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Enhanced oil recovery from high-viscosity oil deposits by acid systems based on surfactants, coordining solvents and complex compounds

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Abstract. Physicochemical aspects of enhanced oil recovery (EOR) from heavy high-viscosity deposits, developed in natural mode and combined with thermal methods, using systems based on surface-active substances (surfactants), coordinating solvents and complex compounds are considered, which chemically evolve in situ to acquire colloidal-chemical properties that are optimal for oil displacement. Thermobaric reservoir conditions, interactions with reservoir rock and fluids are the factors causing the chemical evolution of the systems.

To enhance oil recovery and intensify the development of high-viscosity deposits, acid oil-displacing systems of prolonged action based on surfactants, inorganic acid adduct and polyatomic alcohol have been created. As a result of experimental studies of acid-base equilibrium in the systems with donor-acceptor interactions – polybasic inorganic acid and polyol, the influence of electrolytes, non-electrolytes and surfactants, the optimal compositions of the systems were selected, as well as concentration ranges of the components in the acid systems. When the initially acid system interacts with the carbonate reservoir to release CO_2 , the oil viscosity decreases 1.2-2.7 times, the pH of the system rises and this system evolves chemically turning into an alkaline oil-displacing system. As a result it provides effective oil displacement and prolonged reservoir stimulation. The system is compatible with saline reservoir waters, has a low freezing point (minus 20 \div minus 60 °C), low interfacial tension at the oil boundary and is applicable in a wide temperature range, from 10 to 200 °C.

In 2014-2018 field tests of EOR technologies were successfully carried out to intensify oil production in the test areas of the Permian-Carboniferous deposit of high-viscosity oil in the Usinsk oil field, developed in natural mode and combined with thermal-steam stimulation, using the acid oil-displacing system based on surfactants, coordinating solvents and complex compounds. The pilot tests proved high efficiency of EOR technologies, as far as the oil production rate significantly increased, water cut decreased to intensify the development. The EOR technologies are environmentally safe and technologically effective. Commercial use of the EOR is promising for high-viscosity oil deposits.

Keywords: high-viscosity oils, enhanced oil recovery, physicochemical technologies, acid oil-displacing systems, surfactants, polybasic acids, polyols, coordinating compounds, acid-base equilibrium, CO₂, rheology, viscosity, the Usinsk oilfield, pilot tests

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Introduction

At present, heavy, highly viscous oils are considered as the main reserve of global hydrocarbon production, which determines the relevance of fundamental research work on the formation of new approaches to solving the problems of their most complete extraction from

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© 2019 The Authors. Published by Georesursy LLC This is an open access article under the CC BY 4.0 license (https://creativecommons.org/licenses/by/4.0/) the reservoir (Romero-Zeron, 2016; Muslimov, 2012, Sheng, 2011). To solve the problem of increasing oil recovery of heavy, highly viscous oil deposits, a wide range of different methods is proposed. The most common are thermal methods based on reducing the viscosity of oil when heated, which increases the degree of its extraction from the reservoir (Ruzin et al., 2013; Hascakir, 2017; Burzhe et al., 1989; Kovscek, 2102). Various options of thermal effects are investigated using water vapor and hot water injection into the reservoir, as well as processes of in-situ dry and wet combustion, thermochemical heat generation due to reactions with reservoir water and rock, microwave heating, and geothermal heat. Of the thermal methods, the most effective method that has reached the stage of large-scale industrial use is the method of steam-thermal exposure by the stationary or cyclic injection of water vapor into the reservoir. However, the steam-thermal effect is a technologically complex and high-cost field development system. Therefore, it is promising to use physicochemical methods to intensify the development and enhance the oil recovery of heavy, highly viscous oil deposits in the form of non-thermal "cold" technologies and in combination with thermal steam effects (Altunina, Kuvshinov, 2007, 2008; Altunina et al., 2015).

In the work of the Institute of Petroleum Chemistry of the Siberian Branch of the Russian Academy of Sciences (IPC SB RAS), this approach is implemented by creating "intelligent" compositions based on thermotropic inorganic and polymer sol-forming and gel-forming compositions, as well as oil-displacing compositions with adjustable viscosity and alkalinity for injection into oil reservoirs with the aim of increasing oil recovery, generated directly in the reservoir, reducing the water cut in producing wells and intensifying oil production in complicated operating conditions, including highviscosity deposits x oils developed both using thermal methods and without thermal exposure (Altunina et al., 2013, 2016a, 2017a, 2017b; Kuvshinov et al., 2017).

