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Promising Physical-chemical IOR Technologies for Arctic Oilfields

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Abstract

The results of laboratory and field tests of physicochemical technologies for enhanced oil recovery are presented for oil fields developed by flooding and thermal-steam stimulation. These technologies can be used in extreme climatic conditions of the Arctic. A promising concept has been developed using reservoir energy or that of the injected heat carrier to generate oil-displacing fluid, gels and sols *in situ*. Physicochemical bases for EOR have been developed involving chemical intelligent systems: gel-forming and oil-displacing systems based on surfactants self-regulating a complex of properties, optimal for oil displacement, in a reservoir for a long time. Pilot tests of EOR technologies were successfully carried out in oil fields of Russia, China, Vietnam, Oman and Germany using gel-forming systems and surfactant compositions developed at IPC SB RAS. Such systems are commercially produced in Russia and China. The results of pilot tests and commercial application of the technologies for enhanced oil recovery and water shutoff are presented for oil fields with difficult-to-recover reserves including deposits of high-viscosity oils. For effective development of difficult-to-recover oil reserves and further increase in oil production it seems promising large-scale use of advanced complex technologies for enhanced oil recovery combining basic reservoir treatment by water or steam injections with physicochemical methods increasing reservoir sweep and oil-displacement factor at simultaneous intensification of the development. The achieved scientific and technical level of the works enables to create new EOR technologies for hydrocarbon deposits located in the Arctic shelf of Russia, in the Urals and Siberia, as well as reagents adaptable to works in the extreme climatic conditions.

Introduction

Northern regions are the main reserve of oil-and-gas producing industry in Russia. The specific climatic and geological-physical conditions of hydrocarbon deposits in the northern regions cause troubles in their development. At present major Russian oil fields are produced at a later stage of their development, where current water cut exceeds 80 %. Water-flooded reservoirs contain a considerable portion of residual oil reserves. As a rule, novel oil fields have low permeability, increased oil viscosity and complex geological structures, in other words their reserves are difficult-to-recover. A portion of difficult-to-recover oil reserves in Russia is constantly growing. In this case potential increase in oil reserves due to enhanced oil recovery is of special importance. The reserves of difficult-to-recover oils in the world exceed 1 trillion tons as estimated by the experts. For their effective development it is necessary to create and widely apply EOR technologies [1-4]. There is necessity of science-based technologies for enhanced oil recovery, adapted to the conditions of the North, and development of new chemical reagents to implement these technologies. It is promising to develop the concept of “intelligent” oil-displacing and gel-forming compositions as physicochemical systems with a negative feedback, preserving and self-regulating in the reservoir for a long time a complex of colloidal-chemical properties, being optimal for oil displacement of sweep efficiency.

On the basis of fundamental research a number of high-tech and environmentally safe technologies, has been developed at IPC SB RAS to enhance oil recovery, which are commercially used by oil companies “LUKOIL”, “Rosneft” and others. The systems are commercially produced in Russia.

We have carried out the laboratory research and field testing of new physicochemical EOR technologies involving thermotropic gel-forming and oil-displacing systems oriented to arctic conditions. The gels redistribute filtration flows of fluids in the reservoir and increase conformance at water flooding or thermal-steam stimulation. The oil-displacing systems have low interfacial tension at the boundary with oil, decrease clay swelling and provide after-washing of the residual oil from both high- and low-permeability reservoir zones. The gel-forming and oil-displacing systems, have regulating density ranging from 1.1 to 1.3 kg/m^3 and viscosity from tens to hundreds mPa·s, are low-freezing with a freezing temperature ranging from minus 20 ÷ to minus 60 ^{o}C, compatible with the saline reservoir waters. One can prepare such systems in waters of any salinity including seawater. All system components are environmentally safe products of large-tonnage industrial production. EOR technologies, involving thermotropic gel-forming and oil-displacing systems, can be applied in oil fields developed in extreme climatic conditions of the Arctic.

Gel-technologies intended to increase conformance

During some years the Institute of Petroleum Chemistry SB RAS develops the concept of the treatment of high-viscosity oil pool with surfactant-based systems, which due to a heat carrier generate CO_2 and ammonia buffer solution *in situ* [7-12]. Prior to steam one injects a slug of the system based on surfactant – carbamide – ammonium salt – water. In the reservoir under due to high steam temperature the carbamide is subjected to hydrolysis to yield carbon dioxide and ammonia. In contrast to ammonia the carbon dioxide is more oil- than water-soluble. A coefficient of CO_2 distribution in oil – water system at 35 – 100 ^oC and pressure of 10 ÷ 40 MPa ranges from 4 to 10, whereas for ammonia it does not exceed $6{\cdot}10^{-4}$. Therefore in oil – water system an oil phase will be enriched with CO_2 and an aqueous one – with ammonia, which together with an ammonium salt form alkaline system with maximal buffer capacity at pH of 9 ÷ 10 [7-9], which is optimal for oil displacement. Several useful effects are observed. The solution of CO_2 in oil decreases its viscosity. The presence of CO_2 and ammonia in the vapor phase facilitates the conservation of vapor – gas mixture at the temperature below the temperature of vapor condensation and thereby increases the efficiency of oil components migration via distillation mechanism. Besides CO_2 and ammonia decrease the swelling of clay minerals in rock-reservoir the thereby preserve the initial permeability of the formation. Ammonia buffer system, formed at ammonia dissolution in an aqueous solution of ammonium salt, performs the same function. Due to its alkalinity, pH = 9-10, and the presence of surfactants it intensifies countercurrent soaking and additional oil displacement. Ammonia buffer system decreases interfacial tension and promotes destructing and thinning of high-viscosity layers or films formed in oil – water – rock boundaries, which worsen fluid filtration in the reservoir and decrease oil recovery. [10-12].

The practice of EOR technologies application in oil fields of Russia demonstrated that technologies, increasing conformance with the injected fluid (water, steam, gas and other) or those, which simultaneously increase both conformance and oil displacement factors, are considered as the most promising. Intra-stratal generation of gels is one of the prospective techniques used to increase conformance with water flooding and thermal steam treatment [5 - 7].

There are various methods for gel generation differed in the type of gelation reaction. Hydrolytic polycondensations are the most widely used reactions, which yield inorganic gels of coagulation or condensation-crystallization structures, for example, gels of metal hydroxides and those of silicic acid [4, 8], the reactions forming three-dimensional polymer structures due to cross-linkage of macromolecules of natural and synthetic polymers in the solutions by chemical or coordination bonds (polyacrylamide, cross-linked with chromium salts, polysaccharides cross-linked with borates and others) [8-11], and also phase transitions solution – gel in the systems: polymer with a higher or lower critical temperature – water (cellulose ethers, polyvinyl alcohol and others) [12, 13].

In recent years novel EOR technologies involving thermotropic inorganic and polymer gel-forming systems generating gels *in situ* have been developed at the Institute of Petroleum Chemistry SB RAS to increase conformance with water flooding or thermal steam treatment [5-7, 12-18].

Each oil field has specific geological-physical characteristics. Oil composition and that of reservoir rock, oil viscosity, water salinity, reservoir temperature and pressure vary in wide ranges. Thus reservoir temperature in Yakutia is 8-12 ^oC, in Tatarstan – 20-40^oC, in West Siberia – 50-100 ^oC and in oil fields of South China Sea shelf in Vietnam it is 110-170 ^oC. Water salinity varies from 0 to 300-400 g/L. Therefore in order to use gel-technologies intended to enhance oil recovery it is necessary to develop gel-forming systems with regulated properties.

In the course of some years physicochemical and hydrodynamic aspects of intrastratal generation of gels from aqueous solutions are being studied at the Institute of Petroleum Chemistry SB RAS. Under surface conditions the aqueous solutions are low-viscosity solutions, which under reservoir conditions are converted into gels. Gelation proceeds due to thermal energy of the reservoir or that of the injected heat carrier, as well as the result of the injected solution interaction with the reservoir fluids and rock-reservoir. Kinetics of gelation and also rheological and filtration properties of the gels of different types have been studied for heterogeneous reservoirs with permeability ranging from 0.01 to 10 μm^2. We proposed thermotropic gel-forming systems with different time of gelation – from several minutes to several days – in the temperature range of 30 - 320 ^oC. Based on these systems five gel-technologies have been developed to enhance oil recovery from highly heterogeneous reservoirs and now the technologies are commercially employed in oil fields of West Siberia and in Komi Republic [5-7, 12-18]. Due to environmental safety of the reagents and safety in operation gel-technologies are widely employed in oil fields of Russia and other countries.

