatment cycle. Such approaches and the analysis of previous experimental studies suggest the potential for significant progress in BFZ.

Based on the results of laboratory experiments on cores of domanik deposits of the Bavlinskoye field in Tatarstan with an absolute permeability of  $k_g \approx (3\text{--}4) \cdot 10^{-3} \mu\text{m}^2$  and initial oil saturation, the uncomplicated formation of through channels by alcohol-containing HCl solutions during their filtration was established ~ 0.2 PV at a rate of 2 cm<sup>3</sup>/min, which turned out to be twice lower than for 15 % HCl

[23]. However, the tested SCSs are designated by numbers, which reduce their scientific value.

Modern methods of protecting wells from scaling by pumping inhibitor solutions (ISO) into the wellbore zone using Squeeze treatment technology or before killing wells with calcium-containing liquids with low-volume mini rims squeeze are to apply preliminary injection of alcohol-containing compositions to remove the oil film from the collector surface and enhance the adsorption of ISO [24]. An obvious advantage will also be the ISO injection as part of alcohol compositions, and as a preliminary edging, the injection of a homogeneous acid-hydrocarbon composition, which additionally clears the BFZ from mechanical impurities, WOE and ARP.

### Microemulsion acidic compositions (MCS)

MCS are divided into direct ones – with an external acidic environment, and reverse ones – with an external hydrocarbon environment. To obtain them, high concentrations of nonionic surfactants,  $C_1$ – $C_5$  alcohols, hydrocarbons and HCl or HCl+HF solutions are used [3, 25, 26]. For example, according to [27], a direct microemulsion includes the following ingredients (vol.%):  $AF_9$ -6-5-12, 60 %  $AF_9$ -12 solution in a mixture of: butanol – water – 2-5, diesel fuel – 2.5–10 and HCl solution to a final concentration of 5–12 % – the rest. A similar HAC contains:  $AF_9$ -6-5-12,  $AF_9$ -12-2-5 solution, diesel fuel – 2.5–10, HCl – 6.0–7.5, HF – 2.0–2.5 and water – the rest.

In [28] the composition of the reverse microemulsion is given (wt.%):  $AF_9$ -4 +  $AF_9$ -12 solution (from 2:1 to 20:1)-13-25, mixture of paraffin and aromatic hydrocarbons – 30–45, 22 % HCl solution – the rest.

They are characterized by a low reaction rate with carbonate rock, extremely low  $\sigma_{12}$  values and an increase in the size of the internal phase globules as they react, which allows the development of extended dissolution channels in the carbonate matrix [25, 26].

Apparently, such MCS compositions will not find wide application in domestic OGI.

### Direct acid-containing emulsions (DACE)

DACEs systems are considered "capricious" in their known stabilization variants with nonionic surfactants due to their low thermal and sedimentation stability [4, 7]. In particular, according to experimental data [29], a DACE formulation containing (by volume %):  $AF_9$ -10-1-4, toluene-59-86 and 36 % HCl-10-40, remains stable at 20°C for 24 hours, even though its initial effective viscosity at a shear gradient of 100  $s^{-1}$  ranges from 100 to 1250 mPa·s.

The positive functions of DACE are their high concentration of hydrocarbon phase, which does not disrupt the oil-well flow properties (OFP) in the reservoir and allows for effective dissolution of asphaltenes, prevention of water-oil emulsion (WOE) formation, and hydrophilization of the reservoir rock surface. They have been successfully used in a number of fields in Kazakhstan and Azerbaijan.

Laboratory studies on the channel formation during the DACE acid dissolution, consisting of (by volume %): emulsifier-1, 28 % HCl, and kerosene-66,

conducted on Indiana limestone cores with values of  $k_g = (1-7) \cdot 10^{-3} \mu m^2$  and a 25 % residual water content, indicated a reduction in pore volume (PV) for breakthrough by approximately 2.5 times compared to 15 % HCl due to effectively mitigating fast leakage [30].

In terms of obtaining more stable and effective PCE compositions, the works [4, 7] consider options for obtaining them based on mono spent sulfite liquor and aromatic hydrocarbons with the following volume ratio of components: 10 % MSSL solution in 20–24 % HCl-40–60 and aromatic hydrocarbons – 60–40. The corrosion rate values for steel of such PCE at 20 °C are ~3 g/(m<sup>2</sup>h), and the effective viscosity is 30–200 mPa·c. It is rational to add IR, nonionic surfactants, alcohols,  $CH_3COOH$ , and polymers, which can be the subject of interesting research work, including cores, the formation of acid dissolution channels, as well as the process of acid fracturing.