This paper discusses the physicochemical aspects of enhanced oil recovery of heavy oil fields developed in natural mode and in combination with thermal methods, using cyclic and stationary effects on the formation of chemically evolving surfactant-based systems, coordinating solvents and complex compounds. The factors causing the chemical evolution of systems in the reservoir are thermobaric reservoir conditions, interaction with reservoir rock and reservoir fluids. As a result of the chemical evolution of the injected systems in the reservoir, in the process of oil displacement, successively replacing each other, form effective oil displacing liquids with a high acid-base buffer capacity, adjustable viscosity, as well as emulsion and gas-liquid dispersion systems.

Acid-base equilibria in the systems "polybasic acid-polyol-water"

To increase oil recovery and intensify the development of high-viscosity oil fields, acidic oil-displacing compositions of a new type based on surfactants, coordinating solvents and complex compounds, in particular, coordination compounds of polybasic inorganic acids with polyatomic alcohols (polyols), chemically evolving directly in the formation with the acquisition of colloid-chemical properties that are optimal for oil displacement. As a result of experimental studies of acid-base equilibria in systems with donor-acceptor interactions – polybasic inorganic acid and polyhydric alcohol, the influence of electrolytes, non-electrolytes and surfactants on them, the optimal compositions and concentration areas of acidic compositions were selected.

In the "inorganic polyacid-polyol" systems, due to donor-acceptor interaction, complex acids are formed that are much stronger than the original acid (Shvarts, 1990; Shvarts et al., 2005). Donor-acceptor interaction allows increasing the acidity of oil-displacing compositions and increase the duration of their action in the reservoir by increasing the buffer capacity and expanding the range of the buffer action in the acidic pH range. The donor-acceptor interaction proceeds in the medium of an aqueous solution of a polyol, for example, glycerin, mannitol, sorbitol. Such a solution is a coordinating solvent, the polyol in it is a Lewis base, an electron pair donor. Lewis acids, for example, boric acid, dissolved in a coordinating solvent as well as aqua ions of some metals: calcium, magnesium, iron, and aluminum, are acceptors of the donor electron pair. A donor-acceptor chemical bond possesses the properties of a polarized covalent bond and is called a coordination bond. The interaction of the donor and the acceptor leads to the formation of a donor-acceptor molecular complex, called the coordination compound or adduct. The complex is a much stronger acid than the original Lewis acid. In Russia and abroad, this fact aroused interest in the study of the possibility of using complex acids in physical and chemical technologies for enhancing oil recovery.

Figure 1 shows a diagram of the formation of complex acid and its dissociation into ions by the example of the interaction of boric acid and glycerin.

$\begin{array}{c} H_2C-OH \\ H_C-OH \\ H_C-OH \\ H_2C-OH \end{array} + \begin{array}{c} HO \\ HO \\ HO \end{array} \xrightarrow{OH} \begin{array}{c} HO-CH_2 \\ HO-CH_2 \\ HO-CH_2 \end{array} \rightarrow$	$ \begin{bmatrix} H_2C - O & O & -CH_2 \\ HC - O & BB & O & -CH \\ H_2C - OH & HO - CH_2 \end{bmatrix}^{-} H^+ + 3H_2O $	
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Fig. 1. Donor-acceptor interaction of boric acid and glycerin with the formation of complex glycerinboric acid

Glycerinboric acid of a stoichiometric composition shown in Figure 1, under the conditions of our experiments, is the dominant form of the coordination polyolborate complex.

The oxygen atom of the hydroxyl group in the glycerin molecule, the donor, transfers its lone electron pair to the free orbital of the acceptor, the boron atom in the boric acid molecule. As a result, a molecule of coordination compound, glycerinboric acid, is four orders of magnitude stronger than boric acid from one molecule of boric acid and two molecules of glycerin. Instead of boric acid in this scheme there may be a metal aqua ion with properties of a Lewis acid, for example, a doubly charged cation of calcium and magnesium or a triple charged cation of aluminum and iron. Molecules of the complex acid are able to interact with metal aqua ions due to their hydroxyl alcohol groups. Figure 2 shows the reaction scheme, which reflects the stereochemical feature of the glycerinboric acid molecule – its ability to form soluble outer-sphere cyclic complexes with metal ions due to terminal hydroxyl groups.

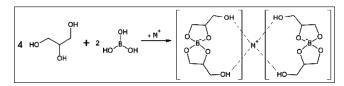


Fig. 2. Diagram of the interaction of glycerinboric acid with a metal cation in solution with the formation of a soluble outer-sphere cyclic complex

The scheme in Figure 2 is hypothetical, based on experimental results (Fig. 3) – abnormally high viscosity of glycerinboric acid in concentrated water-glycerin solutions of salts of divalent and trivalent metals.