Thermotropic inorganic gels for improved oil recovery

The ability of the system aluminum salt – carbamide – water – surfactant to generate inorganic gel and CO_2 *in situ* surved as the basis for a technology intended to increase conformance in water or steam injections in the temperature range of 30 – 320 ^oC [5, 6, 19-23].

It is possible to form free- or connected-dispersed systems (sols and gels) in a reservoir by a condensation method, in particular based on a well known in analytical chemistry principle of “arising reagents (homogeneous precipitation)” [6]. Within the framework of this principle realized due to reservoir thermal energy or that of the injected heat carrier a novel physicochemical method has been proposed to enhance oil recovery. A homogeneous aqueous solution containing a gel-forming system in injected into a reservoir. In the reservoir one of the system components is subjected to gradual hydrolysis due to reservoir heat energy or that of the injected heat carrier. The forming hydrolysates shift prolytic equilibrium of the other component causing hydrolytic polycondensation of monomeric units via a mechanism of cooperative phenomenon. In certain time gel is formed practically instantly in the whole volume of the solution.

A principle of "arising reagents (homogeneous precipitation)" has been realized at the development of a physicochemical method for enhanced oil recovery based on the ability of the system aluminum salt – carbamide – water – surfactant to generate inorganic gel and CO_2 *in situ* [19-23]. Gel-forming fluids based on this system are low-viscosity solutions with pH 2.5-3.5. They are capable to dissolve carbonate minerals of a reservoir rock and decrease (suppress) clay swelling. One can prepare the solutions using water of any salinity. They are injected into a reservoir through injection wells using standard equipment.

In the reservoir due to its thermal energy or that of the injected heat carrier carbamide is hydrolyzed to form ammonium and carbon dioxide; it causes gradual increase in pH of the solution. When pH reaches the value of 3.8-4.2 aluminum ions are hydrolyzed and as a result in certain time the gel of aluminum hydroxide is immediately formed practically in the whole solution volume, Figs. 1, 2. Time of gelation depends on a reservoir temperature and component ratio in the gel-forming system. Due to gelation reservoir rock permeability to water decreases 4-35 times. A degree of permeability decrease is as greater as higher is the initial water saturation and reservoir rock permeability. Static shear stress of the gel ranges from 3 to 40 Pa. The presence of surfactants in a gel-forming solution intensifies reservoir rock wetting and thereby improves penetration and oil displacing capacities of the solution. Besides surfactants have plasticizing effect on the gel of aluminum hydroxide and can foam carbon dioxide and ammonium evolved in the process of carbamide hydrolysis [6].

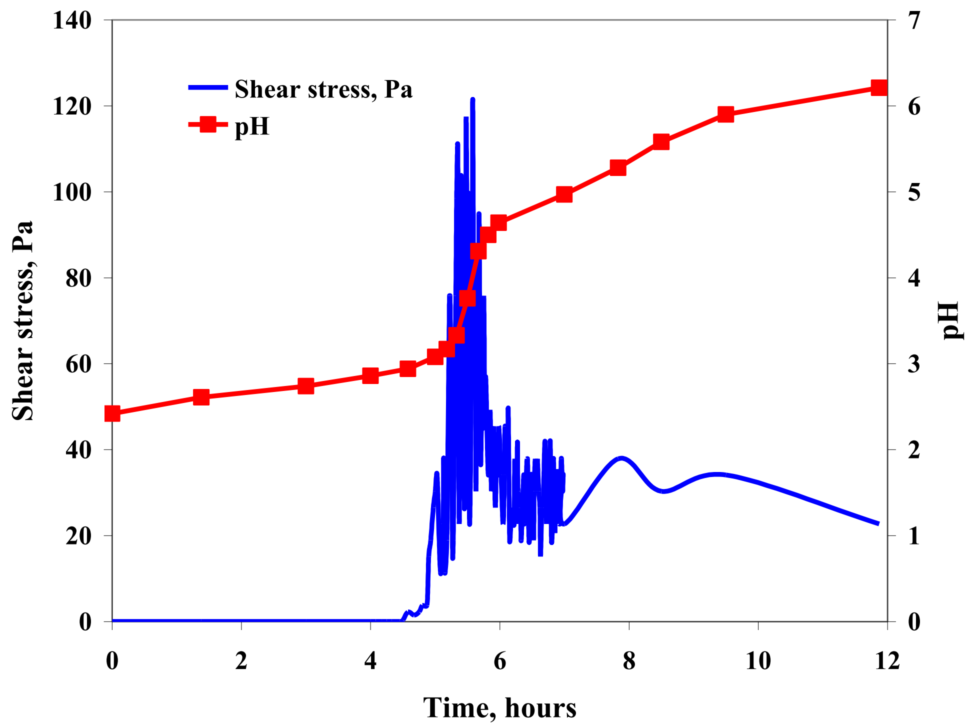


Fig. 1: Changes in pH and shear stress in the system aluminum salt – carbamide – water at gelation during thermostating at 97 °C

Rheological properties of the gel correspond to a thixotropic pseudo-plastic body of a coagulation structure. Gel permeability to an aqueous phase at shear stresses being lower than static shear stress of the gel itself is a distinctive feature of the gel. Gelation causes rearrangement of filtration flows, equalizes injectivity profile of the injection wells and decreases water cuttings of well production. Gel-forming systems are intended for application in oil fields with a high reservoir temperature and high heterogeneity typical to West Siberia, as well as for high-viscosity oil pools developed by thermal methods.

At 70-100 °C kinetics of gelation is determined by carbamide hydrolysis, which proceeds much slower as compared with the process of aluminum hydroxide gelation, carried out as a cooperative phenomenon. The temperature effect on the time of gelation obeys Vant-Hoff rule for chemical reactions: at temperature increase by each 10 degrees the time of gelation increases 3.5 times [6, 19-22].

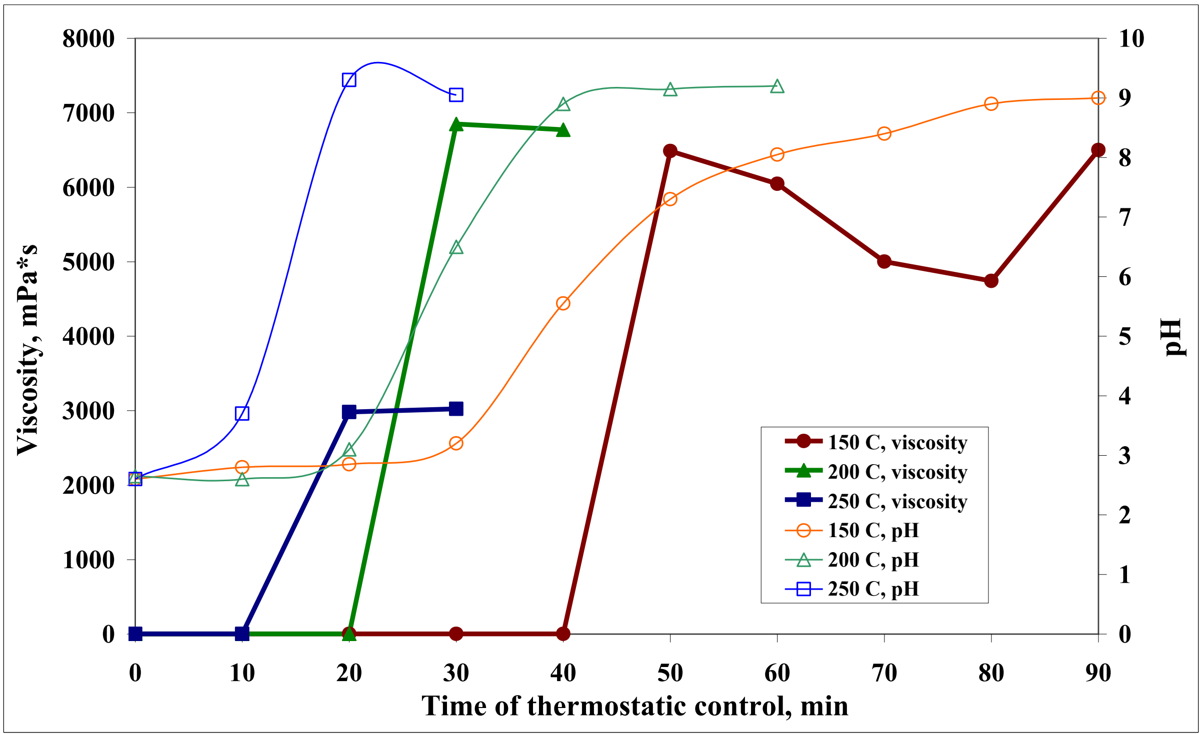


Fig. 2: Changes in viscosity and pH in the system aluminum salt – carbamide – water at gelation during thermostating at 150 – 250 °C

In the temperature range of 100 - 250 °C the effect of temperature on the time of gelation does not obey to Vant-Hoff rule: at temperature increase by each 10 degrees the time of gelation increases 1.2 times. In this range the kinetics of gelation in the system aluminum salt – carbamide – water is determined by a coagulation process of aluminum hydroxide gelation [19-22].

