OIL-DISPLACING SURFACTANT COMPOSITION WITH CONTROLLED VISCOSITY FOR ENHANCED OIL RECOVERY FROM HEAVY OIL DEPOSITS

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Abstract. To improve the efficiency of waterflooding or steam stimulation, enhanced oil recovery and intensification of development a thickened oil-displacing composition NINKA-Z has been created, based on surfactants with controlled viscosity and alkalinity, which is both water-diverting and oil-displacing composition. When exposed to the reservoir with compositions NINKA-Z there is an increase in the final oil recovery by increasing the rate and factor of oil displacement, and sweep efficiency.

The paper gives the results of laboratory studies of thickened oil-displacing composition for enhanced oil recovery from deposits with high temperature and for steam stimulation – solation kinetics, physical-chemical and rheological properties of the composition solutions. The composition has an adjustable viscosity and high oil-displacing ability; it retains, self-regulates in a deposit for a long time complex of colloidal-chemical properties, optimal for oil displacement purposes.

In 2014-2015 pilot tests were successfully conducted of the technology to enhance oil recovery using oil-displacing thickened composition NINKA-Z on the experimental plot of Permian-Carboniferous heavy oil deposit of the Usinsky field that being developed by steam stimulation. Pilot projects have shown high efficiency of the technology, significant effects were received on increasing oil production, reduction of water cut and intensification of development. The technology is environmentally friendly and technologically efficient. The technology is promising for the industrial use in heavy oil deposits.

Keywords: oil-displacing compositions, surfactants, alkaline buffers, urea, hydrolysis, CO_2, kinetics, rheology, viscosity, enhanced oil recovery, physical and chemical technologies, heavy oil, Permian-Carboniferous deposit, Usinsky field, steam stimulation, pilot tests

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Russia is among the top ten countries with the largest oil reserves, on this indicator only being behind countries of the Middle East and Venezuela. The main method of oil fields development in Russia is flooding, with its use about 95 % of oil is produced. Currently, most of the large deposits of Russia are in the late stage of development, the current water cut exceeds 80 %. The newly introduced fields are characterized by low permeability, high viscosity of oil and complex geological structure, i.e. reserves are classified as difficult to recover.

The share of oil reserves difficult to recover in Russia is constantly growing and now exceeds 60 % (including heavy oil – 13 %, low-permeable reservoirs – 36 %) (Yakutseni et al., 2007; Tarasyuk, 2014; Barkov et al., 2015). In these conditions the opportunity of oil reserves increment by increasing oil recovery is of particular importance. The increase of the final oil recovery factor by only 1 % will provide annual increase in production by 20-30 million tons. For effective development of hard recoverable oil reserves, it is necessary to create and widespread use of science-based technologies in oil production, development of new chemicals for implementation of technologies.

Permanent complication of conditions for profitable operation of oil and gas stimulates the emergence of new and improvement of methods used to enhance oil recovery. In the development of methods of enhanced oil recovery, a trend is clear to provide oil-displacing fluid with elements of self-regulation, enabling them to maintain their function in the formation for a long time. The Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences (IPC SB RAS, Tomsk) has implemented one of the options of this trend, based on the ideas of composition for enhanced oil recovery as a physical-chemical system with feedback.

These ideas served as the theoretical basis of physical and chemical principles of compositions selection on the basis of the surfactant considering thermodynamic and kinetic parameters of the system ‘oil – rock – aqueous phase’, affecting the displacement of oil from the porous medium. It was suggested to use alkaline buffering system with a maximum buffering capacity in the range of 9.0-10.5 units of pH to provide negative feedback in the oil-displacing compositions, enabling them to maintain, self-regulate complex of colloidal-chemical properties, optimal for oil displacement (Altunina, Kuvshinov, 2007 a, 2007 b, 2008; Altunina et al., 2019, 2011, 2014).

The choice of alkaline buffer systems is due to the important role of physical and chemical processes with the involvement of hydroxyl ions in the mechanism of oil displacement from capillary-porous media of the reservoir by aqueous surfactant solutions. Such interactions include neutralization of acidic groups, saponification of ester bonds, deprotonation of donor heteroatoms of asphaltene-resin oil components, association of the hydroxyl ions with aromatic fragments of molecules of oil components, influence on the structure of water and thus on hydrophobic binding, conformational mobility of hydrophobic surfactants parts. As a result of these interactions the interfacial tension and interfacial viscosity decrease at the interface of oil – water, rock wettability increases and surfactant losses are reduced due to reduced adsorption onto the rock.

Currently, the effective development of deposits of high-viscosity oils is carried out mainly with the use of thermal effects techniques. Steam is widely used as a coolant. Many researchers continually attempt to find the chemical additives to steam, improving its oil-displacing effect.