With increasing concentration of metal aqua ions in solution, along with cyclic structures, the formation of polymer-like associates is possible, in which metal aqua ions play the role of bridges connecting the complex acid molecules to linear and branched spatial associative structures. As a rule, such a structure formation leads to a significant increase in viscosity. The method of regulating the viscosity and density of the salt additives of these metals may be useful for regulating the physico-chemical and rheological properties of the compositions. In addition, this interaction contributes to the compatibility of complex acids based on polyols with formation waters, especially with highly mineralized, with a high content of calcium and magnesium salts.

The system "boric acid-polyhydric alcoholelectrolytes-water" is of interest as the basis for a new type of oil-displacing fluids, effective at low reservoir temperatures, at which conventional oil-displacing fluids are ineffective. The physicochemical properties of this system are determined by the donor-acceptor interaction of polyhydric alcohols with boric acid, in which the acid anions act as a tetradentate ligand, which is a Lewis acid. As a result, in this system, depending on the pH and the nature of the electrolytes present, various coordination complexes of glycerin and boric acid anions are formed. When interacting with watersoluble non-ionic surfactants, these complexes form effective oil-displacing liquids with high wetting and washing ability.

Boric acid is a weak acid, its pK = 9.2, but with glycerin it forms a sufficiently strong glycerinboric acid (Rakhmankulov et al., 2003; Kreshkov, 1977), in which pK for a concentration of glycerin 1M is 6.5, for a concentration of glycerin 3.5M - 5.7 (Charlot, 1965). Glycerinboric acid and its salts are more soluble in water than salts of boric acid. This is due to the greater hydrophilicity of their molecules and the saturation of the coordination bonds of boron. Therefore, glycerinboric acid and its salts are well compatible with mineralized formation waters.

Experimental studies of acid-base equilibria in systems "boric acid-polyol-water" have been carried out at the IPC SB RAS. The pH values of the solutions were obtained by a potentiometric method using a glass electrode using a microprocessor laboratory pH meter manufactured by HANNA Instruments, the density by the pycnometric method. The measurement of the viscosity of polyol solutions was performed using a vibration viscometer "Reokinetic" with a tuning fork sensor. Studies of the rheological properties of solutions and oil were performed by rotational viscometry using a Reotest-2.1.M viscometer (measuring system of coaxial cylinders S/S2) and a HAAKE Viscometer iQ reometer (measuring system of coaxial cylinders CC16 DIN/Ti) at different shear rates and temperatures.

It was established that during the interaction of boric acid and polyols as a result of the formation of complex acids, the pH value of a 1 % solution of boric acid in aqueous-alcoholic solvents decreases from 5.9 units pH with an increase in the concentration of polyhydric

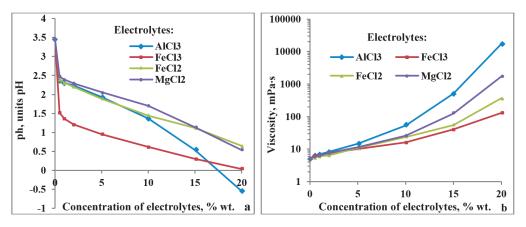


Fig. 3. Dependence of pH(a) and viscosity (b) of solutions containing 5 % wt. boric acid and 50 % wt. glycerin on concentration of electrolytes

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alcohols in the solvent up to 1.7-2.7 units pH, 5 % solution – from 3.4 to 1.5-2.2 units pH and 10 % – up to 1.3-1.8 units pH, Figure 4a is given as an example. In this case, the viscosity of solutions significantly increases (Fig. 4b). The decrease in pH with increasing polyol concentration is monotonous, due to the continuous equilibrium shift of the ionization reaction coupled with the shift of the formation of boric acid complex with the polyol, which is confirmed by the calculated concentration constants of the formation and ionization of glycerinboric acid in the glycerin coordinating solvent.

As a result of studying the effect of electrolytes on acid-base equilibria of solutions in the waterglycerinboric acid system, it was found that aluminum chloride AlCl₃, iron FeCl₃, FeCl₂ and magnesium MgCl₂ (Fig. 3), exert a strong influence on acid equilibrium. The concentration of aluminum chloride in solution to 20 % wt. pH values decrease to minus 0.54 units pH (Fig. 3a) the viscosity values of the solutions increase to 17,500 mPa s (Fig. 3b).

