Russian Chemical Reviews **76** (10) 971 – 987 (2007) © 2007 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2007v076n10ABEH003723

Physicochemical methods for enhancing oil recovery from oil fields

L K Altunina, V A Kuvshinov

Contents

I.	Introduction	971
II.	Trends in the development of enhanced oil recovery methods	971
III.	Compositions of surfactants and alkaline buffer systems used for enhancing oil recovery of low-permeability reservoirs	973
IV.	Surfactant compositions generating carbon dioxide and an alkaline buffer system in the reservoir	977
V.	Thermotropic gel-forming systems for increasing sweep efficiency in water flooding and thermal steam treatment	979

Abstract. Physicochemical methods for enhancing oil recovery from oil fields that are developed using water flooding and thermal steam treatment are considered. The results of pilot testing of processes based on these methods carried out at West Siberian and Chinese oil fields are analysed. The attention is focused on the processes that make use of surfactant blends and alkaline buffer solutions and thermotropic gel-forming systems. The bibliography includes 123 references.

I. Introduction

Currently, Russia is a prominent supplier of hydrocarbon raw materials to the world market. Russia fully satisfies the internal requirements in crude oil and remains simultaneously among the main exporting countries. During the period from 2000 to 2006, crude oil production has steadily increased from 323 to 480 mln t.[1] These are the highest values over the last 20 years. According to data of oil companies, the increase in oil production in Russia due to implementation of enhanced oil recovery (EOR) techniques was ~43 – 45 mln t per year in 2002 – 2006.[1]

The key method for oil field development in Russia is water flooding used to produce ~95% of crude oil. Most of large oil fields are now at a late stage of development, the current water cut being more than 80%. The flooded reservoir rocks contain residual oil reserves. The newly developed oil fields are characterised, most often, by low rock permeability, high oil viscosity and complex geological structures; therefore, these reserves are difficult to recover. In Russia, the fraction of this type of oil reserves constantly increases. Calculations have shown that an increase in final oil recovery by only 1% would increase the annual production by 20 – 30 mln t. Therefore, the possibility of increasing oil reserves by enhancing the oil recovery of water-flooded reservoirs appears significant. According to expert estimates, the oil reserves difficult to recover exceed 10^{12} tons all over the world, and in mature economies, these are regarded not only as an inventory for crude oil production, but also as a main source for its intensification in the near future. Effective development of difficult-to-recover oil reserves and further buildup of production requires the design and wide-scale application of new integrated EOR techniques.[2, 3]

L K Altunina, V A Kuvshinov Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Academichesky prosp. 3, 634021 Tomsk, Russian Federation. Fax (7-3822) 49 14 57, tel. (7-3822) 49 16 23, e-mail: alk@ipc.tsc.ru (L K Altunina), tel. (7-3822) 49 24 11, e-mail: vak@ipc.tsc.ru (V A Kuvshinov)

Received 23 April 2007
Uspekhi Khimii **76** (10) 1034 – 1052 (2007); translated by Z P Bobkova

II. Trends in the development of enhanced oil recovery methods

In oil field development by water flooding, water is injected into an oil deposit through a network of injection wells. The injection of water makes up for the decrease in the formation pressure caused by oil withdrawal through producing wells. Water flooding is interpreted as displacement of oil from the fractured-porous medium by water with the formation pressure remaining the same and with full compensation of the produced oil volume by the injected water volume. In the initial stage of development, producing wells give anhydrous crude oil and later, a fluid comprising an oil – water mixture. The ratio of the amount of the produced water to the amount of the produced fluid is called water cut.

The oil recovery factor (ORF) is the ratio of the produced oil volume to the initial oil reserves. The development target is one or several oil formations developed together. The ORF value can be represented as the product of oil displacement efficiency (K_d) by the sweep efficiency (K_c) of the target by the given treatment method

$$\mathrm{ORF} = K_d K_c .$$

Even in the favourable case where water has penetrated through 70% of the formation volume ($K_c = 0.7$) and has displaced 70% of oil from the penetrated areas ($K_d = 0.7$), the final ORF would not exceed 50%:

$$\mathrm{ORF} = K_d K_c = 0.7 \times 0.7 = 0.49.$$

Computer simulation of oil field development does not imply explicit use of the coefficients K_d and K_c in design documents. Nevertheless, these values are useful as they allow one to distinguish contributions of K_d and K_c to the ORF.

There are several reasons for incomplete oil recovery on water flooding.[4 – 10] They can be divided into three groups. The first group is related to the capillary-porous structure of the reservoir rock and to the enormous overall oil – rock contact

area. The rock surface is always coated with an oil film that is not displaced by water. The film oil can account for 10% – 20% of the total oil volume in the reservoir rock. In addition, ~10% of oil remains in the formation as drops entrapped in narrow sections of capillary pores and rock cracks. The displacement of drops is hampered by the capillary pressure gradient, which may be hundreds (or even thousands) times higher than practicable pressure gradients of oil displacement with water. Therefore, the highest K_d value usually does not exceed 0.7. Thus, the first group of reasons is associated with adverse influence of the ion-molecular surface forces at interfaces in the oil – water – rock system.

The second group is related to the difference between oil and water parameters, *viz*., density and viscosity, resulting in uneven migration of the displacement front of oil by water.