Theoretically, such additives should reduce steam condensation temperature, for example, for the mechanism of azeotrope formation or water solubility in compressed gases, should increase phase permeability of the steam-gas mixture and the like. To date, the best additive is carbon dioxide CO_2. The reasons for the favorable effect of CO_2 are well known – increase of phase permeability by oil, oil viscosity reduction, favorable change in the ratio of oil and water phase mobility.

The IPC SB RAS develops the impact on the heavy oil deposit by thermotropic oil-displacing compositions based on surfactants, which in the formation under the temperature of water vapor or hot water form CO_2 and ammonia buffer system. Physical-chemical mechanism of oil-displacing compositions based on surfactant and alkaline buffer solutions, generating CO_2 directly into the formation, is based on the kinetics of urea hydrolysis in the compositions with ammonia and carbon dioxide formation in the temperature range 70-250 °C.

Previously technology has been developed of the stimulation of NINKA® composition on heavy oil deposit based on surfactants, ammonium salts and urea, which are under reservoir temperature or injected coolant form carbon dioxide CO_2 and ammonia buffer system (Altunina, Kuvshinov, 2007 b; Altunina et al., 2003, 2010). Urea directly in the reservoir at a temperature above 70 ° C is hydrolyzed to form ammonia and CO_2. Carbon dioxide, in contrast to ammonia is much more soluble in oil than in water. Therefore, in the system 'oil – water' oil phase will be enriched in CO_2, water phase – in ammonia.

When CO_2 dissolved, oil viscosity is reduced 2-6 times (Altunina et al., 2003). Ammonia with ammonium salt forms alkaline buffer system with a maximum capacity in the range of pH 9÷10 optimal for the purposes of oil displacement. Moreover, thanks to the presence of alkalinity and surfactants, it contributes to further oil displacement, interfacial tension and destructuring decrease, thinning of viscous layers or films at the boundaries of oil – water – rock, worsening fluids filtering in the reservoir and reducing completeness of oil extraction (Altunina, Kuvshinov, 2007 b; Altunina et al., 1992; 2010).

In order to increase oil recovery, not only by increasing the oil displacement factor, but also by increasing the sweep efficiency, thickened oil-displacing composition NINKA-Z has been created with adjustable viscosity and alkalinity, which is both water diverting and oil-displacing composition. The composition is the result of research in the concept development of using reservoir energy or injected coolant to generate *in situ* of chemical 'smart' systems – compositions based on surfactants and alkaline buffer systems, preserving, self-supporting in the formation set of properties for a long time, optimal for oil displacement purposes (Altunina, Kuvshinov, 2007 b; Altunina et al., 1992; 2010).

NINKA-Z composition can be used to improve the efficiency of waterflooding or steam stimulation, increasing the ultimate oil recovery factor: for enhanced oil recovery from reservoirs with high natural reservoir temperature (above 70 °C), developed by flooding, as well as deposits of heavy oil with natural low reservoir temperature, developed by technology of areal injection of coolant (steam, hot water) and cyclic-steam stimulation for producing wells.

When injecting thickened composition NINKA-Z in the water or steam injection wells, controlled increase in viscosity of the composition occurs directly in the formation. This helps equalizing the mobility of displaced and displacing agents and increasing the sweep impact, reducing the viscosity instability of displacement front, limiting the working injected fluid breakthroughs in reacting production wells, and connection of low-permeability interlayers. Furthermore, there is an additional reduction in the oil viscosity and additional oil washing from washed zones. As a result, there is an increase in sweep efficiency, oil recovery and stimulation of oil production.

To obtain thickened composition NINKA-Z in the composition NINKA® based on surfactants, aluminum salt is additionally introduced, changing the concentration of which it is possible to adjust the composition viscosity. At temperatures above 70 °C resulting in urea hydrolysis directly in the formation pH of the solution increases, hydrolysis of aluminum ions occurs to form aluminum hydroxide (Altunina, Kuvshinov, 2007 b; Altunina et al., 1992; 2003), resulting in increased viscosity of oil-displacing composition after a certain time.

The research has been made to find out the influence of components concentrations of thickened oil-displacing composition NINKA-Z on rheological properties of solutions and sols in particular, the dynamic viscosity (mPa·s). Measuring of solution viscosity was performed by rotation and vibration methods using a vibrating viscometer with tuning-fork sensor "Reokinetika" (Bogoslovskiy, Altunina, 1985). At certain concentrations of aluminum salt, sol is formed directly in the reservoir – mobile free-dispersed system with high oil-displacing properties.