At 70-100 °C gelation time depends on concentration and aluminum salt – carbamide ratio in the solution, at the temperatures higher than 150°C this dependence is not so great. The lower carbamide concentration the longer is gelation time. Varying aluminum salt – carbamide ratio it is possible to regulate gelation time adapting it to concrete reservoir temperature [19, 20].

The gelation process in the system aluminum salt – carbamide – water was studied by vibratory viscosimetry using a vibratory viscometer "Reokinetika" equipped with a tuning sensor [24-26] at an atmospheric pressure. At aluminum salt concentration of 4.0 wt. % the solution viscosity during gelation increases from 1.2 - 1.6 mPa·s to 300 - 3500 mPa·s and at salt concentration of 8.0 wt. % – from 1.8 - 2.5 mPa·s to 1800 – 7500 mPa·s. At 100 – 250 °C aluminum salt concentration has the major effect on gel viscosity. Component ratio and temperature have no considerable effect.

Gel-forming capacity of the solutions in the system aluminum salt – carbamide – water was studied via viscosity and shear stress measurements using a rotary viscometer Haake RheoStress 600 at the temperatures ranging from 20 to 150 °C and pressure up to 50 atm. under dynamic conditions at uniform compression. At 100-150 °C in several minutes the solution converts into a solid-like gel of a coagulation structure with pronounced thixotropy and yield point of 25-90 Pa, Fig. 3. Yield point value increases with increase in a rate of loading.

It should be noted that under the conditions of uniform compression at high pressures at shear rates ranging from 0.01 to 3 s^{-1} the values of shear stress and gel viscosity in the system aluminum salt – carbamide – water are by several orders of magnitude higher, Fig. 3, as compared with those observed at atmospheric pressure. Therefore one can use thermotropic gel-forming systems based on aluminum salt – carbamide – water to regulate injectivity profile in injection wells and for water shutoff in production wells and also to enhance oil recovery at combined thermal-steam and cyclic-steam treatments.

Gel-forming GALKA® and GALKA®– surfactant systems have been developed based on the results of the studies on gelation kinetics and rheological characteristics of the system aluminum salt – carbamide – water – surfactants.

In 1996 IPC SB RAS in association with Stock Company "Nefteotdacha" organized commercial production of liquid GALKA® system using alumina-containing industrial waste. In 2000 IPC SB RAS in association with Stock Company "AURAT" organized the commercial production of the following solid GALKA®-thermogel systems: GALKA®-C for reservoir temperatures ranging from 70 to 320 °C, GALKA -U for reservoir temperatures ranging from 40 to 70 °C, and GALKA®-NT for reservoir temperatures ranging from 20 to 40 °C. Regulated temperature of gelation, homogeneity and low viscosity of aqueous solutions, solid commercial form and low freezing-points of the solutions are the main distinctive features of GALKA®-thermogel systems. Therefore one can use GALKA® systems: i) in a wide temperature range (20-320 °C), including thermal-steam treatment of reservoirs; ii) for low-permeable reservoirs; iii) to inject into a well by dosing directly into a conduit without preliminary dilution; and iv) under winter conditions [5, 7, 15], including the Arctic ones.

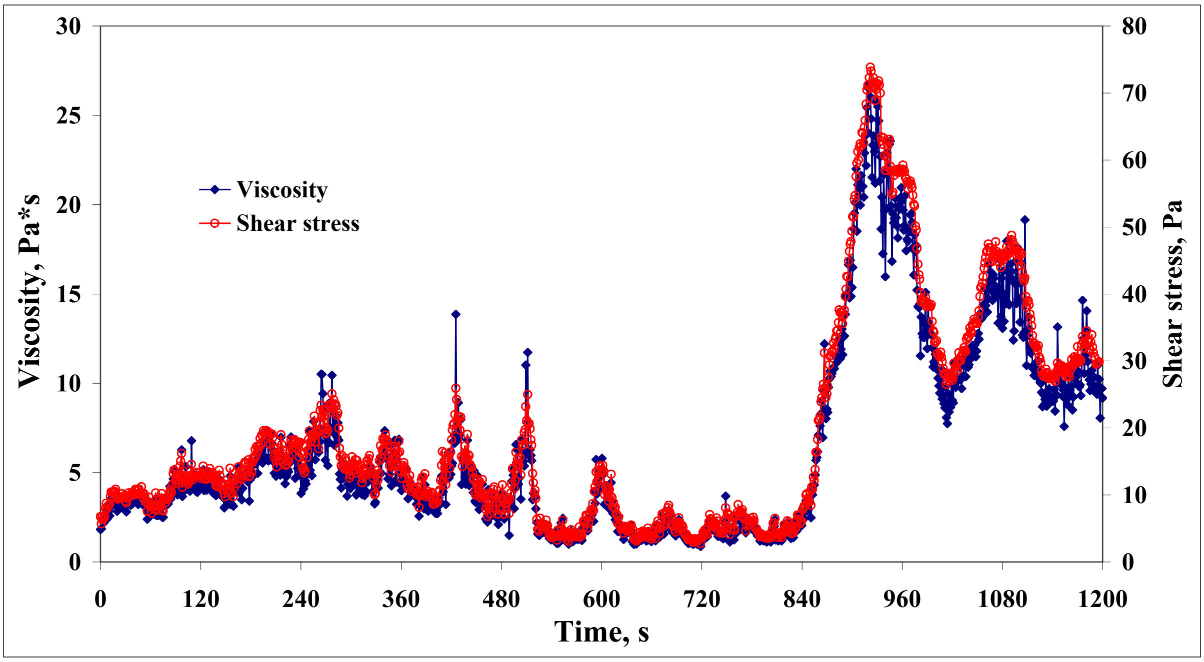


Fig. 3: Time-dependent changes in viscosity and shear stress for the solution of GALKA®-C system (thermostating at T=150 ^{o}C and shear rate 3 s^{-1})

The study of the effect of GALKA®-C system, generating carbon dioxide and ammonia at thermal treatment, on oil viscosity demonstrated that after thermostating at 250 ^{o}C during 4 hours with GALKA-thermogel-C system at oil: system ration of 1:1 oil viscosity decreased 3.6 – 4.0 times at the temperatures range of 20 – 50 ^{o}C (Fig. 4).