The third group is related to geological and physical heterogeneity of the reservoir (mainly, heterogeneous structure and properties of the reservoir rock at macro- and micro-levels) and is manifested as incomplete sweep of the rock by water flooding, *i.e*., K_c is < 1. Finally, this enhances the variance of hydrodynamic and energy and mass exchange processes in the formation.

Enhanced oil recovery can be attained by using physicochemical methods of productive formation treatment, in particular, by introducing chemical reagents, which (*e.g*., surfactants, solvents, carbon dioxide) eliminate partially or fully the adverse influence of capillary forces. Other materials (polymer solutions, gels, emulsions and foams) change the rheological properties and structure of the filtration flows of the formation fluids (oil, water or emulsions with dissolved gases) and decrease the hydrodynamic anisotropy of the oil formation.

The long experience of using diversified methods for enhancing oil recovery at West Siberia oil fields has shown that methods that increase the sweep efficiency of the injected water are most promising. This is due to the fact that in many deposits progressive increase in the water content in the produced oil (water cut $> 70\%$) is observed even at early stage of development due to the low sweep efficiency ($K_c \simeq 0.1 - 0.2$). Meanwhile, the K_d value for high-permeability, flooded-out formation zones is close to the maximum attainable value, oil displacement by water is close to the frontal drive and $K_c \simeq 0.6 - 0.7$.

The EOR methods that increase K_d (for example, injection of dilute surfactant and polymer solutions) proved to be of low efficiency under field conditions. Meanwhile, the methods that increase K_c (or both coefficients) provided engineering and economic benefits irrespective of the particular impact mechanism.[11–18] These methods include the following:

— hydrodynamic methods changing the direction of filtration flows (various versions of non-stationary cyclic water flooding);[19]

— physicochemical methods for the control of filtration flows: injection of concentrated solutions of surfactants, oil-displacement compositions, cross-linked polymeric and polymer-dispersion systems, viscoelastic and gel-forming systems, gas, emulsions and foam and generation of such systems *in situ*, directly within the oil formation, by using thermotropic gel-forming compositions, organosilicate systems, *etc*.[5,8,9,20]

From the standpoint of subsurface gas- and hydrodynamics, the problem of coverage of an oil-bearing formation with water flooding is reduced to the control of the filtration flows of formation fluids.[21] Currently, the predominant view considers EOR methods as efficient means for the control of filtration flows, increase in the sweep efficiency of waterflooding or another active treatment. The same goal is pursued in using hydraulic fracturing of the formation, horizontal drilling and branch wellbore drilling.[22–24] These methods give rise to a fracture crack network and enhance oil production. However, after that, the water cut of producing well fluid rapidly increases. This also suggests using physicochemical methods to control the sweep efficiency and intensify the capillary counter-current impregnation of low-permeability blocks of the fractured reservoir matrix. Physicochemical methods for the control of filtration flows by creating gel barriers in the formation are promising.

The oil remaining in the reservoir after water flooding is called residual. On the basis of expert estimates, the residual oil reserves are classified in the following way:[4]

— oil remaining in low-permeability interlayers and sections not swept by water, 27%;

— oil in stagnant pockets of uniform formations, 19%;

— oil remaining in lenses and at impermeable barriers not exposed by wells, 24%;

— oil retained in capillaries and films, 30%.

Thus, the oil not swept by water flooding due to reservoir heterogeneity accounts for 70% of all residual reserves and represents the main source for enhancing oil recovery. For the production of residual oil, it is important to systematically select the EOR method and to schedule various types of stimulation of producing and injection wells in a definite order with time matching.[25,26]

In recent years, the fraction of high-viscosity oils in the total amount of crude oil produced in the world has increased. The reserves of high-viscosity oils exceed ~5 times the recoverable reserves of low- and medium-viscosity oils (according to estimates, 810 and 162 bln t, respectively).[27] Large reserves of high-viscosity oils are found in Canada, Venezuela, Mexico, USA, Russia, Kuwait and China.

Of the modern methods for production of high-viscosity oils, thermal steam treatment of formation by stationary or cyclic (huff-and-puff) steam injection is most efficient.[28–30] Most often, the injected steam has a temperature of 310 to 320 °C at the wellhead and dryness of 70% – 80%. The injection pressure usually does not exceed 15 – 18 MPa. Combustion of 1 t of oil in a steam generation plant gives from 10 to 15 t of steam. The treatment is considered efficient if this gives 1 t of additional produced oil per 3 – 4 t of steam. The stationary steam injection is accomplished continuously though a network of steam injection wells, while oil is produced through a network of producing wells. The cyclic (huff-and-puff) stimulation consists of three stages: first, steam is injected into producing well, then the well is closed and kept for some period for formation warming up, and after that, oil production is resumed. When oil no longer enters the well, the huff-and-puff cycle is repeated. In this case, the first cycle is most effective, the efficiency of subsequent cycles being lower.

The efficiency of thermal steam treatment can be increased by combining it with physicochemical methods that use gel-forming and oil-displacing compositions. The use of gels increases the sweep efficiency of steam injection, while the use of oil-displacing compositions ensures additional oil recovery. Integrated methods that combine thermal steam and physicochemical treatment of formation are at an early stage of development (the number of these projects is small but they arouse considerable interest).