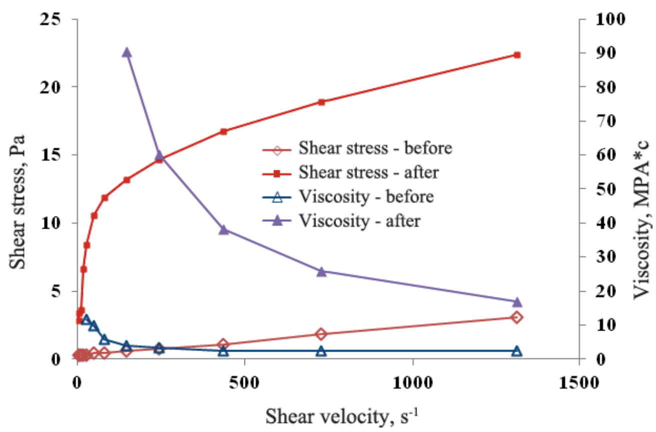

Figure 1. The complete rheological flow curves and the dependence of solution viscosity of sol-forming oil-displacing composition NINKA-Z with adjustable viscosity and alkalinity (2.5 % of aluminum salts) before and after 5 hours of thermal regulation at 150 °C: before thermal regulation composition solution is a Newtonian fluid, after the sol formation- viscoplastic fluid.

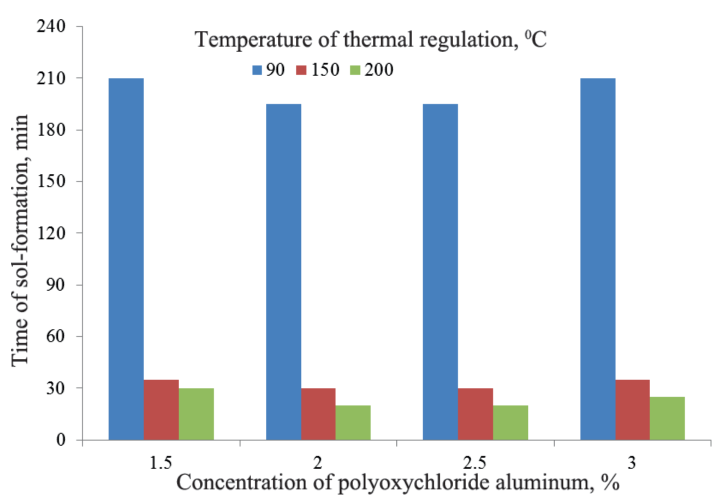

Figure 2. Thickening time (gel or sol formation) of sol-forming oil-displacing composition solutions with controlled viscosity and alkalinity, depending on the content of aluminum salt and thermal regulation temperature.

Figures 1 and 2 show the results of sol generation kinetics in the composition solutions at temperatures of 90, 150 and 200 °C.

Studies of sol formation kinetics and rheological properties of sols and solutions prepared at 90, 150 and 200 °C showed that after thermal regulation of solutions of sol forming oil-displacing composition with controlled viscosity and alkalinity, depending on the concentration of aluminum salt, viscosity of the composition solutions increases by 6-78 times, pH of the composition solutions after thermal regulation increases to 7.7-10.1 units pH.

As an example, Figure 1 shows the study results of rheological properties of the composition solution (concentration of aluminum salt 2.5 %) before and after the formation of a sol by thermal regulation at 150 °C for 5 hours. Measurements were carried out after cooling the solution to 20 °C. As can be seen from the figure, before thermal regulation, composition solution is a Newtonian fluid, after the sol formation – viscoplastic fluid having properties of both solid and liquid, and the ability to show the properties of elastic shape recovery after stress relief (Figure 1).

The time of sol formation in the solution of oil-displacing composition depends on aluminum salt concentration and thermal regulation temperature and ranges from 20-35 minutes at 150 and 200 °C and 3-3.5 hours at 90 °C (Figure 2), that is, by increasing the thermal regulation temperature between 90 and 150, 200 °C, the time of sol formation is reduced 6-9 times.

Research of the rheological properties changes of the Usinsk oil field after thermal regulation with solutions of sol-forming oil-displacing composition with controlled viscosity and alkalinity showed that after heat treatment at 150 °C of heavy oil from the Usinsk field with composition, oil viscosity as compared to the original oil (non-heat treated) is reduced by 2-3 times (Figure 3). Composition solutions have demulsifying action; the amount of water in the oil is reduced 10-220 times.

The developed compositions have the following physical-chemical parameters: pH of solutions – 3.4-4.1 units pH; pH of sols and gels – 7.7-10.1 units pH; viscosity of solutions – 1.6-3.5 MPa·s; viscosity of sols – 9.7-260 mPa·s; solution density – 1161-1178 kg/m^3; gel formation time – from several minutes to several days depending on the temperature and composition of the solution; freezing temperature – minus 20.4 – minus 21.2 °C.