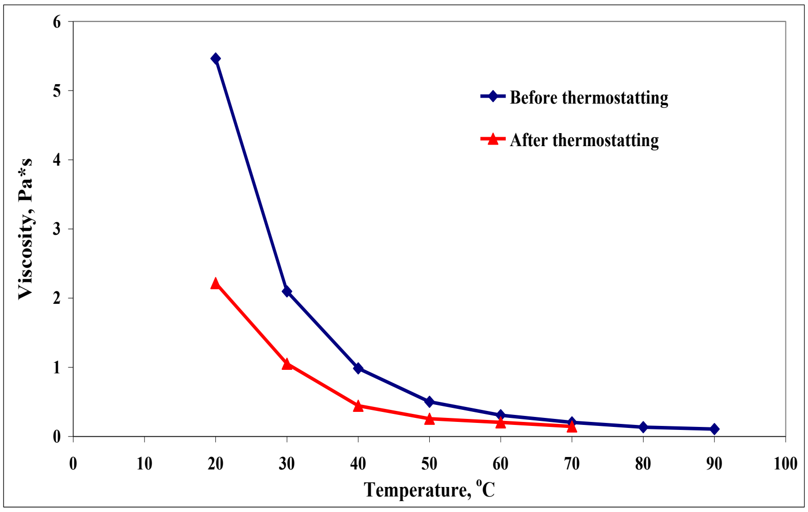


Fig. 4: Temperature dependence of oil viscosity before and after thermostating with GALKA®-C system in 2:1 ratio during 4 hours at 250 ^{o}C (heating process)

At 70-250 ^{o}C we studied filtration characteristics and oil-displacing capacity of gel-forming GALKA® systems in a heterogeneous reservoir model in respect to the conditions of oil fields developed by flooding and thermal-steam treatment [6, 7, 15-22]. It has been determined that the system entered mainly into a high-permeability reservoir model. Gelation causes rearrangement of filtration flows, decreases filtration rate in high-permeability seams and increases filtration rate in low-permeability seams, levels liquid mobility. It is accompanied with oil after-washing from both low- and high-permeability zones of a reservoir model. Oil displacement factor increases by 10-23 % to achieve high absolute coefficients of oil displacement and lower residual oil saturation.

GALKA®-C system includes carbamide, which forms carbon dioxide at a high temperature. Due to carbon dioxide release at thermal-steam or cyclic-steam treatments the pressure can increase by 20-30 atm. to increase oil recovery.

Thus, the studies on physicochemical, rheological and filtration properties, as well as on oil-displacing capacity of gel-forming GALKA® systems proved their effectiveness to regulate filtration flows, increase conformance and for thermal-steam treatment. One can use GALKA® systems for thermal-steam and cyclic-steam treatments of a reservoir at the development of high-viscosity oil pools and also to increase conformance and for water shutoff in oil fields with formation temperatures ranging from 20 to 320 °C. GALKA® system is suitable for both an early and later stages of oil field development.

Application in West Siberia

In 1989-1995 pilot tests of the technology intended to enhance oil recovery using inorganic gel-forming GALKA® systems were successfully carried out in oil fields of West Siberia. Since 1996 EOR technology is commercially employed in West Siberia. The application of EOR technology promotes rearrangement of filtration flows, increases conformance and as a result increases final oil recovery by 5-8 %. Additional oil recovery ranges from 400 to 3000 tons per one well treatment [5-7, 15].

In 1996-1997 pilot tests of GALKA® systems based on alumina-containing wastes of industrial production were successfully carried out in West Siberia. The use of wastes reduced the cost of the system 3-5 times. GALKA® system was injected into 14 injection wells. One injected 13-46 m^3 into each well. In 2-3 months after the injection production wells, which were hydrodynamically connected with injection ones, responded by decreased water production and increased oil production rate. In 1996 jointly with Stock Company "Nefteotdacha" arranged the production of a liquid marketable form of GALKA® system based on alumina-containing wastes. Such GALKA system is delivered by rail tank cars. It is a low-freezing liquid, the freezing point of which is minus 20 - 25 °C. Therefore one can use GALKA® system all the year round.

In 1997 - 2000 Stock Companies "Yuganskneftegaz", "LUKOIL-Langepasneftegaz" and "LUKOIL-Pokachevneftegaz" commercially employed EOR technology using GALKA® system. Due to injection of GALKA® system into 6 injection wells in Pokamasovskoye and Pokachevskoye oil fields (formations YuV_1) one recovered in addition 5.4 thou tons of oil. One injected GALKA® system into 17 injection wells of volume 41-157 m^3 into each well in oil fields developed by Stock Company "Yuganskneftegaz". As a result additional oil recovery amounted to 163.8 thou tons of oil, the effect continued for more than 10 months and specific effect was 9.6 thou tons of additional oil per one well treatment [19-23, 27, 28].

In 1999 GALKA® system was injected into 41 injection wells in 8 oil fields of West Siberia (Russia) – Yuzhno-Surgutskoye, Pravdinskoye, Severo-Salymskoye, Sredne-Asomkinskoye, Vostochno-Surgutskoye, Petelimskoye and Mayskoye. In Mayskoye oil field the injection was carried out in 26 wells using group pumping station. Additional oil recovery amounted to 225.5 thou tons of oil and specific technological effect was 3.4 thou tons per one well treatment at the effect duration more than 12 months. The period of payback was 5-9 months. In 2000 the technology involving GALKA® systems was introduced in 5 oil fields developed by Stock Company "Yuganskneftegaz" within investment projects. For the first 6 months one treated 50 wells including 1 well in Mayskoye oil field, which was treated twice. One injected 12 thou m^3 of the solution (1184 t of commercial reagent). Additional oil recovery on October 1, 2000 amounted to 31.3 thou tons and specific technological effect was 1.6 thou tons per well treatment. The effect is still in progress. Good results were obtained for high- temperature reservoirs in Yuzhno- and Vostochno-Surgutskoye oil fields, where specific technological effect was 1.6-2.2 thou tons per well treatment. Thus four injection wells in Vostochno-Surgutskoye oil field were treated in the zone of the greatest oil withdrawals in June 2000; water cut decreased to 7 % and thereby additional oil recovery amounted to 9.0 thou tons. The increase in oil production amounted to 30 % and the effect is still in progress [14, 15, 28].

Pilot tests of the gel-technology using GALKA® systems were successfully carried out in White Tiger oil field (Vietnam) [14, 15].

Application at thermal-steam treatment

Due to unique capacity of inorganic GALKA® gels to withstand temperatures up to 300–320°C they were used to increase coverage by thermal-steam treatment at the development of high-viscosity oil pools [28-30]. In 2002-2006 pilot tests of IOR technologies were carried out in the area of thermal-steam stimulation PTV-3 on Permocarbonic deposit in Usinskoye oil field at a later stage of its development. One used GALKA® systems at thermal-steam and cyclic-steam stimulations. Since 2007 IOR technologies are used on commercial scale.

In 2002-2004 GALKA®-C system was injected in the test area into 5 steam-injection wells. Incremental oil production from 29 surrounding production wells amounted to 33 thousand tons, water cut decreased by 3-45 %, oil production rate increased on average by 23%, Figure 5, whereas fluid production rate decreased by 19.8 %. In 2008-2009 GALKA®-C system was injected into 22 injection wells. By the results of production wells operation in the test area average monthly incremental production of oil was 101.7 – 747.6 ton, providing the increase in incremental production by 50-90% relative to additionally produced oil due to steam injection.

Objective evidence of the effective influence of the injected GALKA®-C thermogel on the operation mode of injection well № 4023 on Permocarbonic deposit of high-viscosity oil in Usinskoye oilfield was obtained using unique heat-resistant «Scientific Drilling» equipment, which enabled to register down-hole parameters of the heat carrier in the running wells, Figure 6.

In the process of steam injection on May 17, 2011 in the well with «Scientific Drilling» equipment were instrumentally recorded the following down-hole conditions of heat carrier absorption: according to flow meter readings out of the perforated with two intervals (20 m + 30 m) thickness of reservoir-rocks it was an upper part of the lower perforated zone, total thickness 5 m, which actively absorbed the steam. At the depth of upper perforated hole (1136 m) the steam pressure was 7.69 MPa and temperature +290 °C. Because of low injectivity of upper and lower perforated zones the injectivity profile was rather uneven and reservoir coverage was low.