In 1981, works on enhancing oil recovery by using physicochemical methods were started at the Institute of Petroleum Chemistry of the Siberian Branch of the RAS (IPC SB RAS). A new approach to the development of efficient oil-displacing compositions based on surfactants and alkaline buffer systems has been proposed. A set of original devices and methods for investigation of the physicochemical and rheological properties of the surface and bulk phases in the oil – rock – surfactant solution system have been developed. A promising concept of using the reservoir or injected heat carrier energy for *in situ* generation of oil-displacing fluids, gels and sols directly in the reservoir has been proposed. The physicochemical grounds for

EOR methods making use of gel-forming systems and surfactant compositions were proposed. The principles of selection of oil recovery-enhancing compositions were implemented within the concept considering oil-displacing liquids as physicochemical systems with negative feedback, which maintain self-adjusting properties optimal for oil recovery in the producing formation for a long period of time. In recent years, development of new techniques using inorganic and polymeric gel-forming systems capable of generating gels directly in the formation has been in progress. By using these techniques, it is possible to create diverting barriers and control filtration flows, which would increase oil production and decrease water cut in the producing well product.

The chemical reagents used in industrial oil production should be relatively cheap, environmentally safe and commercially available on a large scale. Their application should not induce irreversible changes in the environmental situation in oil producing regions. The search for new cheap raw material sources for the use in EOR techniques is of special value. In this respect, good promise is given by the joint work of the Institute of Petroleum Chemistry and the Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the RAS dealing with the preparation of soluble compounds from plant stock (cellulose, rice hulls and so on) using mechanochemical treatment and coordinating solvents [31] and with the use of large-scale industrial products manufactured in Russia, wastes from chemical and petrochemical plants and Kuznetsk Basin coal industry and so on.[32]

The specialists of the IPC have developed eight EOR techniques, which are used at West Siberian and other oil deposits. Annually, 150–200 wells are treated according to these techniques. The additional oil production is on average 1–3 th t per treated well and the payback period is 5–10 months. Due to the use of the developed technologies at the West Siberia oil fields, >1.5 mln t of oil were additionally produced during the last 5 years alone. These technologies are cost effective and environmentally safe; they make use of large-scale products available as wastes of various industrial processes in Russia. The pilot tests of gel technologies were successfully carried out in the White Tiger offshore field in South China Sea (Vietnam).

Currently, new technologies for enhancing oil recovery, in particular, for high-viscosity oil fields, are developed. For increasing the efficiency of cyclic steam treatment of high-viscosity oil reservoirs, it was proposed to combine this method with physicochemical methods, in particular, those using polymeric and inorganic gels (for water shutoff) and surfactant compositions and generating, on thermal treatment, carbon dioxide and alkaline buffer system (for decreasing oil viscosity and for additional oil displacement). A set of laboratory studies has been performed. The first field tests of thermotropic gel-forming compositions for water shutoff and surfactant-based oil-displacing compositions were carried out between 2003 and 2006 as applied to cyclic steam treatment of high-viscosity oil reservoirs of the Usinskoye oil field (Komi Republic) and Liaohe and Gaosheng oil fields in China.

III. Compositions of surfactants and alkaline buffer systems used for enhancing oil recovery of low-permeability reservoirs

1. Effect of pH on oil displacement by water

A key factor hampering oil displacement by water is structuring of the adsorption layers in the oil–rock–formation water system. These layers contain tars, asphaltenes, heteroatomic compounds, high-molecular-mass paraffins, mineral colloidal particles.[33–42] As a result, gel-like layers (films), possibly microemulsions, having high viscosity are formed at the interface. These layers (films) create a structure-mechanical barrier, which accounts for the kinetic stability of the disperse system and prevents thermodynamically favourable processes.[43] Therefore, of interest are investigations of boundary layers in the oil–water–surfactant system, especially those carried out by low-frequency vibration methods.[44–46] These methods allow one to measure rheological parameters of contacting bulky and surface phases under conditions of continuous deformation with small amplitude (this type of deformation occurs in an oil drop or film on filtration through a water-saturated capillary-porous formation material).

For enhancing oil recovery, it is insufficient to ensure low oil–water interfacial tension. The interfacial tension is a thermodynamic value equal to the free energy of the interface; the lower the interfacial tension, the thermodynamically more favourable the oil displacement process.[47,48] However, thermodynamically favourable process often cannot be accomplished due to its too long duration. In the case we consider, adsorption layers rearrange slowly upon mechanical impact due to the sharp increase in the structural viscosity or, what is the same, due to the appearance of relaxing shear elasticity following a decrease in the layer thickness. Consequently, during water flooding at the formation pressure gradients, the structured adsorption layers behave as non-thixotropic mechanically strong films, which deteriorate filtration of formation fluids and reduce oil recovery.[33–42,49,50] Thus, to enhance the oil recovery, it is necessary to find practicable ways for destructuring of the adsorption layers and decreasing the interfacial tension.

When aqueous solutions inmiscible with oil are used for oil displacement, the interfacial films can be destructured by chemical reagents, namely, by surfactants and/or low-molecular-mass inorganic compounds dissolved in the injected water that are able to destroy hydrogen bonds and weaken hydrophobic interactions between the oil components constituting these films.[51–55] The surface activity of surfactants should be higher than that of oil components to provide the possibility of displacing them from the adsorption layers. However, surfactants should not form structured interfacial films. None of the commercially manufactured surfactants fully meets these requirements. The properties of the colloidal surfactants used can be improved by adding low-molecular-weight organic co-surfactants and by forming surfactant compositions with low-molecular-mass inorganic chemicals that ensure destructuring (fluidisation) of adsorption layers.