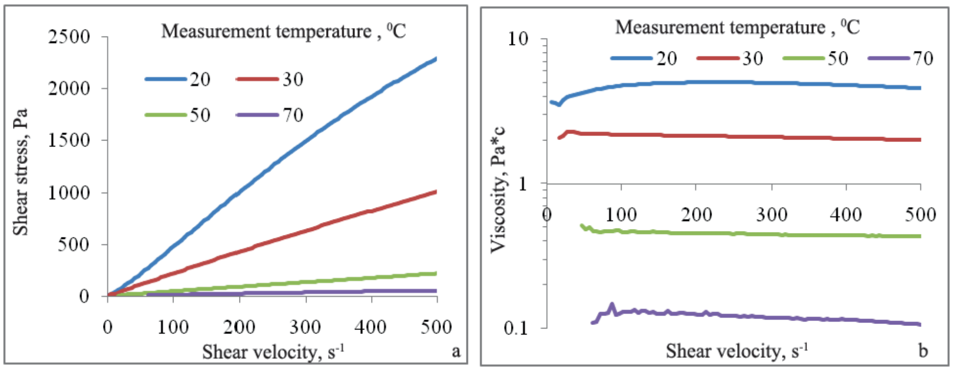

Figure 3. Rheological flow curves (a) and dependences of oil viscosity from Permian-Carboniferous deposit of Usinsk field and shear rate (b) after thermal regulation at 150 °C for 24 hours with solution of sol-forming oil-displacing composition measured at different temperatures.

Experimental study of filtration properties and oil-displacing ability of sol-forming compositions with controlled alkalinity and viscosity (thickened composition NINKA-Z) with respect to the conditions of heterogeneous reservoirs in Western Siberia, developed by flooding, and Permian-Carboniferous deposit of heavy oil of Usinsk field, being developed using steam and cyclic steam stimulation, showed their high efficiency.

So, on the basis of experimental studies we have found that the injection of composition with controlled alkalinity and viscosity – thickened composition NINKA-Z with thermal steam and cyclic steam stimulation on the formation with respect to the conditions of Permian-Carboniferous deposit of heavy oil of Usinsk field leads to a redistribution of filtration flows, reduction of filtration rate on highly permeable streaks and increase of the filtration rate on low permeable seams, leveling of fluid mobility in a heterogeneous reservoir model, which is accompanied by an additional oil wash from low-permeability zones, and zones of high permeability reservoir models.

This increases the factor of oil displacement by water in the whole model. Oil displacement factor increment ranges from 5 to 39 %, at the same high absolute oil displacement coefficients and low residual oil saturation are achieved (Figure 4).

On Permian-Carboniferous deposit of heavy oil of the Usinsk field, in the plot PTV-3, developed by cyclic steam and thermal-steam stimulation, according to the technological instruction the testing was conducted of the technology to enhance oil recovery, oil production stimulation and water shut-off using thermotropic sol-forming composition NINKA-Z. The work was carried by LLC "OSK" on the Usinsk field (Figure 5), LLC "LUKOIL-Komi".