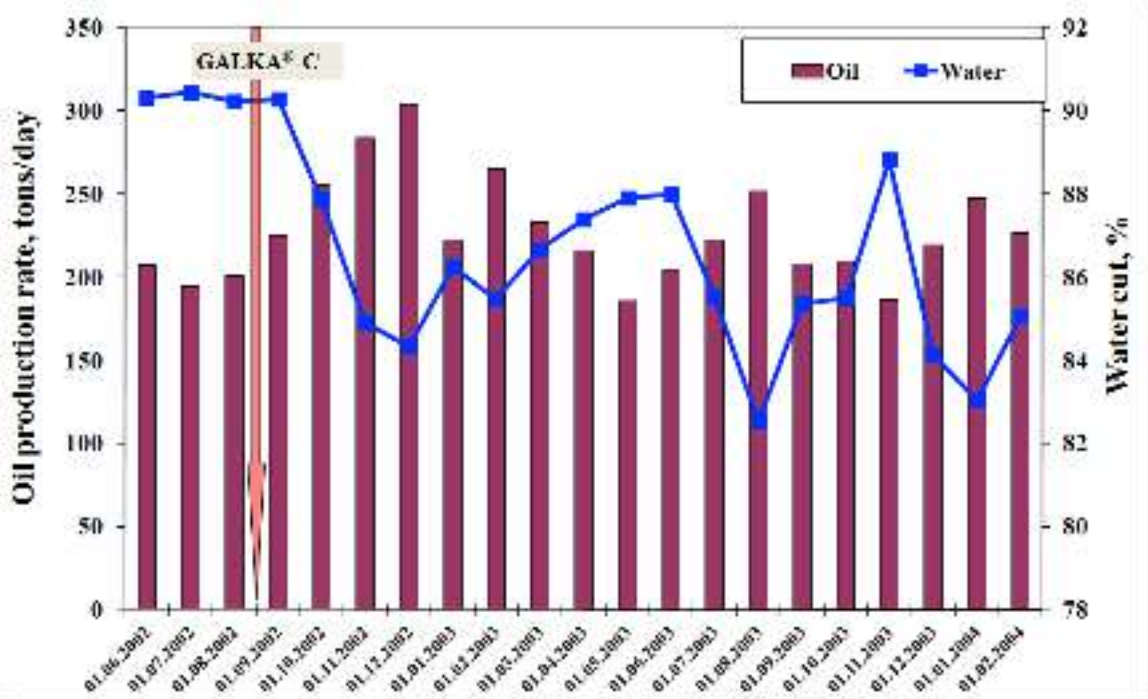


Figure 5 Dynamics of monthly oil production and water cut from June 2002 to February 2004 for 29 wells in the test area after the GALKA®-C injection in Usinskoye oilfield

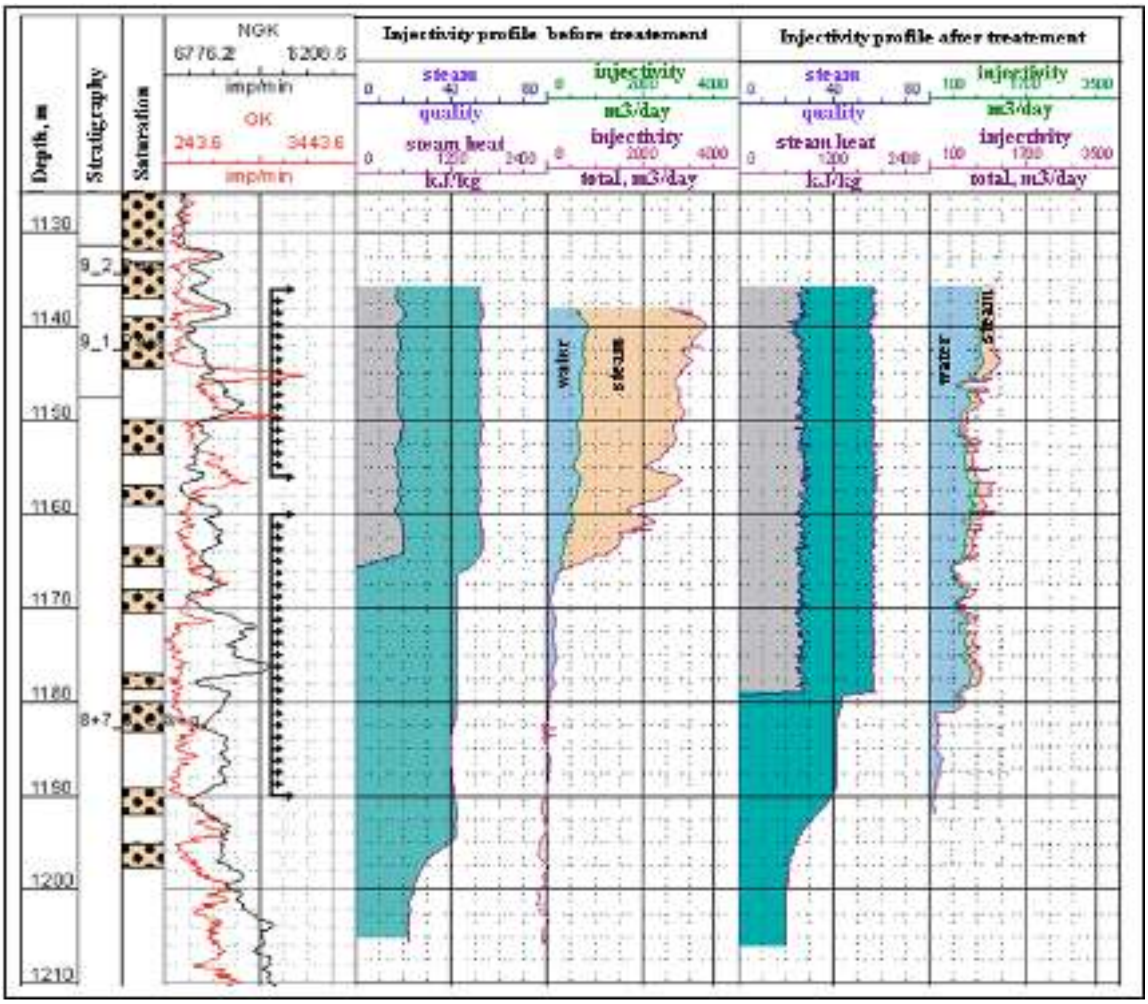


Figure 6 Injectivity profiles of well № 4023 on Permocarbonic deposit in Usinskoye oilfield before and after stimulation with GALKA®-C system

Reinvestigation of the process of steam injection into well № 4023, carried out after the injection of GALKA®-C thermogel on September 8, 2011 in the amount of 120 m^3, revealed that discharge pressure increased up to 7.82 MPa, thickness of the receiving perforated zone increased from 5 to 19 m and the reservoir coverage increased from 10.0 to 38.0 %.

Thus, the injection of GALKA®-C system caused redistribution of filtration flows and increased thickness of the receiving perforated zone and reservoir coverage with thermal-steam stimulation.

In 2007-2010 87 wells were treated to improve the efficiency of cyclic-steam stimulation (CSS) – water shutoff using GALKA®-C systems. The volume of the injected system varied from 80 to 160 m^3. The results of thermographic analysis of cyclic-steam well № 8353 carried out in 2011 before and after the injection of GALKA®-C system, Figure 7, showed that the stimulation with GALKA®-C thermogel caused redistribution of filtration flows and increased reservoir coverage with thermal-steam stimulation. After the injection of GALKA®-C system oil production rate increased from 2.5 to 24 t/d, Figure 8, by 20–30% higher as on average due to CSS, and water cut decreased up to 33-35%; the efficiency of the works was about 90 %, the average additional production amounted to 981 tons per one well stimulation and the average increase in oil production rate was 6.0 t/d.