In the oil–water–rock system, the key role in structuring (strengthening) of interfacial layers belongs to hydrogen bonds, although hydrophobic interaction also plays a role at high formation temperatures. The interfacial layers can be destructured most readily and efficiently using alkaline chemicals as parts of oil-displacing compositions to destroy hydrogen bonds and weaken hydrophobic interactions between the oil components of these layers.[56,57]

The destructuring of interfacial layers by solutions of alkaline reagents is caused by various chemical reactions involving hydroxyl ions, specifically, neutralisation of acid groups (carboxy, phenolic and thiol); saponification of ester bonds; deprotonation of donor heteroatoms (nitrogen, sulfur); association of hydroxyl ions with aromatic fragments of the oil components; and influence on the structure of water and thus on hydrophobic bonding, the conformational mobility of hydrophobic parts of surfactants, *etc*. These reactions involving hydroxyl ions reduce the oil–water interfacial tension (Fig. 1),[58–60] change the electric double layer,[61–63] decrease the viscosity of interfacial layers [58,64] and increase the wettability of the reservoir rock and oil phase by water.[65–69]

Among all anions, the hydroxyl ion has the highest adsorption potential with respect to the rock oxide minerals in an aqueous medium and the highest mobility and exerts the

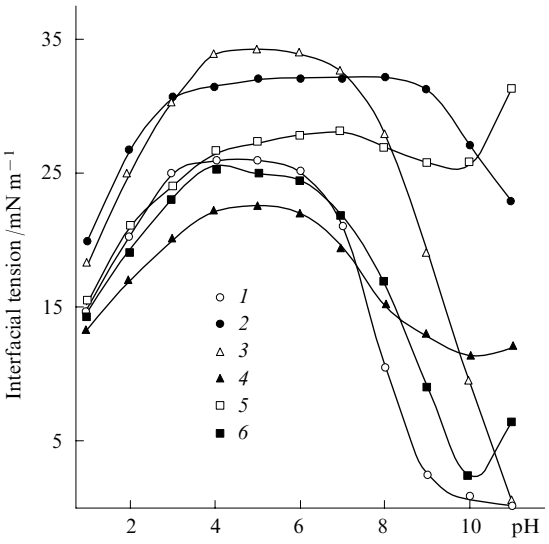


Figure 1. Oil interfacial tension for the AV_1 formation of the Sovetskoye (*1*, *4*), D_1 formation of the Romashkinskoye (*2*, *5*) and PK_{1-2} formation of the Russkoye deposits (*3*, *6*) *vs.* pH of the aqueous phase of different compositions.[5]
Aqueous solution: (*1*–*3*) 0.1 M HCl + NaOH; (*4*–*6*) 0.1 M HNO_3 + NH_3.

most pronounced ordering effect on water. In an alkaline solution, the initially hydrophobic sections of the rock become hydrophilic and the thickness of the stable aqueous interlayer between the rock and oil increases. The adsorption of hydroxyl ions increases the surface density of the negative charge of the rock and decreases the number of adsorption sites able to form hydrogen bonds.[65, 70] This is favourable for improving rock wetting by water and for decreasing adsorption of both anionic and non-ionic surfactants.[71–75] When surfactants are adsorbed from alkaline solutions onto a negatively charged rock surface, the orientation of surfactant molecules in the adsorption layer is such that the hydrophilic character of the rock does not change. For alkaline solutions of non-ionic and anionic surfactants, a low interfacial tension and neutral wetting in the rock–oil–aqueous phase system can be implemented simultaneously, which is confirmed by the results of testing of selective wetting in a model system with controlled properties of interfaces.[76–78] This results in high capillary numbers so that the oil-displacing ability of surfactant solutions increases.[5, 79, 80]

In view of the foregoing, it appears promising to develop compositions containing surfactants and alkaline chemicals and combining the useful features of alkaline water flooding and water flooding using surfactant solutions.[4, 47, 48, 81, 82] Analysis of the features of oil displacement process by alkaline solutions of surfactants [5] attests to the presence of an optimal alkalinity range (pH 9.0–10.5) in which the surfactants are chemically stable and have the highest oil-sweeping ability.[79] In addition, it is in the range of pH 9.0–10.5 that suspensions of clay minerals have the lowest viscosity and adhesion to the reservoir rock,[83] which is important for water flooding of low-permeability reservoirs. In this pH range, no noticeable dissolution of rock minerals and precipitation of alkaline-earth metal hydroxides from formation or injected water are observed, whereas at pH > 10.5, calcium and magnesium hydroxides can precipitate and rock minerals dissolve. In highly alkaline media, non-ionic surfactants like hydoxyethylated phenols undergo denaturation resulting in a sharp increase in the critical micelle concentration.[71]