The addition of surfactants does not significantly affect the acid-base equilibria of solutions in the waterglycerinboric acid system and their physico-chemical characteristics of the solutions (pH, viscosity, density).

To increase oil recovery of high-viscosity oil deposits, along with acid-base properties, the rheological behavior of oil-displacing compositions is important. In this regard, the rheological properties of solutions compositions based on the surfactant-glycerin-oric acid-electrolytes system using rotational viscometry using the Reotest-2.1.M rotational viscometer (measuring system of coaxial cylinders S/S1) were investigated. At various shear rates, rheological curves of solution flow were obtained, and viscosity values were determined. It has been established that compositions based on the "surfactant-glycerin-boric acid-electrolytes" system are Newtonian fluids, that is, the dependence of stress on shear rate is linear, and the viscosity does not depend on shear rate (Fig. 5), despite the high values of solution viscosity.

Thus, the introduction of polyols, for example, glycerin, mannitol, sorbitol in the composition of

oil-displacing compositions based on surfactants and polyatomic acids leads to an increase in their acidity, a decrease in pH and freezing temperature of solutions, an increase in their viscosity and density, and an improvement in their compatibility with saline stratum waters. The study of acid-base equilibria in systems "boric acid-polyol-water" with donor-acceptor interactions, studying the effect of electrolytes, nonelectrolytes and surfactants, allowed us to establish the regularities of the formation of coordinating compounds and choose the composition and concentration of components to create acidic compositions with colloidal chemical properties optimal for oil displacement.

Physico-chemical and rheological properties of oil-displacing acidic compositions based on surfactants, boric acid and polyol

On the basis of the conducted research in the IPC SB RAS, an acid oil-displacing composition of prolonged action on the basis of surfactant, boric acid and glycerin adduct (GBK composition), realizing the concept of chemically evolving systems, was created. The composition is compatible with saline stratal waters, has a low freezing point (minus 20 °C \div minus 60 °C), low interfacial tension at the border with oil (below 0.001 mN/m at the border with oil of the Usinsk field). The density of the composition can be adjusted from 1100 to 1300 kg/m³, viscosity – from tens to hundreds of mPa·s.

The composition is applicable to enhance oil recovery and intensify oil production by increasing the permeability of reservoir rocks and the productivity of producing wells in a wide range of temperatures, from 10 to 200 °C, most effective in carbonate reservoirs, in particular, the Permian-Carboniferous reservoir of the Usinsk field. The composition has a delayed reaction with carbonate rocks. High oil displacing ability, compatibility with saline stratal waters, reduction of clay swelling leads to additional flushing of residual oil from both highly permeable and low permeable zones of the formation.

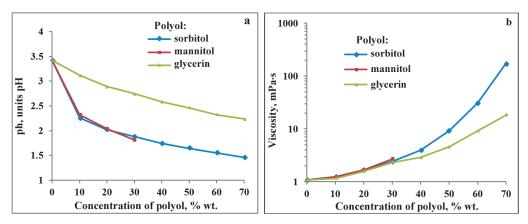


Fig. 4. Dependence of pH (a) and viscosity (b) of solutions containing 5 % wt. boric acid on concentration of polyol

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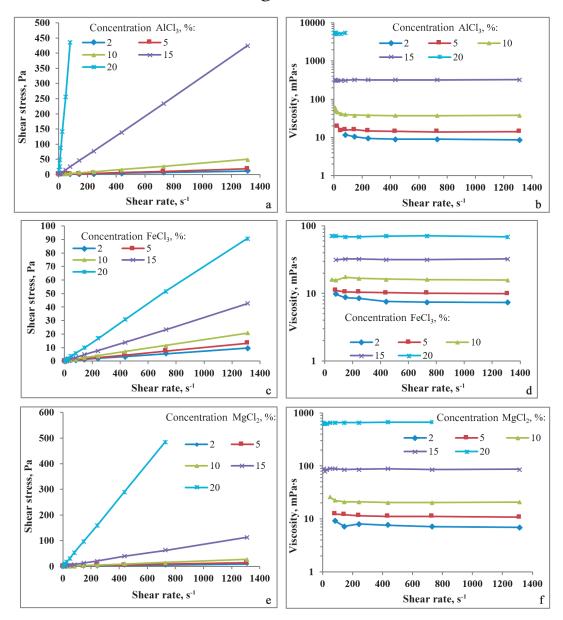


Fig. 5. Rheological curves of flow (a, c, d) and the dependence of viscosity (b, d, e) of solutions containing surfactants, boric acid, glycerin and electrolytes, on the shear rate

As a result of the interaction of the acidic composition with the carbonate reservoir, CO_2 is released, which dissolves in oil and reduces its viscosity, and contributes to an increase in the degree of oil recovery. In addition, at high temperatures, greater than 70 °C, the pH of the composition increases from 2.8-3.1 to 8.8-10.0 (Fig. 6), and it evolves chemically, becoming alkaline composition, providing effective oil displacement and prolonged exposure to the reservoir. After thermostating with the composition and carbonate reservoir at temperatures above 70 °C, the viscosity of the oil decreases 1.2-2.7 times (Fig. 7).