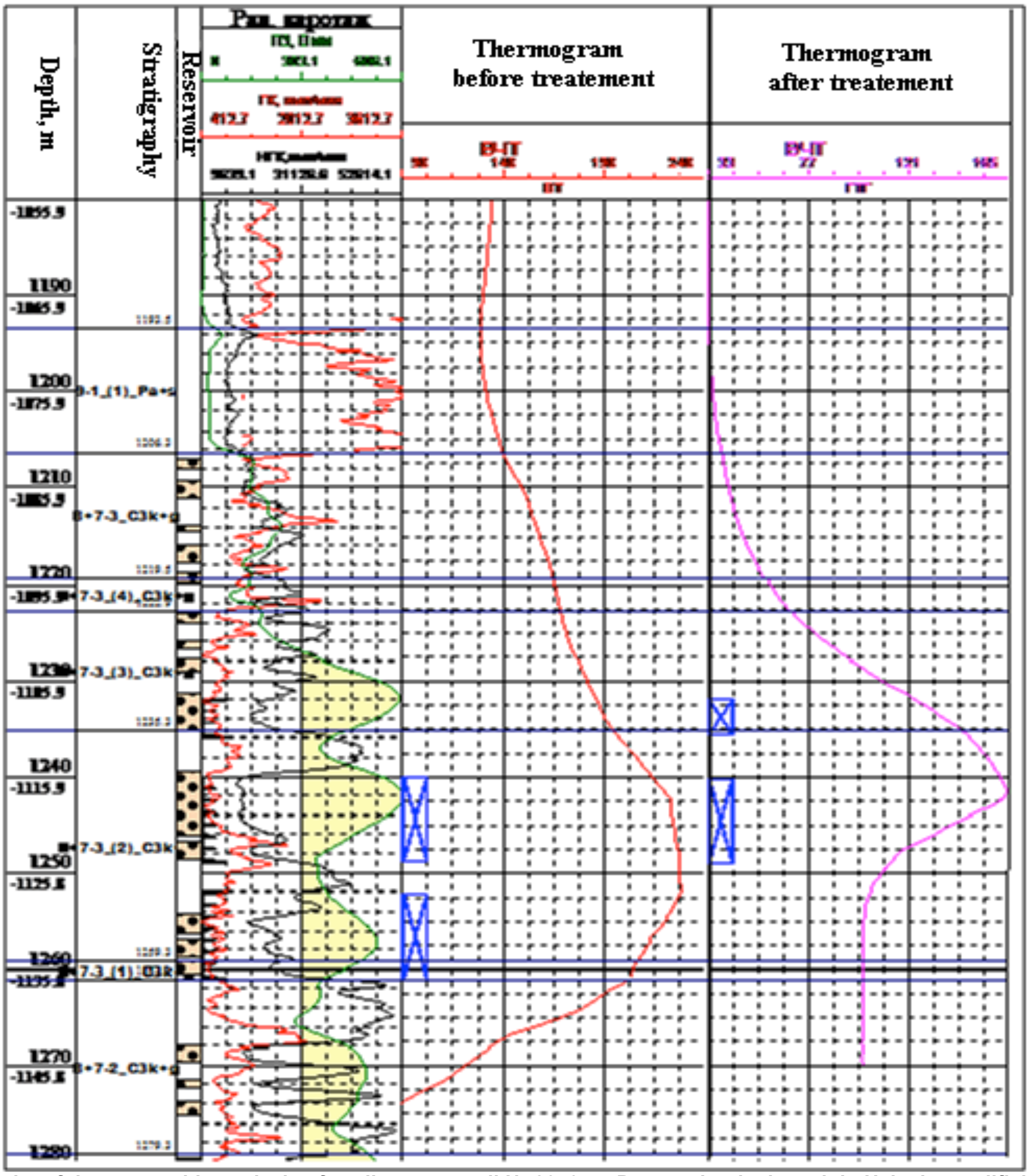
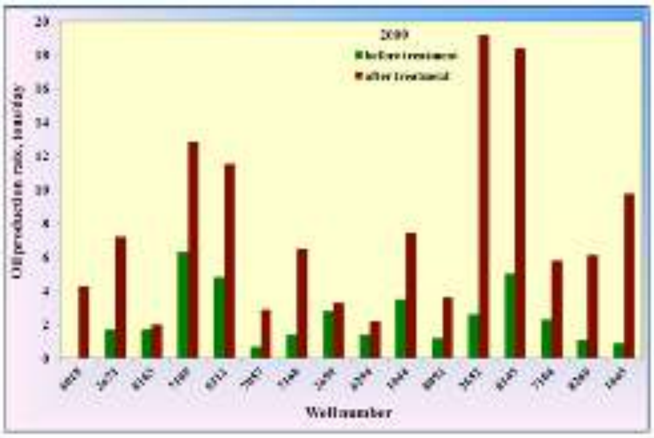


Figure 7 The results of thermographic analysis of cyclic-steam well № 8353 on Prmocarbonic deposit in Usinskoye oilfield before and after stimulation with GALKA® system

Thus, application of inorganic gels to improve oil recovery and for water shutoff on Permocarbonic deposit of high-viscosity oil in Usinskoye oilfield being at a later stage of its development resulted in increased reservoir coverage with steam injection, decreased water cuttings of well production by 3-45%, increased oil production rate by 11-33 % and increased fluid production rate by 14-25%.



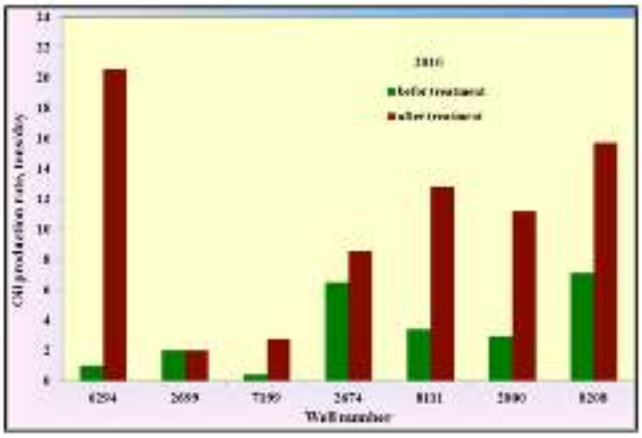


Figure 8 Increase in oil production rate after the injection of GALKA®-C system into 23 cyclic-steam wells in Usinskoye oil field in 2009 and 2010

Increase in oil-displacement factor by surfactants

During some years the Institute of Petroleum Chemistry SB RAS develops the concept of enhanced oil recovery with surfactant-based systems, which due to reservoir heat or that of the injected heat carrier generate CO_2 and ammonia buffer solution *in situ* [5, 7, 12, 14, 18, 21, 28, 31-34]. One injects a slug of the system based on surfactant – carbamide – ammonium salt – water. In the reservoir due to high temperature of the reservoir or the injected steam the carbamide is subjected to hydrolysis to yield carbon dioxide and ammonia. In contrast to ammonia the carbon dioxide is more oil- than water-soluble. A coefficient of CO_2 distribution in oil – water system at 35 – 100 ^oC and pressure of 10 ÷ 40 MPa ranges from 4 to 10, whereas for ammonia it does not exceed $6 \cdot 10^{-4}$. Therefore in oil – water system an oil phase will be enriched with CO_2 and an aqueous one – with ammonia, which together with an ammonium salt form alkaline system with maximal buffer capacity at pH of 9 ÷ 10 [5, 7, 12, 14], which is optimal for oil displacement. Several useful effects are observed. The solution of CO_2 in oil decreases its viscosity. The presence of CO_2 and ammonia in the vapor phase facilitates the conservation of vapor – gas mixture at the temperature below the temperature of vapor condensation and thereby increases the efficiency of oil components migration via distillation mechanism. Besides CO_2 and ammonia decrease the swelling of clay minerals in rock-reservoir the thereby preserve the initial permeability of the formation. Ammonia buffer system, formed at ammonia dissolution in an aqueous solution of ammonium salt, performs the same function. Due to its alkalinity, pH = 9-10, and the presence of surfactants it intensifies countercurrent soaking and additional oil displacement. Ammonia buffer system decreases interfacial tension and promotes destructing and thinning of high-viscosity layers or films formed in oil – water – rock boundaries, which worsen fluid filtration in the reservoir and decrease oil recovery [12, 14, 18, 21].

Oil-displacing systems based on surfactants, carbamide and ammonium salts (NINKA®) have been developed to enhance the efficiency of thermal-steam treatment of high-viscosity oil fields. They are capable to generate CO_2 and ammonium buffer system *in situ* under the action of injected steam temperature. To optimize the composition and physico-chemical properties of oil-displacing systems we studied kinetics of carbamide hydrolysis proceeding in water and in oil-displacing systems at the temperature interval ranging from 100 to 250 ^oC [12]. Activation energy and preexponent in Arrenius equation for carbamide hydrolysis in water and in oil-displacing NINKA® systems were equal to 44.6 kJ/mole; $4.01 \cdot 10^4$ h^{-1} and 50.8 kJ/mole; $10.9 \cdot 10^4$ h^{-1}, respectively. Buffer capacity of carbamide solutions in water and in oil-displacing systems was determined both before and after thermostatting at 100-250 ^oC. The highest buffer capacity of the solutions was observed only in the presence of ammonium salt. Buffer capacity of NINKA® system was 2-4 times higher as compared with that of carbamide solutions in water under the same conditions. Rheological properties in the system oil - NINKA® solution were studied at 100 – 250 ^oC using vibration, rotary and high-pressure viscosimetries. After thermostatting carried out at 100 - 250 ^oC during 3 – 48 hours with oil-displacing solution at the ration of oil : solution ranging from 4:1 to 1:1 oil viscosity decreased 3-10 times at the temperature interval ranging from 20 to 50 ^oC. The higher was thermostatting temperature the lower was oil viscosity and wider concentration range, in which decreased oil viscosity was observed.