Thus, selection of an appropriate alkaline reagent is crucial for the development of effective oil-displacing compositions based on surfactants. A self-maintained, self-adjusted pH value in the range from 9.0 to 10.5 can be ensured by using buffer systems with maximum buffer capacity in this pH range. In terms of more general views on an oil-displacing composition as a physicochemical system, the presence of an alkaline buffer solution generates a negative feedback and thus imparts the composition with self-adjustment property, *i.e.*, maintenance of its functions in the formation for a long period of time. In physicochemical systems, self-adjustment is necessarily accompanied by a change in the component concentrations and has natural concentration limits within which the parameter characterising the self-adjustment efficiency reaches a maximum. For buffer solutions, the buffer capacity is such a parameter. The condition for maximum capacity is met if the concentrations of the acid (base) and salt composing the buffer system are equal. The thermodynamics of buffer solutions was considered previously.[84, 85] The effects of dilution, neutral electrolyte and non-electrolyte additives, temperature and pressure on the buffer capacity have been described in detail in a monograph.[86]

Despite the enormous number of substances capable of forming buffer solutions, only some organic and only four inorganic buffer systems are suitable for the required pH range (9 to 10.5): phosphate (tripolyphosphate), silicate, ammonia and borate systems. The tripolyphosphate system can be used to enhance oil recovery of high-permeability reservoirs with low temperature. In the case of low-permeability reservoirs of the West Siberia oil fields, its use is problematic, because sodium tripolyphosphate rapidly hydrolyses above 323 K being converted into trisodium phosphate, which forms insoluble salts with calcium, magnesium and iron ions present in injected and formation waters. The use of silicate systems (specifically, their field preparation) is faced with technical difficulties caused by the tendency of sodium silicate to hydrolytic polycondensation and poor compatibility with oil field brine. It is noteworthy that phosphate and silicate systems are used in the techniques implementing the precipitation and gelation effects for selective isolation of highly permeable zones of the reservoir.

Ammonia, borate and mixed ammonia–borate systems are the systems of choice. They are prepared from ammonia, ammonium nitrate, sodium tetraborate and boric acid. These compounds are rather cheap commercial chemicals manufactured on a large scale.

The use of compositions of non-ionic surfactants with an alkaline reagent at high formation temperatures requires that they contain anionic components, which increase the cloud point of the non-ionic surfactant.[87] Additionally, in order to enhance the oil-sweeping ability and improve the compatibility with oil field brine and injected water, it is desirable to introduce low-molecular-mass organic compounds that combine the functions of a non-colloidal co-surfactant and a precipitation inhibitor for hydroxides and hardness calcium or magnesium salts. Taking into account the above requirements, a number of compositions based on ionic and non-ionic surfactants (oxyethylated alkylphenols: OP-10, Neonol AF 9-12 and its analogues) were developed and laboratory tested.[5]

2. IPC compositions based on surfactants and alkaline buffer systems

Analysis of the development of physicochemical methods for enhancing oil recovery reveals a clear tendency to impart self-adjustment feature to the oil-displacing fluid, which allow the fluid to maintain its functions in the reservoir rock for a long period of time.[88] The development of physicochemical principles for selection of surfactant compositions taking into account the thermodynamic and kinetic parameters of the oil–rock–aqueous phase system, which affect the oil displace-

ment from the porous rock, carried out at the IPC SB RAS is based on the concept of an oil-displacing fluid as an above-mentioned physicochemical system with negative feedback. It was proposed that alkaline buffer systems with a highest buffer capacity in the pH range of 9.0 – 10.5 would be used in the oil-displacing compositions of the IPC series.

Systematic studies of the effect of pH and the ionic strength of aqueous electrolyte solutions on the interfacial tension of oils showed that the pH dependence of the interfacial tension (see Fig. 1) has extreme points: a maximum in the pH range from 4.5 to 5.5 and a minimum at pH 9 – 10. The maximum is due to the presence of natural surfactants in oil.[5] These are heteroatomic compounds present as parts of tars and asphaltenes, the most high-molecular-mass oil components. The functional groups of the cationic surfactants present in oil include pyridine, quinoline and other, mainly heterocyclic, basic groups and also tetrapyrrole fragments of oil metal porphyrins. The anionic surfactants present in oil typically contain carboxy, phenolic and thiol functional groups. The decrease in the interfacial tension upon the shift of the aqueous phase pH to the acidic region with respect to the maximum is due to protonation of functional groups of cationic surfactants in the interfacial layer, while that upon the shift of pH to the alkaline region from the maximum is due to neutralisation of the carboxy, phenolic and thiol groups of anionic surfactants. The pH dependences of the interfacial tension for crude oils of West Siberia and the Ural – Volga region are different. In the alkaline region, the interfacial tension decreases substantially for West Siberian crudes, whereas for the sour crudes of the Ural-Volga region, this decrease is slight, which may be attributed to the presence of saturated sulfides having weakly basic properties. For all crudes studied, the interfacial tension varied inversely to the ionic strength of the aqueous phase.

At the oil – aqueous phase interface, the natural surfactants of oil form an amphoteric adsorption layer. The ionisation of the polar ionic groups in the oil natural surfactants in acidic or alkaline medium gives rise to an electric double layer at the interface. The maximum in the dependence of the interfacial tension of oil at the interface with the aqueous phase *vs*. pH of the aqueous phase corresponds to the isoionic state of the adsorption layer. The maximum pH value corresponds to the isoionic point of the layer (pH_i); it can be calculated as the half-sum of the acid constant indexes (pK_a) of the strongest acidic and basic functional groups in the adsorbed molecules. The strongest acidic groups present in oil surfactants are carboxy groups ($pK_a = 5.6$), while the strongest basic groups are pyridine ($pK_a = 4.6$) or quinoline groups ($pK_a = 4.9$). The calculated pH_i value equal to 5.3 virtually coincides with the experimental pH_i 5.2.