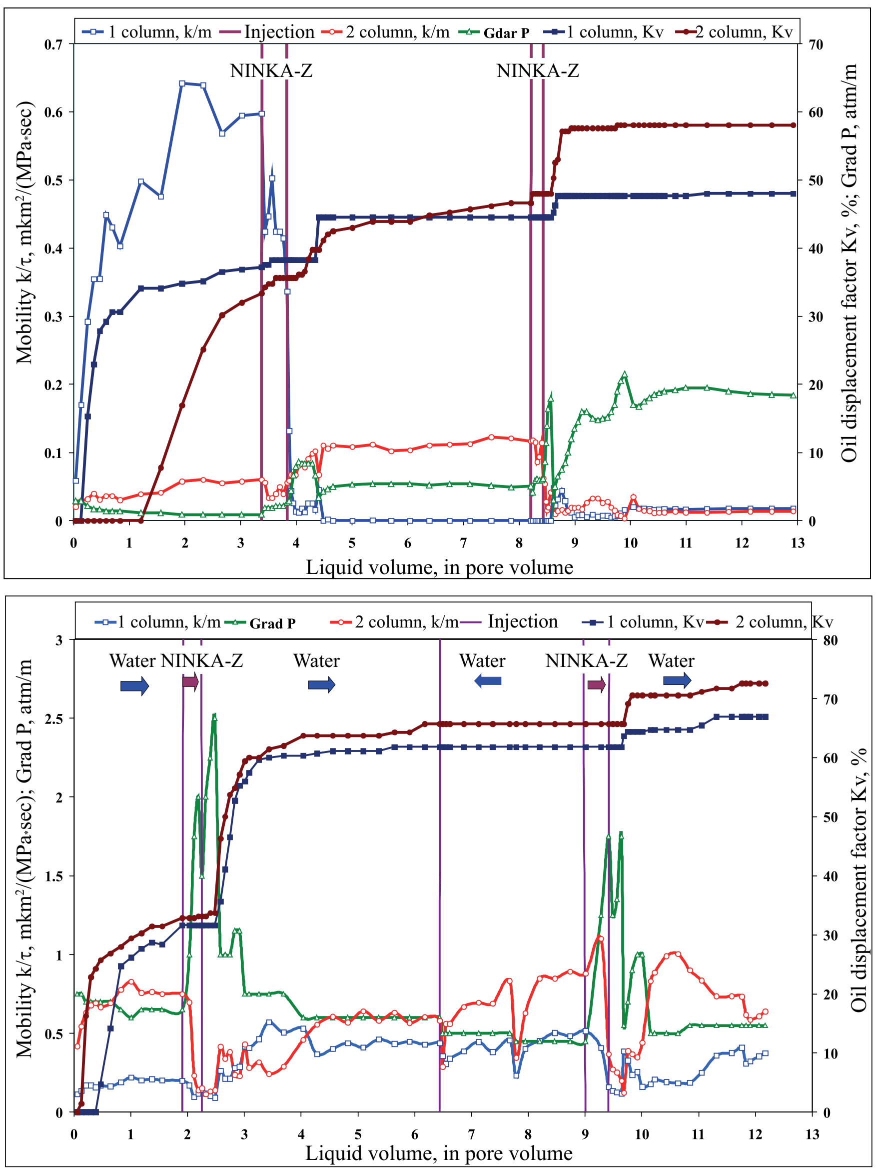

Figure 4. Alignment of filtration flows and additional wash of oil at 150 °C after injection of thickened composition NINKA-Z in heterogeneous oil-saturated reservoir model under conditions simulating steam stimulation on Permian-Carboniferous deposit of the Usinsk field. The initial gas permeability of models: (a) 1 column – 0.730 mm², 2 column – 0.091 mm²; (b) 1 column – 0.374 mm², 2 column – 1.918 mm².

Figure 5. Usinsk field on the map of the Komi Republic.

Permian-Carboniferous deposit of the Usinsk field is located in the depth interval 1100-1500 meters. At the initial conditions oil of Permian-Carboniferous deposit is characterized by high values of dynamic viscosity of about 710 mPas, due to the high content of asphalt-resin components. Permian-Carboniferous sediments have extremely inhomogeneous geological structure, reservoirs of complex type: cavern-porous, fractured-porous, fractured- cavern-porous.

Industrial development of the deposit is carried out since 1977. To date, deposit is half drilled by inclined-directional wells. A significant part of the deposit is developed on the natural water drive. In order to reduce the oil viscosity and enhance oil recovery in the steam stimulation zone, since 1992 areal steam injection has been applied and steam-cyclic treatment of wells has been held.

The current state of deposit development is characterized by high water cut at low development of geological oil reserves, which creates prerequisites for the use of various methods of enhanced oil recovery, in particular for the use of chemical compositions.

In 2014-2015 field tests were conducted of enhanced oil recovery technology by using thickened composition NINKA-Z on the experimental plot of steam stimulation (PTV-Southwest) in Permian-Carboniferous deposit of the Usinsk field (Figure 6).

In 2014, 485 tons of composition NINKA-Z was injected into 5 steam injection wells, located on the same plot. In August 2015 further 2 steam injection wells were treated on the same plot. Injection volume was 80-110 m^3 per well. Tracking the effect was carried out by 75 production wells of the plot. The effects of injections in 2015 was analyzed separately for 25 production wells surrounding treated injection wells; this effect is also taken into account in the overall operation dynamics of the plot in 2014-2016.

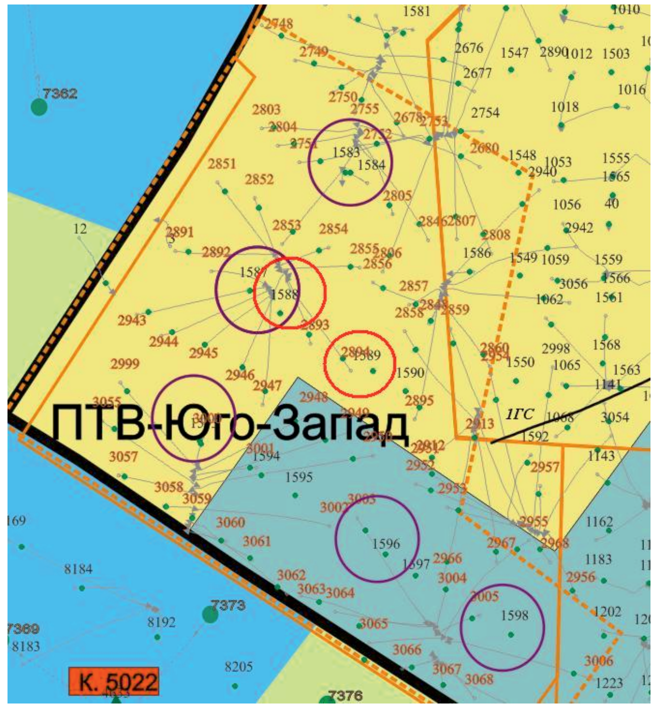

Figure 6. Map of the plot of PTV-Southwest in Permian-Carboniferous deposit of the Usinsk field; purple circles designate steam injection wells, in which the composition NINKA-Z was injected in 2014, red circles – in 2015.