Under the laboratory conditions using a filtration high-pressure installation at 150-200^oC the effects of oil-displacing NINKA® system concentrations (from 10 to 50 % mass) and slug sizes (from 0.1 to 1 pore volume of reservoir models) on a factor of oil displacement from reservoir models with different permeability (from 0.072 to 1.918 μm^2) were studied with regard to conditions of high-viscosity oil pools: Usinskoye and Yaregskoye oil fields, Russia, Liaohe and Fluarty oil fields, China

It has been determined that alternation of steam slugs and oil-displacing NINKA® system increases oil displacement factor as compared to thermal-steam treatment. The injection of the first system slug contributes to oil displacement factor increase. The highest increases in oil displacement factor up to 30-32 % were observed at the concentration of oil-displacing system of 30-50 % mass, where high absolute values of oil displacement factor – up to 75-78 % were achieved. At concentration of the system of 10-20 % mass the increase in oil displacement factor did not exceed 20 %.

Generalizing dependencies of oil displacement factor and increase in oil displacement factor on the accumulated volume of the system injection were deduced. Based on the experiments program «SteamODC_v2»: computer simulation of alternating thermal-steam and physicochemical treatments was created using Borland Delphi. Computer program "NINKA_calc" has been developed at Institute of Petroleum Chemistry SB RAS to calculate the volumes of NINKA® system at planning treatment of bottom-hole areas of cyclic-steam wells in high-viscosity oil pools. Using this program we calculated the recommended volumes of NINKA® system for several cyclic-steam wells

Thus the study of filtration characteristics and oil-displacing capacity of the surfactant based NINKA® system, generating CO_2 and alkaline buffer solutions *in situ* at thermal-steam and cyclic-steam treatments as regards to the conditions of pools with high-viscosity oil, proved their efficiency both at thermal-steam and cyclic-steam treatments and at a later stage of oil field development.

In 2002-2010 pilot tests of the technology were successfully carried out in oil fields of Russia and China at later stage of their development to enhance oil recovery from high-viscosity oil pools by surfactant-based NINKA® systems at thermal-steam and cyclic-steam stimulations [31-33]. In 2002 NINKA® system was injected into steam-injection wells 4029, 4040 and 4596, in 2008 – into well 4030 in Usinskoye oilfield. The application of IOR technology at the stationary steam injection resulted in decreased water cuttings of the production well by 10-20%, increased oil production rate on average by 40% at the increase in fluid production rate on the average by 5-10% (Figure 9). From September 2002 to February 2004 the incremental oil production for three test areas of wells №№ 4029, 4040 and 4596 totally amounted to 44.3 thousand tons, Table, or 14.7 thousand tons of additionally produced oil per one well treatment.

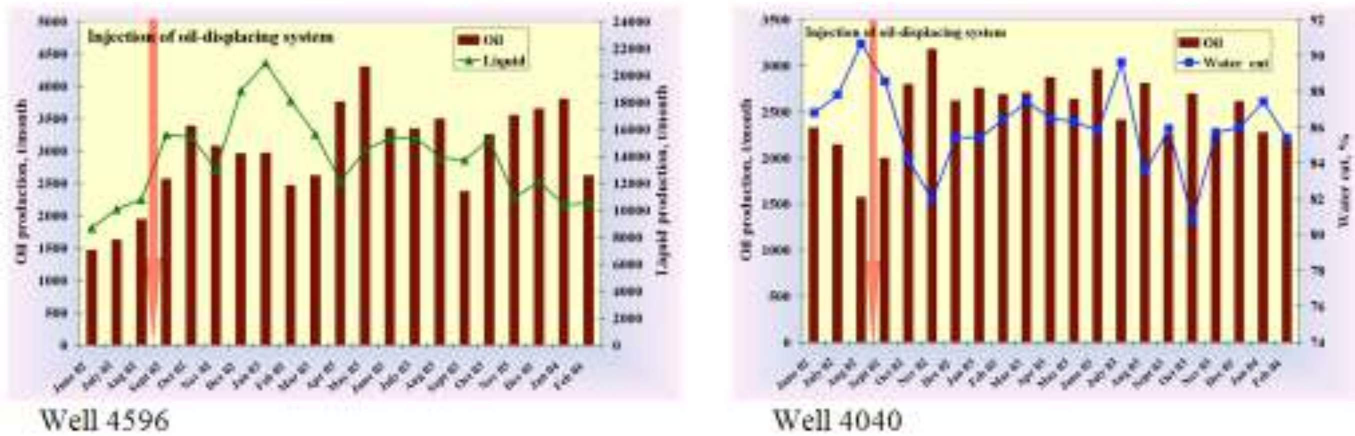


Figure 9 – Dynamics of water cut, oil and liquid production rates for the production wells in the test area of Permocarbonic reservoir in Usinskoye oil field after the injection of NINKA system into steam-injection wells 4596 and 4040.

Table – Calculation of extra oil production from October 2002 to February 2004 in the test areas after NINKA® system injection

Injection well	Object	Extra oil recovery, thou. t	Increase in average monthly production rate of production well, %
4029	lower	11.2	31
4040	lower	14.0	41
4596	upper	19.1	49
Total		**44.3**	**On average by 40 %**

In 2003-2005 pilot tests of the EOR technology were successfully carried out in 8 wells of Liaohe oil field (China) to stimulate high-viscosity oil pool via alteration of physicochemical and cyclic-steam treatments using NINKA system. At cyclic-stem treatment due to application of the EOR technology oil production increased 1.8-2.3 times as compared with steam injection and the period of oil production was prolonged for 3-5 months, for example Fig. 10. Besides viscosity of the produced oil decreased 3 times and oil congelation point decreased by 10-22 ^{o}C. Solid form of NINKA-1 system is commercially manufactured by Liaoyang Oxiranchem Co., Ltd in Laoning Province of China.

In 2008-2010 900 m^3 of NINKA® system were injected into 9 cyclic-steam wells on Permocarbonic deposit in Usinskoye oilfield, the incremental oil production amounted to 11300 tons, the average incremental production was 1250 tons per one well treatment and the average increase in oil production rate was 8.0 t/d.

Pilot tests carried out in oil fields of Russia and China at thermal-steam and cyclic-steam treatments of high-viscosity oil pools, proved the efficiency of the EOR technology and its ecological safety.

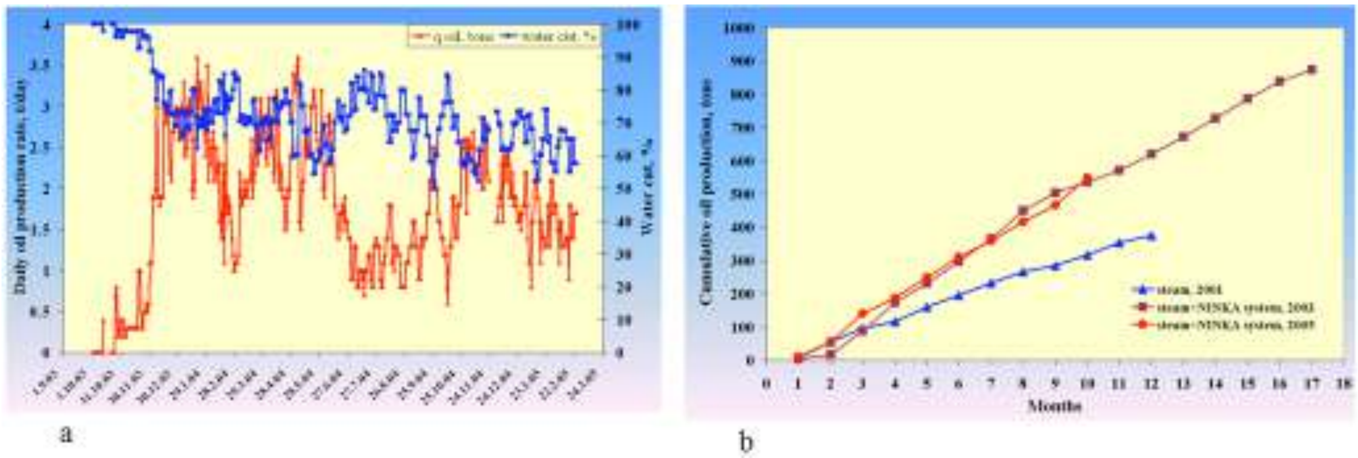


Figure 10 – Dynamics of: (a) daily oil production and water cut, well Qi 108 3-2 Quanxiling area, Liaohe oil field (China) in the cycle of steam and NINKA system injections; (b) accumulated oil production, well 3-2 in the cycle of steam injection (2001) and in the followed cycles of steam and NINKA system injections (2003, 2005)