Taking into account the experimental dependences of the interfacial tension on pH and the ionic strength of the aqueous phase, an electrocapillary model of the interfacial layer has been developed.[5,89] According to this model, the interfacial layer (amphoteric adsorption layer of the natural surfactants present in oil) has the properties of ion exchange membrane. The extremal pattern of dependence of the interfacial tension of oils on pH of the aqueous phase is caused by the presence of an electric double layer arising due to ionisation of the ionisable groups in natural surfactants of oil. The model establishes relationship between the oil composition and the physicochemical parameters of the interfacial layer, which dictates the mechanism of oil displacement by aqueous solutions (due to the change in the interfacial tension, adsorption of the natural surfactants of oil, the composition and concentration of electrolytes in the aqueous phase). In terms of this model, the dependence of the interfacial tension of oil (σ) on the aqueous phase pH is given by the equation

$$\sigma = \sigma_i - b\vartheta^2[-\log(a_{H^+} + KI) - pH_i]^2 +$$

$$+ c\vartheta^4[-\log(a_{H^+} + KI) - pH_i]^4 - 2.303\Gamma_0 RT\log(1 + K_aI),$$

where σ_i is the interfacial tension in the isoionic point; b is the integral capacity of the electric double layer; $\vartheta = 2.303RT/F$, R is the universal gas constant, T is temperature, F is the Faraday number; a_{H^+} is the proton activity in the aqueous phase; K is the ion exchange constant for the interfacial membrane; I is the ionic strength of the aqueous phase; c is a parameter characterising the dependence of the integral capacity of the electric double layer on its potential; Γ_0 is the limiting adsorption of electrolyte ions in the interfacial layer; K_a is the adsorption constant for electrolyte ions in the interfacial layer.

As an example, Fig. 2 shows the dependences of the interfacial tension on pH, one calculated using the above equation (line) and one experimental (dots) for the crude of the Sovetskoye oil field (AV_{1-2} formation) at the interface with an aqueous electrolyte solution with a constant ionic strength.

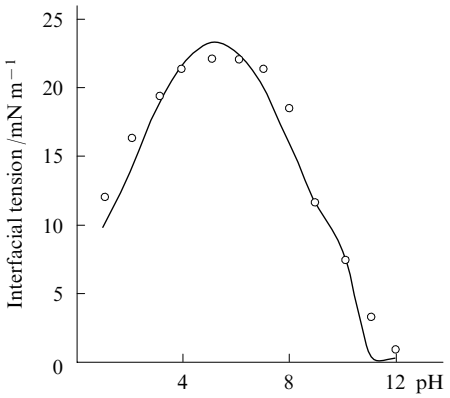


Figure 2. Oil interfacial tension *vs*. pH for the oil of Sovetskoye field (AV_{1-2} formation) at the interface with an aqueous solution of a 1 : 1 electrolyte with a constant ionic strength $I = 0.1$ mol per kg of water.[60]

On the basis of investigation of the thermodynamic and kinetic parameters of the oil – rock – water – surfactant systems, the most promising IPC compositions involving surfactants and ammonia buffer based on ammonia and ammonium nitrate (cheap commercial products) were proposed for the industrial use at the oil fields of West Siberia. These compositions combine the advantages of alkaline water flooding and water flooding with surfactant solutions.

A distinctive feature of IPC compositions is the fact that they contain constituents of the geochemical nitrogen, carbon or oxygen cycles. This accounts for their environmental acceptability and multifunctionality: the components serve as the nutrition sources for the reservoir microflora, natural indicators (tracer agents) of the filtration flows in the oil accumulation, *etc*.

Waxy IPC compositions IHN-60 and IHN-100, low-viscosity non-combustible liquids with freezing points ranging from −33 to −55 °C were proposed for winter injection in Northern regions. The use of IPC compositions increases the oil displacement efficiency by 10% – 20%. They can be employed over broad ranges of formation temperatures and compositions of formation water and for the development of low-permeability and heterogeneous reservoirs. Upon oil displacement by IPC compositions, the mobility of filtered fluid increases 3 – 7-fold, which attests to the possibility of appreci-

able increase in the injectivity of injection wells on treatment of the bottomhole formation zone.[90] The specific loss of the surfactant caused mainly by adsorption on the core material during oil displacement equals 0.2 – 0.6 mg g^{-1}.

3. Pilot testing of EOR processes using IPC compositions

Two processes making use of IPC compositions have been developed: treatment of the bottomhole zones with small volumes of the compositions; injection of large-volume slugs (portions) of compositions in order to affect the interwell space of the formation.