### Reverse acid-containing emulsions (RACE)

RACE possess a wide range of positive properties for effective application in predominantly fractured carbonate reservoirs [1, 3, 5, 31]. These properties arise from the variability of effective viscosity with the presence of acid phase globules, allowing them to be selectively filtered in the networks of the most permeable channels and fractures at low leak rates to form extended channels with minimal pore volume. Due to the low reaction rate with carbonate rock even under high temperatures (> 100°C) and insignificant corrosive aggressiveness towards steel while maintaining increased viscosity, these properties are applicable to high-temperature operational fields. The high content of the hydrocarbon medium does not significantly disrupt the oil-well flow properties in the reservoir. Additional ingredients can include stabilizers such as  $Fe^{3+}$  ions and polymeric anti-filters, specifically 1–2 % of starch or other additives [1].

In terms of the potential RACE improvement, the following experimental studies can be recommended. Specifically, as a dispersion for the acid-containing phase, it is effective to pre-thicken it with temporarily stable polymers (such as hydrolyzed polyacrylamide, hydroxyethyl cellulose, etc.). These compositions exhibit lower viscosity values, as illustrated in Fig. 2, as well as reduced fluid losses and reaction rates with carbonates. Furthermore, after the breakdown of RACE, the polymer-thickened HCl solutions retain their reactivity for a longer time [1].

By analogy, it is advisable to use a mixture of water-based or glycol solutions of MSL with HCl. Such RACEs have effective viscosity values of 10–100 mPa·s with prolonged interaction with carbonates even after destruction and lower thermal stability.

For high-temperature objects, water-based solutions of acid-generating compounds ( $NH_4Cl + CH_2O$ ,  $AlCl_3$ , glycols +  $H_2O_2$ , etc. [1], as well as  $CH_3COOH$  solutions [32]) can be tested as the internal phase.

The innovative solution for the RACE spontaneous generation lies in the simple mixing of a hydrocarbon solution of non-ionic surfactant and an emulsifier with a water-based solution of HCl. The resulting stable microemulsion, upon increasing the temperature, inverts into an RACE with a sharp increase in viscosity.

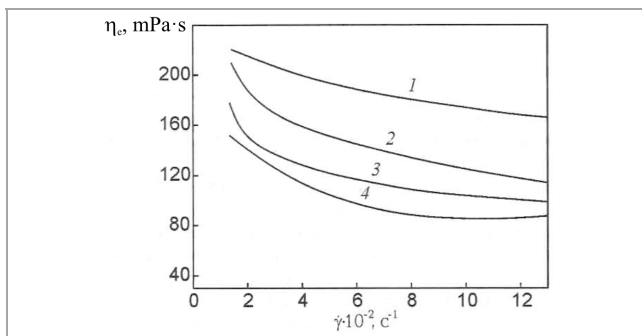


Fig. 2. Rheological flow curves of a 3.3 % solution of HEC in 12 % HCl (1), RACE using (3, 4), and RACE based on 12 % HCl (2), stabilized with various emulsifiers at a volumetric ratio of v/m – 60/40; 2, 3 – tarin (5 vol.%), 4 – emulgal

Table 5

Research data

Parameter	Value							
<i>t</i> , °C	20	30	40	50	60	70	80	90
$\eta_e$ , mPa·s	25	7	423	613	331	261	211	56

This is illustrated in data below, demonstrating a shear rate of 81 s<sup>-1</sup> for one of the compositions, which includes (vol. %): non-ionic surfactant – 4.5, emulsifier – 5.0, and 10 % HCl – 85.5 (see Table 5).

This technological approach has been widely applied in oil and gas production since the early 1980s and is summarized in works [1, 3]. Specifically, in the Perm Krai region, 177 such acid treatments were carried out from 2017 to 2020 on layered heterogeneous carbonate formations with water content exceeding 30 %, achieving a success rate of 89 % [9]. For a number of wells, a decrease in water cut by an average of 15 % and an increase in reservoir pressure were noted, indicating the connection of previously unused oil-saturated interlayers.

To facilitate the blockage of previously injected emulsion in perforation holes and against oil-saturated thicknesses, it is suggested to introduce fine-dispersed chalk or Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> into the emulsion. Their reaction with HCl promotes the rapid breakdown of the emulsion within the surface film. The optimal decision would be to use water-based solutions of Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> during the emulsion preparation stage. Another acceptable option is to introduce demulsifiers into the injected emulsion.

Since these acid treatments are conducted on highly water-saturated formations, it would be rational to include an intermediate stage of injecting a hydrocarbon flush after the emulsion to "wash away" the water deeper into the formation, thereby creating more favorable conditions for forming acid channels. For instance, according to [33], the amount of acid required for making through channels in water-saturated cores using 15 % HCl was 4.46, in oil-saturated cores it was 1.49, and in water-saturated cores with residual oil it was 0.68, all at identical injection rates.