According to the results shown in Figure 7 (according to the monthly operating reports as of August 2015), we can see a steady decline in water cut and increase of oil production after the injection, which is especially noticeable in 3 months after the treatment, due, apparently, to the speed of fluid front movement between injection and production wells. The total effect on the plot, according to different methods of assessment, is 60-80 thousand tons of additional oil production.

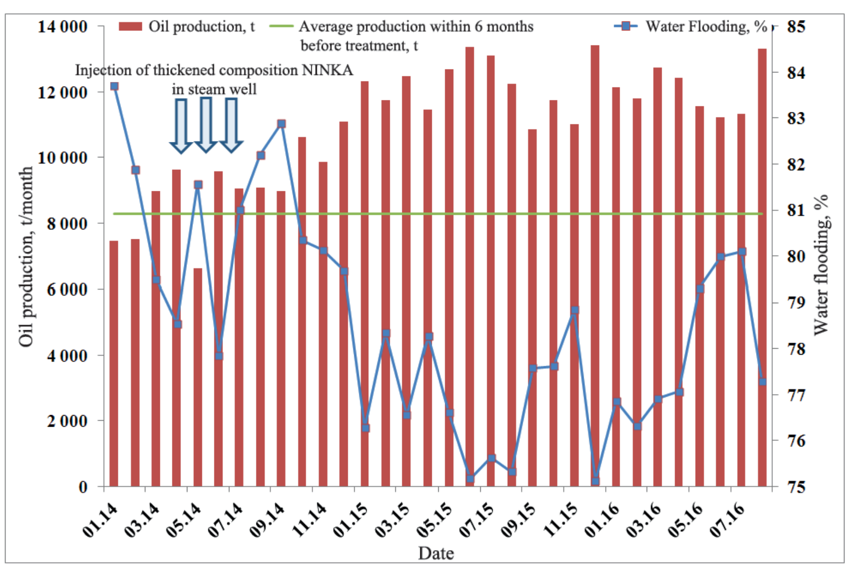

Figure 7. Production rate of oil and fluid before and after injection of NINKA-Z composition at thermal-steam stimulation in 2014-2015 on the experimental plot PTV-Southwest of Permian-Carboniferous deposits of the Usinsk field.

Figure 8 shows a reaction of producing wells on the plot PTV-Southwest on injection of thickened composition NINKA-Z in steam injection wells in 2014: dependence of cumulative oil production from accumulated fluid extraction; divergence of real and predictive curve before and after injection of the composition NINKA-Z, characterizing an additional oil production.

Figure 9 shows the operation dynamics of others 25 production wells around the injection wells treated in 2015. The effect for this plot, calculated separately, is 9500 tons of additional crude oil, as of August 2016.