From 1984 to 2006, treatment of the bottomhole zones of more than 150 injection wells was carried out under different geological conditions in the oil fields of the Tomsk and Tyumen Regions. This process increases the well injectivity 1.5 – 2.5-fold, decreases the injection pressure by 30% – 40%, increases the efficiency of the producing wells that are hydrodynamically connected to injection wells. The duration of the effect is 6 to 16 months. The additional oil production is 20 – 30 t per t of the injected composition. The technology is cost effective, the payback time being 4 – 9 months; it is applicable to formations with temperatures of 10 – 130 °C and permeability of 0.005 – 0.500 μm^2, the effect being most pronounced for low-permeable heterogeneous reservoirs of Jurassic and Cretaceous deposits typical of West Siberia.[5]

The pilot testing of technology with injection of large-volume slugs of IPC compositions with controlled alkalinity was carried out from 1985 to 1989 under different geological conditions in the pilot sites of oil fields of West Siberia: AV_1 formation of the Sovetskoye field, YuV_1 formation of the Vakhskoye field, AV_{1-3}, AV_{2-3}, and BV_{10} formations of the Samotlorskoye field, BV_{10} formation of the Lor-Yeganskoye field, Yu_1 formation of the Malo-Chernogorskoye field, and AS_4 formation of the Mamontovskoye field (Table 1), and in pilot sites of the V_3 formation of the Severo-Savinoborskoye field (Komi Republic). Altogether > 30 th t of IPC compositions was injected. The slug volume was 0.2% – 0.4% of the oil-saturated pore volume of the pilot site formation.[5, 18]

Analysis of the state of the art of development of the pilot sites resorting to the results of geophysical, hydrodynamic and physicochemical studies showed that IPC compositions improve the water flooding process: the water cut of producing wells decreases, remains constant or increases at a lower rate; the parameters of the bottomhole zone of injection wells and the reservoir (productivity, hydroconductivity, piezoconductivity and permeability) are improved; the dynamic liquid levels in producing wells increase; the residual oil saturation decreases; oil displacement parameters are improved; and the effective formation thickness either increases or remains the same. The injectivity of the injection wells increases, resulting in more intense development. The IPC compositions move along the formation as a whole entity, being gradually diluted with the formation water. The migration of the composition front is accompanied by a decrease in the water cut of oil, to the utmost, by 30% – 40% and a pH increase from 6 – 7 to 8 – 10. Some components of the IPC composition can be found in reliably determinable concentrations (0.001% – 0.1%) in the producing well product for long periods of time, up to 2 – 3 years, the highest surfactant and ammonium nitrate concentrations being 0.2% – 1.0%. The production of the components from different wells occurs in comparable amounts, which indicates that the formation has been swept throughout the whole pilot site. The diagrams of the space distribution of surfactant and the oil production according to wells are similar, *i.e.*, an increase in the surfactant production is accompanied by an increase in the specific oil production.[5, 18]

The produced water is less corrosive in the presence of IPC compositions than the injected water. Thus the rate of corrosion of the test samples mounted in the oil-gathering systems in the pilot sites of the Lor-Yeganskoye field was 0.1 mm per year. The IPC compositions present in produced water in concentrations of 0.5% enhance oil dehydration processes.

The engineering and cost efficiency of using IPC compositions at the West Siberia oil fields was evaluated (see Table 1). The increase in the oil recovery was from 2.8% to 27.5% (on average, 8.2%). This technology provides from 9.8 to 68 t (on average, 26.2 t) of oil produced additionally per t of the composition or 183 t of oil per t of the surfactant. A computer model of the process was designed.[5] The industrial production of the IPC compositions IHN-60 and IHN-100 was organised in Russia (at the CJSC KHIMEKO-GANG and CJSC Polyex plants).

The field tests revealed the stimulating effect of IPC compositions on the development of the reservoir microflora.[91 – 93] The components of the ammonia buffer system are involved in the geochemical nitrogen cycle and serve as additional nitrogen nutrition for anaerobic and aerobic bacteria in trophic chains of the microbial biocenosis of the oil-bearing formation. Microbiological studies carried out in injection areas of IPC compositions IHN-60 and IHN-100 into the AV_1 formation of the Sovetskoye oil field, AV_1, AV_{2-3} and BV_{10} formations of the Samotlorskoye oil field, YuV_1 formation of the Vakhskoye and BV_{10} formation of the Lor-Yeganskoye oil fields have shown that the amount of denitrifying and heterotrophic bacteria, including *Pseudomonas* and *Actinomices*, is much higher than in reference sites. The count of sulfate-reducing bacteria in the produced water in the pilot sites was much lower than that in the injected water or in the produced water in the reference sites. The geochemical activity of the denitrifying bacteria is directed at the oxidation of organic compounds present in oil to give carbon dioxide, biosurfactants and other substances enhancing the oil recovery.

Table 1. Oil production with the use of IPC compositions on the pilot sites of West Siberia oil fields.[18]

Oil field			Oil in place reserves /th t	Amount of the injected IPC composition /th t	Gain in ORF (%)	Additional oil production	
name	formation	number of the injection well				th t	t per t of the IPC composition
Samotlorskoye	AV_{1-3}	4110	1576.0	5.0	12.8	201.7	40.3
	BV_{10}	12168	369.0	2.3	27.5	101.5	44.1
	BV_{10}	12162	403.9	1.6	3.9	15.8	9.9
	AV_1^{1+2}	15930	582.9	1.7	5.3	30.9	18.2
	AV_1^3	15618	589.0	1.5	2.8	16.5	11.0
Lor Yeganskoye	BV_{10}	site 1 (wells 129, 132 133, 134)	706.9	2.1	2.9	20.5	9.8
	BV_{10}	site 3 (wells 85, 86 87, 88)	901.2	4.2	8.3	74.8	17.8
Malo-Chernogorskoye	Yu_1^1	239	551.6	1.8	3.7	20.4	11.3
Sovetskoye	AV_1	644	2458.0	5.8	7.5	184.4	31.8
Mamontovskoye	AC_4	2054	768.0	0.8	7.1	54.5	68.1