The method of rotational viscometry was used to study the rheological properties of the oil of the Usinsk field before thermostating and after thermostating of the original oil with the oil-displacing acidic composition GBK at temperatures of 70, 90 and 120 °C. At various shear rates and temperatures in the range from 20 to 90 °C, rheological curves of oil flow were obtained and viscosity values were determined (Fig. 8). Oil from the Usinsk field is a colloid-dispersed system with poorly pronounced non-Newtonian properties. Temperature control with an oil-driving acidic composition significantly reduces the oil viscosity. Oil loses its non-Newtonian properties and becomes a Newtonian fluid, that is, the dependence of stress on shear rate becomes linear.

In addition, the proton magnetic resonance (PMR) method using an AVANCEAV 300 Fourier transform spectrometer (Bruker) (Germany) found that oildisplacing acidic compositions of GBK have demulsifying properties. From the PMR spectra, it follows that the result of heat treatment of oil with GBK compositions at different temperatures is that the water content in the oil phase of the "oil-composition" system decreases; the higher the heat treatment temperature, the less water remains in the oil phase.

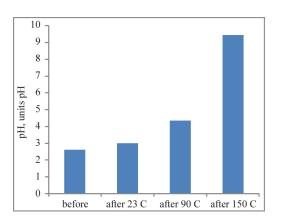


Fig. 6. The pH value of the composition of GBK before and after thermostating with a carbonate reservoir at different temperatures

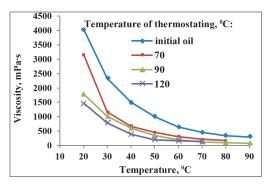


Fig. 7. Temperature dependence of oil viscosity of the Usinsk field before and after thermostating with the composition of GBK at various temperatures

Pilot works with the use of acid oil-displacing GBK composition

Acid oil-displacing composition of GBK of prolonged action on the basis of surfactant, boric acid adduct and glycerin can be used in the treatment of bottomhole zones of injection and production wells using different injection schemes: one rim, several rims, alternating injection of the rims of gas cylinder in different concentrations. When alternating injection of the rims of GBK composition, the rim of the composition is diluted 3-10 times (optimally 5 times), then the rim of GBK composition, diluted 2 times is first pumped, then the rim of composition, diluted 3-10 times, etc. After the total volume has been injected, the GBK composition is forced into the reservoir from tubing with a buffer volume of water (8-10 m³). The exposure time of the GBK composition on the well bottom zone is from 12 hours to 1-3 days, for this period the well should be closed.

To increase oil recovery and to intensify the development of deposits of heavy, highly viscous oils without heat exposure, "cold" physical and chemical technologies have been proposed using "intelligent" oil-displacing compositions based on surfactants, coordinating solvents and complex compounds. To increase the flow rates of low-productive producing wells of the Permian-Carboniferous reservoir of the Usinsk field for oil and liquid without thermal steam effects,

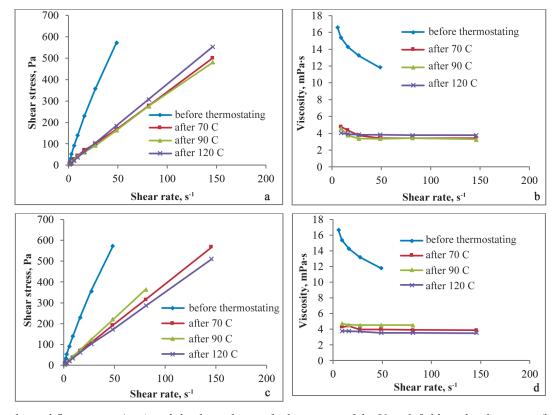


Fig. 8. Rheological flow curves (a, c) and the dependence of oil viscosity of the Usinsk field on the shear rate (b, d) before and after thermostating at different temperatures with the composition of GBK (a, b) and with the composition of GBK with the addition of carbonate rock (c, d). Measurements were carried out at 20 °C.