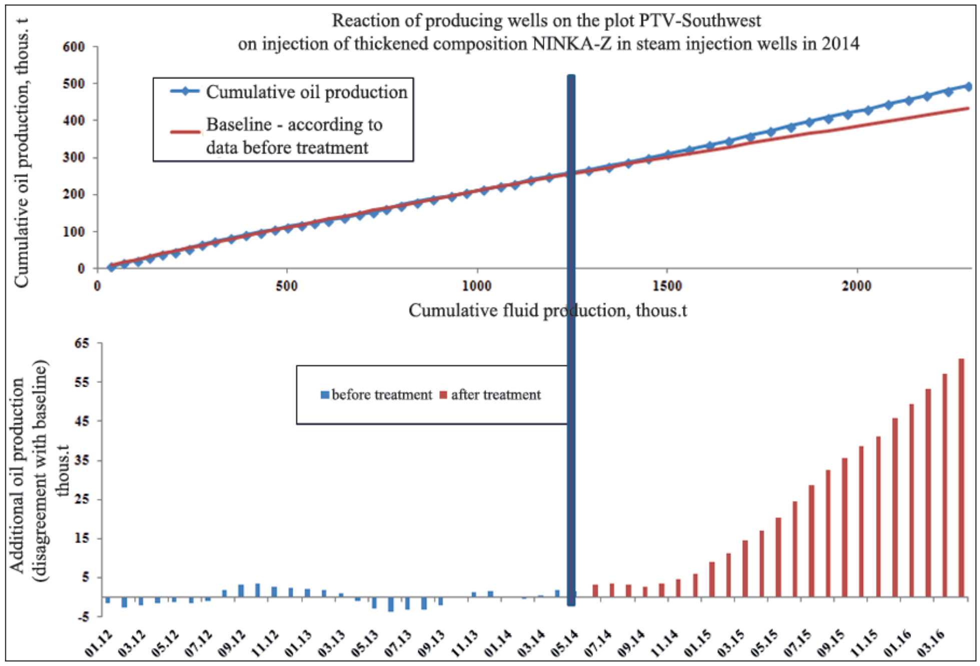

Figure 8. Dependence of cumulative oil production from cumulative fluid production and additional oil production on the plot PTV-Southwest of Permian-Carboniferous deposit of the Usinsk field after injection of NINKA-Z composition.

Figures 10-13 show typical responses of production wells on injection of composition NINKA-Z in the injection well. It is evident that the main front of the composition takes place in the drainage area of wells within 2-4 months after the injection. This is also confirmed by the sampling of these wells, which found reagents characteristic to composition NINKA-Z (urea, urea decomposition products and so forth). In these wells the greatest effect is observed on the additional oil produced, as in most hydrodynamically connected with the injection wells and thus fall under the injected composition.

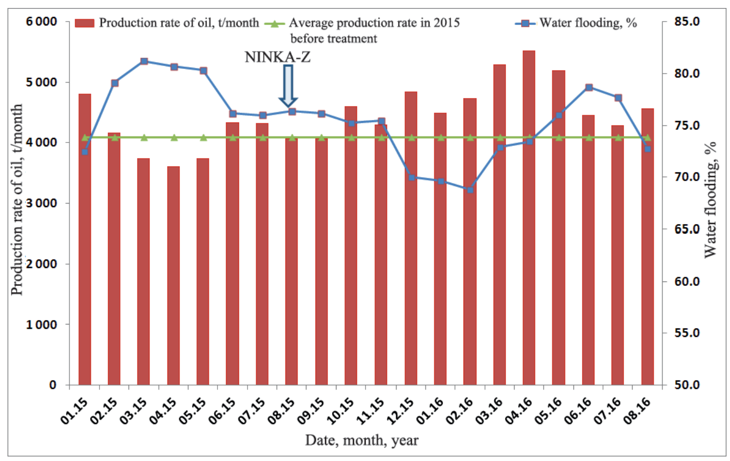

Figure 9. Production rate of oil and fluid before and after the injection of NINKA-Z composition at thermal-steam stimulation in 2015 on the experimental plot PTV-Southwest of Permian-Carboniferous deposit of the Usinsk field.

In the production well 2949 (Figure 13), we can clearly see the effect of injected NINKA-Z composition both in 2014 and 2015. In this case, the effect of the second injection is more as steam injection wells 1589 is closer to the well 2949.

The results of the studies conducted show the prospects of the use of thickened oil-displacing compositions NINKA-Z with adjustable viscosity and alkalinity for enhanced oil recovery in Permian-Carboniferous deposit of heavy oil of the Usinsk field both by areal steam (hot water) injection, and cyclic steam stimulation.

Thus, thickned oil-displacing composition NINKA-Z with adjustable viscosity and alkalinity, low interfacial tension on the border with oil is both water-diverting and oil-displacing composition and can be used to improve development efficiency by increasing the sweep efficiency and the coefficient of oil displacement; it can be injected into the injection, steam injection and cyclic steam wells.

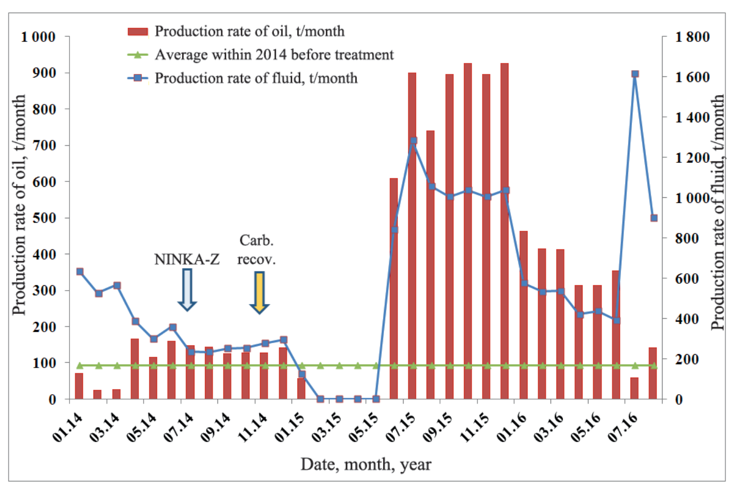

Figure 10. The effect from treatment with composition NINKA-Z in the production well 2946 at experimental plot PTV-Southwest of Permian-Carboniferous deposit of the Usinsk field.