By varying the type of non-ionic surfactant, emulsifier, and their ratios, it is possible to adjust the viscosity, thermal inversion, and other properties of RACE.

**Directional acid treatment (DAT) technology using reverse emulsions**

Finally, we consider it necessary to conduct experiments on core samples to study the formation of acid channels using the DAT method, as we have not found such data in the researches.

**Acid treatment of low-temperature dolomite reservoirs**

Large oil and gas condensate fields are being developed in Eastern Siberia such as Verkhnechonskoye, Kuyumbinskoye, Srednebotuobinskoye, Talakanskoye, Yurubcheno-Tokhonskoye and others, confined to dense dolomitized carbonate deposits of the Osinsky, Preobrazhensky, Danilovsky, Ust-Kutsky, and Erbogachevskoye horizons with reservoir temperatures of 8–12 °C. A research is being carried out for methods of their effective exploitation, including the use of the AT BZF.

It is clear that the most acceptable options for enhancing the connectivity of the reservoir with the remote part of the formation, due to the involvement of natural fractures and cavities in conditions of extremely low matrix porosity, are deep perforation, acid and proppant fracturing, as well as larger volume hydraulic fracturing (HF) [34]. For example, at the N.A. Savostyanov field, the AT BZF of Ust-Kut and Erbogachev horizons in 8-meter, the perforation interval was carried out by sequential injection of 8 m<sup>3</sup> of 12 % HCl + 3.2 m<sup>3</sup> of 20 % Na<sub>2</sub>CO<sub>3</sub> + 4 m<sup>3</sup> of 12 % HCl with wells stopped for reaction after each stage for 12 hours to transfer part of the contained in gypsum reservoirs in the form of CaCO<sub>3</sub> [4]. The efficiency of such OPP was comparable to low-volume proppant hydraulic fracturing.

In this context, it is logical to consider the creation of extended channels for acid dissolution within the bottomhole formation zone with minimal consumption of hydrochloric acid (HCl) solutions. However, in real conditions, the kinetic regime of the hydrochloric acid reaction with dolomites impedes this [3, 5].

To achieve effective dissolution and formation of extended channels within the bottomhole formation zone it is essential to transition the process into the diffusion region, which, according to different data sources, begins at temperatures around 50 °C or 75 °C. This necessitates laboratory confirmation for specific materials; however, relevant studies have still to be conducted by the interested scientific departments.

For instance, the study [37] assessed the efficacy of the imported DEEPA composition, which enzymatically generates a 2 % solution of formic acid (HCOOH) over a period of 3 to 4.5 hours on dolomitized samples from the Kuyumbinskoye field at a temperature of 30 °C, with a filtration rate of 0.1 cm<sup>3</sup>/min, and a soaking time of 48 hours. Naturally, such a low concentration of formic acid and

the low temperature resulted in only negligible dissolution of the filtration channel walls and fractures, limiting the penetration depth into the core. The effectiveness of such treatment could be significantly enhanced by optimizing the reaction conditions and using more suitable acidic solutions.

In work [38], an additional introduction of water-repellent (WR) agents is recommended to increase the reaction rate of dolomite reservoirs with HCl solutions for the conditions of the Yurubcheno-Tokhomskoye field. However, this is only a palliative measure that does not solve the problem.

In work [39], an unqualified conclusion was made regarding the diffusion kinetics of dolomite samples dissolution from a number of wells in the same field using HCl solutions at 27 °C. Nevertheless, the authors eventually acknowledged: "To provide recommendations on the formulations and technology for hydrochloric acid treatment of wells, it is essential to thoroughly study the kinetics of the discussed reaction." Subsequently, the authors recommend injecting methanol to remove water from the bottomhole formation zone, as well as performing hydrophobization of the surface using a 0.06–0.36 % solution of polymethylhydroxysiloxane in diesel fuel as a "water-repellent" agent. However, they fail to consider that water will subsequently filter through these hydrophobized channels at a faster rate compared to oil (see Fig. 1).

The authors of work [40] studied certain patterns of dolomite sample dissolution from the Osininskaya horizon of the Srednebotuobin field in HCl solutions at temperatures of 8–9 °C, based on an incorrect assumption regarding its diffusion kinetics. It has been noted that the dissolution of calcite and dolomite was observed at approximately 50 °C. The recommendations highlight the necessity of soaking 15–20 % HCl solutions in the bottomhole formation zone for 3–5 hours or heating the bottomhole formation zone to 30–40 °C using 20–24 % HCl solutions.