a reagent-cyclical was proposed (similar to a steam cyclic) with the use of acidic oil-displacing composition GBK of a prolonged action based on surfactant, boric acid adduct and glycerin. The rim of the surfactant composition is pumped into the production well, then water is pumped, after that an exposure of 7-14 days is made (similar to impregnation at the steam cyclic) and then the well is put into operation. Oil production is carried out in the form of low-viscosity direct emulsion. After completion of oil production in the well in the first cycle, the next cycle is carried out – injection of alternating rims of the surfactant composition and water, as in the first cycle, holding and then extracting oil from the well. As a result, there is an increase in oil production from both high-permeability and low-permeability zones of the formation.

From May 29, 2014 to July 26, 2014, pilot works were carried out on the Permian-Carboniferous reservoir of the Usinsk field using the acidic GBK composition of prolonged action according to the reagent-cyclical variant. OSK LLC pumped the GBK composition into 10 low-productive production wells. The injection volume of the composition was in the range of 30-50 m³, the volume of the concentrate of the composition was 9-15 m³. Figure 9 shows the characteristic reaction of the wells immediately after injection, and Figure 10 shows a generalized schedule for increasing oil and liquid flow rates for all 10 wells in the observation period after treatment for 19 months and average monthly oil flow rates for individual wells before and after processing composition GBK (up to 19 months).

After injection of the GBK acid composition of prolonged action based on surfactant, inorganic acid adduct and polyol, an increase in oil flow rates by 5.5-14.8 tons/day, an increase in liquid flow rates by 15-25 m³/day is observed. The average oil flow rate for one well before treatment was 80 tons/month, based on the results of 19 months after treatment – 185 tons/month, that is,

the increase in oil flow rates amounted to an average of 104 tons/month per well. Additionally, the oil produced during the observation period of 19 months amounted to $\sim 20,000$ tons over 10 wells, $\sim 2,000$ tons/well; the effect was not over.

According to the results of the work carried out, the use of prolonged-action GBK acid composition to enhance oil recovery and intensify oil production by increasing the permeability of carbonate reservoir rocks and increasing the productivity of low-productive production wells was recommended for industrial use.

On the Permian-Carboniferous deposit of the Usinsk field in 2017-2018 the technology has been successfully tested to restore the injectivity of a horizontal well and enhance oil recovery under thermal effects by injection of an acidic oil-displacing GBK composition of prolonged action based on surfactant, boric acid adduct and glycerin. In 2017, in the South-Eastern experimental area of the Permian-Carboniferous reservoir of highviscosity oil from the Usinsk field, LUKOIL-Komi LLC, jointly with the IPC SB RAS, a branch of LUKOIL-Engineering LLC, PermNIPIneft, and OSC LLC, injection of gelling and oil displacing compositions with the subsequent restoration of liquid injectivity and enhanced oil recovery using acidic composition based on surfactants, coordinating solvents and complex compounds: treatment of horizontal hot water injection wells 10GS and 11GS with compositions GALKA® and NINKA-Z in June-September 2017, followed by treatment of the 10GS well with GBK acid composition based on surfactant.

Inorganic gel-forming compositions GALKA[®] in surface conditions are low-viscosity aqueous solutions, in reservoir conditions – turn into gels. Gelation occurs under the action of thermal energy of the reservoir or the injected coolant, without cross-linking agents. For the preparation of compositions water of any mineralization is used, suitable for inhomogeneous formations with

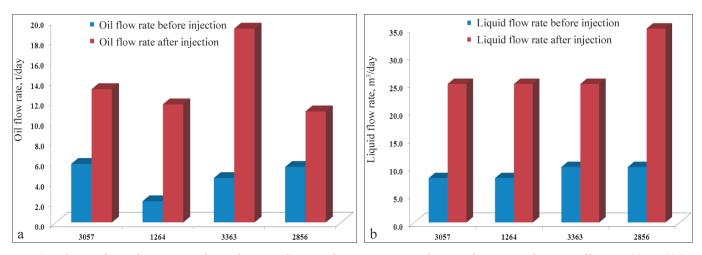
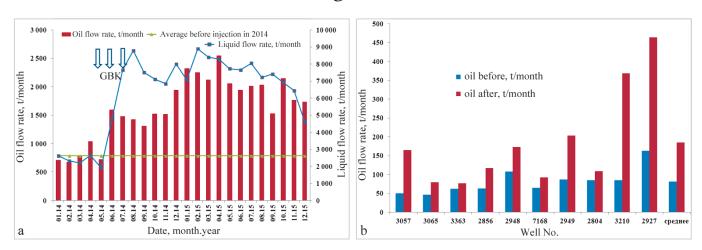