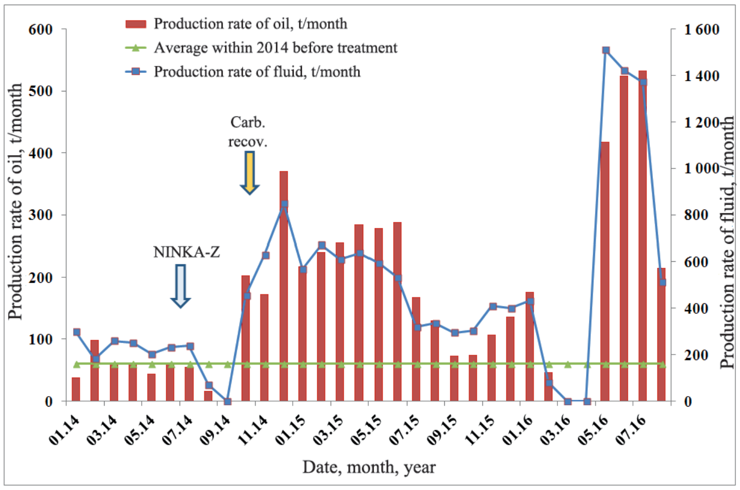

Figure 11. The effect from treatment with composition NINKA-Z in the production well 3059 at experimental plot PTV-Southwest of Permian-Carboniferous deposit of the Usinsk field.

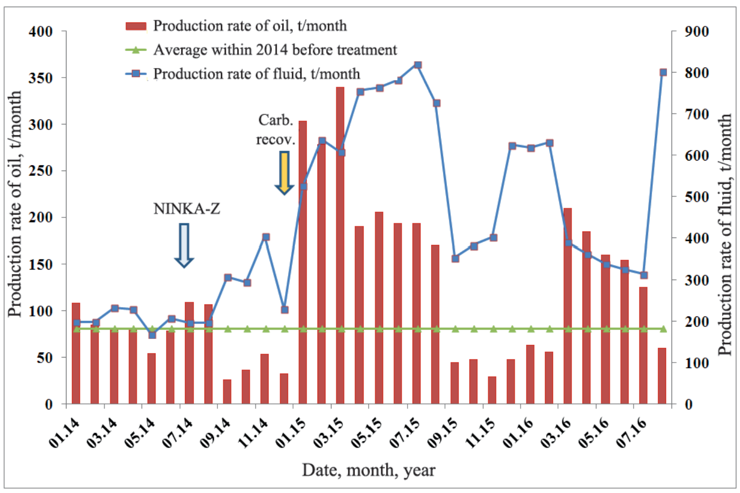

Figure 12. The effect from treatment with composition NINKA-Z in the production well 3066 at experimental plot PTV-Southwest of Permian-Carboniferous deposit of the Usinsk field.

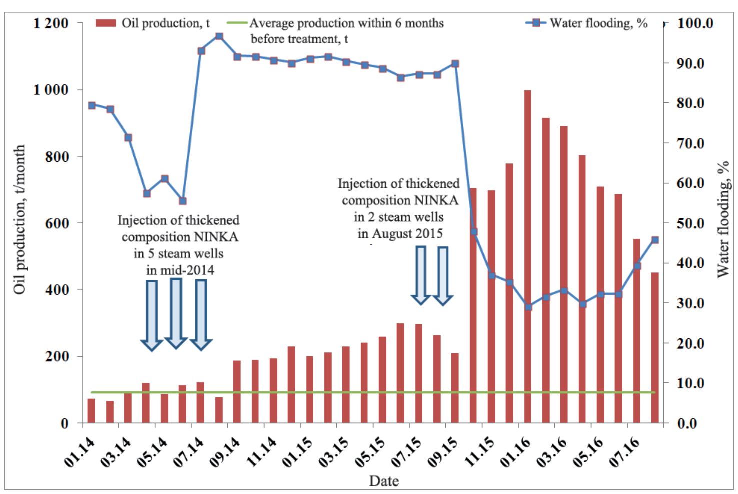

Figure 13. The effect from treatment with composition NINKA-Z in the production well 2949 at experimental plot PTV-Southwest of Permian-Carboniferous deposit of the Usinsk field.

Thickened oil-displacing composition NINKA-Z is a low-viscosity waxy fireproof liquid, making it technologically possible to apply in the winter season. For the preparation and injection of the thickened composition, standard oil field equipment is used in field conditions. Composition NINKA-Z is applicable to both early and late development stages with reserves difficult to recover, including heavy oil deposits.

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