Thus, through many researches an understanding of the necessity for heating the bottomhole formation zone is achieved.

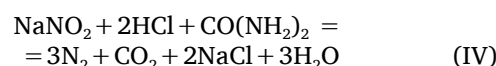
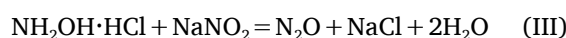
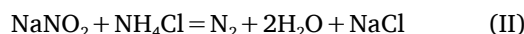
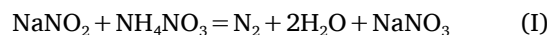
According to data from [41], even at 75 °C, it took approximately 25 pore volumes of HCl solutions to form through channels in dolomite cores with a permeability of about  $1 \cdot 10^{-3} \mu\text{m}^2$ , and at 50 °C, about 35 pore volumes were required. It indicates the need for even higher temperatures to achieve effective channel formation and dissolution in dolomite samples.

This is also supported by the results from [42], which documented the formation of volumetric channels in Devonian dolomite cores from the Timan-Pechora province with a permeability of  $\text{kg} \approx 1 \cdot 10^{-3} \mu\text{m}^2$ , requiring about 5 pore volumes of HCl solutions at 92 °C.

It is reasonable to consider the implementation of thermochemical treatment of bottomhole formation zone in such objects.

This approach could potentially enhance the efficiency of acidizing treatments by taking advantage of the increased temperatures to improve channel formation and dissolution rates in the dolomite reservoirs.

Until the early 2000s, the technology of downhole heat generation by injecting HCl solutions through perforated containers filled with chips, granules, or rods made of magnesium (Mg) or aluminum (Al) was widely used in fields. These solutions were introduced into the bottomhole formation zone in a heated state [3]. Such approaches have good mathematical and kinetic justifications for the reactions taking place. Later on, more effective heat-generating compositions (HGCs) were proposed, which aimed to enhance the efficiency of thermal treatments and acidizing processes within the reservoir rocks, improving hydrocarbon recovery in various geological conditions:



The kinetics of such reactions, depending on the pH of the environment and the amount of heat generated, are discussed in [3].

In a number of wells in the Gulf of Mexico reservoir, at depths exceeding 1220 meters and with hidden layer thicknesses of 6–36 meters, the separate injection of saturated solutions of sodium nitrite ( $\text{NaNO}_2$ ) and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) was carried out at a total flow rate of 32  $\text{m}^3$ . This resulted in temperature increases in bottomhole formation zone reaching 177–232 °C, while in the perforation interval, the temperature rose to 267 °C [43].

In 2011, at well 3003 of the Permian-Carboniferous formation of the Usinskoye field, separate injection of 20 tons of 66 %  $\text{NH}_4\text{NO}_3$  and 6 tons of 50 %  $\text{NaNO}_2$  was carried out with a 1  $\text{m}^3$  water buffer [44]. At the end of injection in the perforated interval at a depth of 1401 m the temperature was 250–325 °C, which extended to the bottomhole formation zone. However, above the packer in the wellbore, the temperature remained at a level of 18–20 °C.

Obviously, such temperatures are unnecessary for the AT BFZ, and the volumes of reagents can be reduced.

There are patented solutions for the safe delivery of heat-generating composition components in the form of two AEs, that mix in the BFZ: one contains a solution of  $\text{NaNO}_2 + \text{CO}(\text{NH}_2)_2$ , and the other contains HCl [3]. The next option involves the injection of crystalline hydrazine hydrochloride and  $\text{NaNO}_2$  into a viscous hydrocarbon liquid, which mixes with formation water in the BFZ to generate heat.

There is significant potential for creative exploration in this area. For instance, a solution of hydrochloric acid (HCl) could be injected into the porous reservoir system (PRS), followed by an emulsified mixture of sodium nitrite ( $\text{NaNO}_2$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) while maintaining its temporary stability. Once the reaction initiates, the target HCl solution could be reintroduced to initiate dissolution channels,



supplemented with a demulsifier and/or alcohols to ensure the complete breakdown of the emulsified mixture upon entering the PRS.

There is significant potential for creative research in this area. For instance, a solution of HCl could be injected into the BFZ, followed by an emulsified mixture of sodium nitrite (NaNO<sub>2</sub>) and ammonium

chloride (NH<sub>4</sub>Cl) while maintaining its temporary stability. Once the reaction initiates, the target HCl solution could be reintroduced to initiate dissolution channels, supplemented with a demulsifier and/or alcohols to ensure the complete breakdown of the emulsified mixture upon entering the heat-generating compositions.

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