Fig. 9. Pilot work results using prolonged-action GBK acid composition on low-productive producing wells Nos. 3057, 1264, 3363, 2856 of the Permian-Carboniferous reservoir of the Usinsk field: an increase in flow rates for oil (a) and liquid (b) immediately after injection



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Fig. 10. Pilot work results using prolonged-action GBK acid composition on low-productive producing wells of the Permian-Carboniferous reservoir of the Usinsk field: (a) – a total of 10 producing wells, an increase in oil production rates, a decrease in water content; (b) – the average value of monthly oil flow rates for individual wells over the observation period of 19 months for individual wells before and after treatment with the GBK composition

permeability from 0.01 to 30 μ m². The gelation time is from several minutes to several days in the temperature range 10-320 °C. With their use, five gel-technologies for enhanced oil recovery have been developed, which are industrially used in the fields of Western Siberia and the Komi Republic (Altunina, Kuvshinov, 2008, 2007; Altunina et al., 2015, 2017a). Ecological safety of the reagents, their harmlessness to humans makes it possible to widely use gel technologies in the fields of Russia and other countries.

The thickened composition NINKA-Z is simultaneously flow-diverting and oil-displacing composition, used to increase both the oil-displacement ratio and the coverage ratio of high-viscosity oil deposits developed by the steam-heat effect (Altunina et al., 2015, 2011, 2016b). In the formation, under thermal action, carbamide is hydrolyzed, forming CO₂ and NH₂, which, with the ammonium salt, provides an alkaline ammonia buffer system, optimal for oil displacement purposes. An increase in pH causes the hydrolysis of the aluminum salt to form an aluminum hydroxide sol, while the viscosity of the composition increases by 1-2 orders of magnitude, which leads to an increase in the formation's thermal coverage, the connection of low-permeability streams, a decrease in oil viscosity and its additional washing out. As a result, an increase in the reservoir coverage ratio, an increase in oil recovery factor and an increase in oil production occur.

The wells number 10GS and 11GS are located in the South-Eastern experimental plot (Fig. 11), pumping hot water into the lower development object. The southeastern section (cluster of wells 7OC) is a part of the southern current section. Until 2012, the site was developed in the natural mode. At the time of the implementation of the reservoir pressure maintenance system, the weighted average reservoir pressure was 8.58 MPa, the average daily fluid flow rate was 22 tons/day, the average daily oil flow rate was 10.4 tons/day, water content – 52 %. With the organization of simultaneous injection of hot water into wells No. 10GS, 11GS in December 2012 with an intake capacity of 400 tons/day (total daily injection of 800 tons/day), the reservoir pressure stabilized and at the time of analysis is 9.2 MPa, but as a result water breakthroughs sharply increased the water content of surrounding wells in February 2013, from 57 to 65 %, after which the injection volumes were adjusted. Since June 2013, wells No. 10GS, 11GS have been operated cyclically for 30 days, the daily injection capacity of one well is about 400 m³/day. After switching to the cyclic injection mode, the average flow rate of the surrounding wells was 30 tons/day, the average oil flow rate was 9 tons/day.

On the injection well No. 10GS of 30-31.07.2017, measures were taken to inject the gel-forming composition GALKA[®] for the redistribution of filtration flows, to limit water inflow, pumped 100 m³. Injectivity capacity before treatment was 720 m³/day, after treatment – 640 m³/day. Measures to inject oil-displacing and flow-

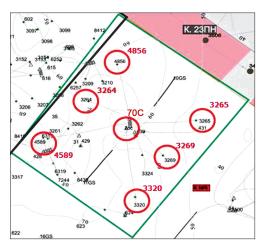


Fig. 11. Plot of pilot works in the area of the well cluster number 70C

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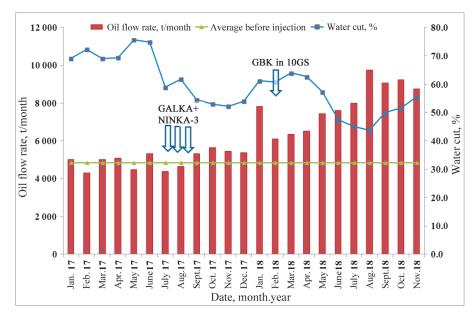


Fig. 12. Results of complex treatment with GALKA + NINKA-Z compositions, with additional treatment with the acid GBK composition of injection wells 10GS and 11GS in 2017-2018

deflecting composition NINKA-Z for leveling the intake profile and washing out residual oil were performed on 09-11.08.2017, 200 m³ were injected. Injectivity capacity before treatment was 640 m³/day, after 640 m³/day. In general, according to the results of the work, the injectivity of the well is reduced by 80 m³.