Complex technology for improved oil recovery involving gel-forming and oil-displacing systems at thermal-steam stimulations

A complex IOR technology has been developed for high-viscosity oil deposits, the oils from which are produced by thermal-steam stimulations. It consists in injecting gel-forming GALKA®-C and oil-displacing NINKA® systems based on surfactants, capable to generate at thermal stimulation carbon dioxide and alkaline buffer solution [5-7, 12]. In 2008-2011 at area steam injection GALKA®-C and NINKA® systems were injected into 41 steam-injection wells on Permocarbonic deposit in Usinskoye oilfield. Injection volume of each system was 100-220 tons per one well-treatment. After the injections of the systems the production wells, which were hydrodynamically connected with injection wells, responded by increased oil production rate by 4-12 t/s and decreased water cut by 5-20%, for example, Figures11. The IOR technology is effective for low permeable and highly heterogeneous reservoirs at early and later stages of oilfield development.

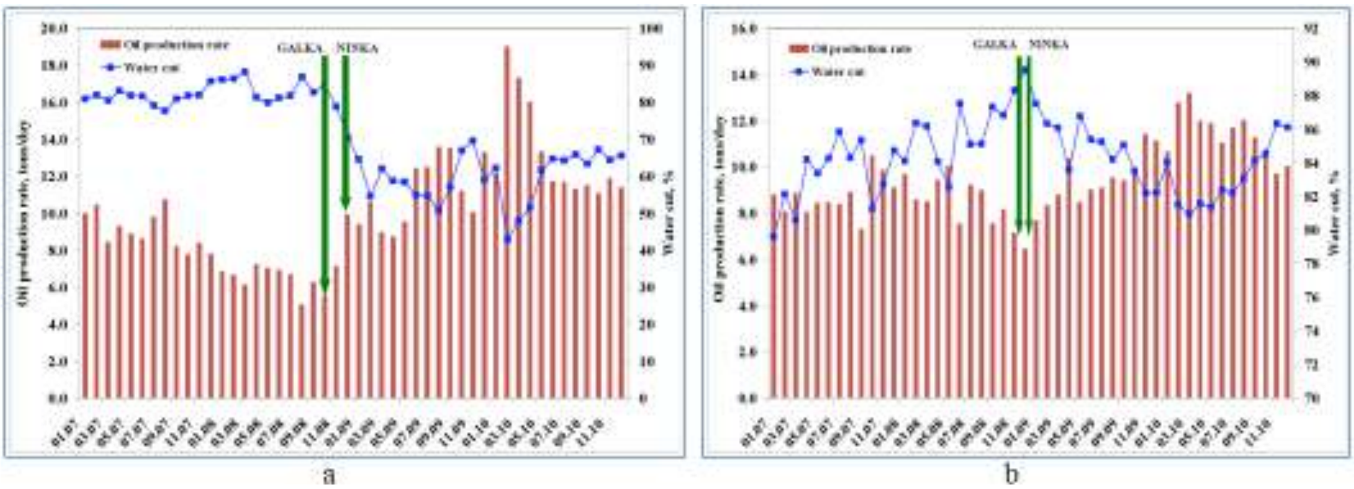


Figure 11 – Increase in oil production rate and decrease in water cut for the test area of steam-injection well № 6168 (a) and № 4233 (b) on Prmocarbonic deposit in Usinskoye oilfield after the injections of the gel-forming GALKA® -C and oil-displacing NINKA® systems.

The general analysis of all wells by years also showd the effectiveness of IOR technologies, Figure 12. Based on this analysis we can state that the program used in Usinskoye oilfield in 2008-2011 to improve oil recovery was effective and a part of the effect was due to application of IOR technologies developed at IPC SB RAS.

The results of the work show synergism of thermal-steam reservoir stimulation and physicochemical methods involving gel-forming and oil-displacing systems, the prospects of their combined application to improve oil recovery on deposit of high-viscosity oil. For effective development of high-viscosity oil deposits and further increase in oil production it seems promising to use complex IOR technologies, combining thermal-steam and cyclic-steam stimulations of reservoirs with physicochemical methods, on a large scale to increase reservoir coverage and the oil-displacement factor at simultaneous intensification of the development.

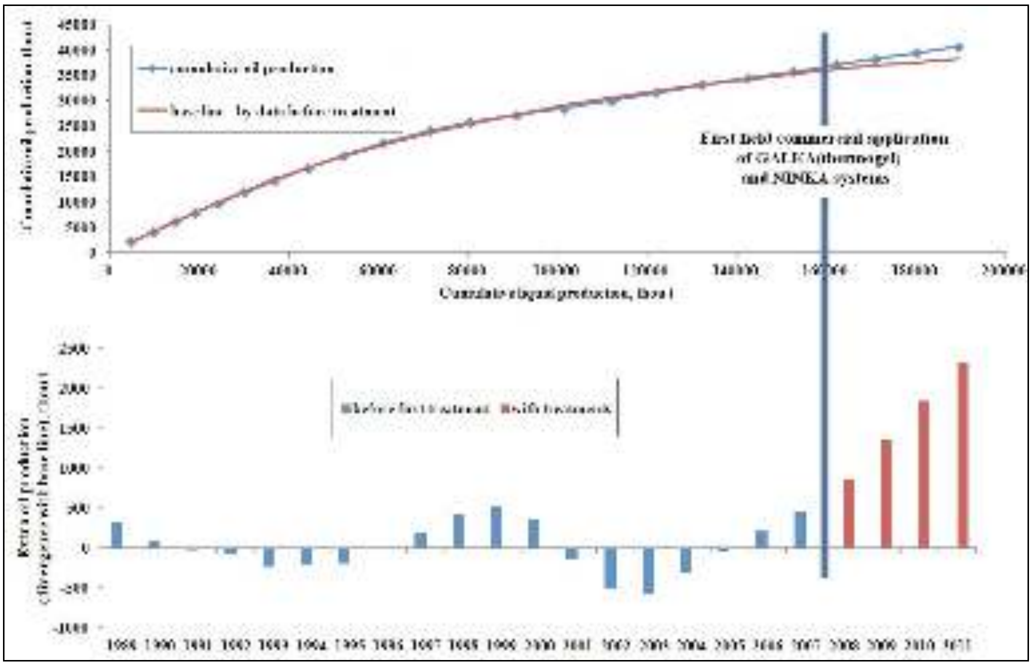


Figure 12 – Efficiency analysis of the commercial application of IOR technologies in Usinskoye oilfield within 2008-2011: increase in oil production wells due to injections of GALKA®-C and NINKA® systems into 41steam-injection wells

To improve oil recovery in oilfields with highly heterogeneous reservoirs, it is promising to combine thermotropic gels and oil-displacing systems developed at IPC SB RAS. Using IOR technology one can effectively redistribute filtration flows and involve those reservoirs into the development, which were not previously subjected to thermal-steam stimulation. The technology is effective to improve oil recovery from low-permeable highly heterogeneous deposits being both at early and later stages of the development of high-viscosity oilfields.

The achieved scientific and technical level of the works enables to create new EOR technologies for hydrocarbon deposits located in the Arctic shelf of Russia, in the Urals and Siberia, as well as reagents adaptable to works in the extreme climatic conditions. It seems promising to create interactive database of predictive value, capable to integrate experience in using EOR methods in oil fields of the world. The database will include oil properties, geological and physical conditions of deposits and techno-economic characteristics of the techniques in operation.

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