On injection well No. 11GS, on 27-28.08.2017, measures were taken to inject the GALKA[®] composition, 80 m³ were injected. Intake capacity before treatment was 720 m³/day, after 520 m³/day. Measures for the injection of the composition NINKA-W were carried out on September 14-15, 2017, 160 m³ were injected. Injectivity capacity before treatment was 510 m³/day, after 520 m³/day. In general, the results of the work show a decrease in the injectivity of well by 200 m³. Due to the fact that the wells are located in one area of the reservoir and the injection of compositions was performed in approximately one period, then their influence on the production wells is considered together.

In December 2017, when the well No. 10GS was operating, there was an increase in pressure on the 7OC furnace, after which the furnace was transferred to a 2 mm choke, but this did not lead to a decrease in pressure. To reduce the pressure on the furnaces, the nozzle at well No. 11GS was increased. Indirectly, this indicates about a decrease in injectivity in the well number 10 GS. To intensify injectivity, a decision was made in the well No. 10GS to perform an bottomhole zone treatment using an oil-displacing acid GBK composition based on surfactant, boric acid adduct and glycerin. In January 2018, the acid composition was injected into the well 10GS 50 m³, the edges of 5 m³, with alternating changes in the composition: water concentration equal to 1:1 and 1:9, according to the developed technical plan and instructions for using the composition.

Figure 12 shows the work schedule for the 20 production wells in the area surrounding wells 10 and 11GS. The figure shows the moments of processing compositions. It can be seen that in the first months the effect was not too noticeable, which can be explained as a delay effect of 2-4 months for the treatment of production wells, due to the time of redistribution of the flow and passage of the fluid front between the injection and production wells, and a decrease in the injectivity in the well 10GS.

After carrying out measures to increase the injectivity at the well 10GS with the injection of the acid composition of the cylinder head, the graph shows a steady increase in oil production. The decrease in the water content was recorded almost immediately after treatment. The whole time of observation of the effect it was maintained. Currently, the duration of the effect is 14 months; additional oil production in the area is 35,400 tons, or ~ 4.2 tons/day for each production well, that is, there is an increase in oil production and development intensification, which confirms the effectiveness of the GBK composition and the proposed technology.

Thus, the possibility of using an acid GBK composition based on surfactants, coordinating solvents and complex compounds, if necessary, to restore or increase the injectivity of the injection well, including after treatments with gel-forming and/or highly viscous compositions, is shown.

Conclusion

To increase oil recovery and intensify the development of high-viscosity oil fields, acidic oil-displacing compositions based on surfactants, coordinating solvents and complex compounds have been created that chemically evolve directly in the reservoir with the acquisition of colloidal chemical properties that are optimal for oil displacement.

The main physicochemical factors for increasing oil recovery are the interaction of the initially acidic composition with a carbonate reservoir with the release of CO_2 and a decrease in oil viscosity by 1.2-2.7 times, leading to an increase in the pH of the composition and its transformation into an alkaline oil-displacing composition with a large buffer capacity. These factors provide effective oil displacement and prolonged impact on the reservoir in a wide range of dilution with water during in-situ filtration.

The presence of surfactants and polyols in the composition ensures its compatibility with mineralized formation water, low freezing temperature (minus $20 \div$ minus 60 °C), low interfacial stress at the interface with oil (below 0.001 mN/m) and applicability over a wide range of reservoir temperatures (from 10 up to 200 °C). Moreover, the compositions are Newtonian fluids with a high viscosity (from tens to hundreds of mPa·s), commensurate with the viscosity of the oil.

All reagents used in the GBK compositions are products of large-tonnage industrial production. The compositions have high manufacturability, including in the northern regions, since they are low-fouling, standard oil-field equipment is used for their preparation and injection.

The use on an industrial scale of acidic oil-displacing compositions of a new type based on surfactants, coordinating solvents and complex compounds that implement the concept of chemically evolving systems, as well as environmentally safe technologies using them that have high technological and economic efficiency, will extend the cost-effective operation of fields located in the late development stage, and to engage in the development of a field with difficultly recoverable hydrocarbon reserves, including deposits of highly viscous oils and deposits of the Arctic region.

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