IV. Surfactant compositions generating carbon dioxide and an alkaline buffer system in the reservoir

It was noted above that development of high-viscosity oil fields involves thermal treatment techniques. Steam is used most often as the heat carrier. Many researchers have attempted to find chemicals for the addition to steam to improve its action.[28,30,94] Theoretically, the use of such additives may decrease the temperature of steam condensation, for example, by formation of an azeotropic mixture or water solubility in compressed gases, increase the reservoir permeability for a steam – gas mixture and so on. Carbon dioxide is the additive of choice. The grounds for the beneficial effect of CO_2 are well-known; they include the increase in the reservoir rock permeability for oil, the decrease in the oil viscosity, *i.e.*, a favourable change in the mobility ratio of oil and the aqueous phase, and so on.[48]

For a number of years, the concept of high-viscosity oil formation stimulation by a surfactant-based compositions, which form CO_2 and an ammonia buffer system under the action of formation temperature, has been developed at the IPC SB RAS.[5,95] Prior to steam injection, a slug of a composition representing an aqueous solution of a blend of non-ionic and anionic surfactants, carbamide and ammonium salts, are introduced into the well. In the oil-bearing formation, carbamide is hydrolysed under the action of high steam temperature to give carbon dioxide and ammonia. Unlike ammonia, carbon dioxide is soluble in oil much better than in water. The partition coefficient for carbon dioxide in the oil – water system in the temperature range of 35 – 100 °C and the pressure range of 10 – 40 MPa is between 4 and 10, whereas this value for ammonia does not exceed 6×10^{-4}. Therefore, in the oil – water system, the oil phase is enriched in carbon dioxide and the aqueous phase in enriched in ammonia, which forms, together with the ammonium salt, an alkaline system with the maximum buffer capacity at pH 9.0 – 10.5, as in IPC compositions. This gives rise to several useful effects. The dissolution of carbon dioxide in oil decreases oil viscosity. In the vapour phase, carbon dioxide and ammonia help to maintain vapor – gas mixture at a temperature below the vapour condensation point; therefore, the efficiency of transfer of oil components by the distillation mechanism increases. Carbon dioxide and ammonia reduce swelling of clay minerals of the reservoir rock and thus help maintaining the initial reservoir permeability. The same role is played by the ammonia buffer system, which is formed upon dissolution of ammonia in an aqueous solution of ammonium salts. In addition, owing to its alkalinity (pH 9 – 10) and the presence of surfactants, it promotes intensification of the counter-current impregnation of the formation and oil displacement.

1. Kinetics of carbamide hydrolysis in water and surfactant-based compositions

The physicochemical mechanism of action of oil-displacing compositions comprising surfactants and alkaline buffer solutions producing CO_2 *in situ* is based on the kinetics of carbamide (urea) hydrolysis in water and compositions at 80 – 250 °C.

Carbamide dissolved in water is rather stable up to 80 °C. Above this temperature, it is hydrolysed to give ammonia and carbon dioxide according to the overall reaction

$$CO(NH_2)_2 + H_2O \longrightarrow CO_2 + 2NH_3. \quad (1)$$

Detailed information about the physicochemical properties of components, phase equilibria and reaction kinetics in the carbamide – water – ammonia – carbon dioxide system have been reported;[96,97] the kinetics of carbamide hydrolysis has been described.[96] The hydrolysis takes place in two steps. The first step is isomerisation of carbamide to ammonium isocyanate

$$CO(NH_2)_2 \rightleftharpoons NH_4OCN. \quad (2)$$

The second step is hydrolysis of ammonium isocyanate to give ammonium carbonate

$$NH_4OCN + 2H_2O \rightleftharpoons (NH_4)_2CO_3. \quad (3)$$

A kinetic study of carbamide hydrolysis in water and in compositions has shown that the reaction follows the first order kinetics with respect to carbamide in the carbamide concentration range from 0.5% to 20% at 80 – 100 °C. The average temperature coefficient was 2.4, *i.e.*, the Van't Hoff rule was fulfilled.

For the temperature range of 100 – 250 °C, the following kinetic parameters were found: the activation energy and the pre-exponential factor for the Arrhenius equation for carbamide hydrolysis in water are 44.6 kJ mol^{-1} and 4.01×10^4 h^{-1}; for hydrolysis in compositions, 50.8 ± 1.5 kJ mol^{-1} and 10.9×10^4 h^{-1}, respectively.[98] The increase in the activation energy in the latter case is due to the effect of the ammonium salt.

The activation energy for carbamide hydrolysis in the temperature range of 80 – 100 °C is twice as high as that in the 100 – 250 °C range. In the 80 – 250 °C range, the rate-limiting step of the reaction changes, as indicated by a change in the slope of the temperature dependence of the reaction rate constant (Fig. 3). At 80 – 100 °C, the rate-limiting step is carbamide isomerisation (2), which has a higher activation energy than reaction (3). At 150 – 250 °C, the rate of carbamide decomposition increases and the solution pH reaches 9 – 10.5 where reaction (3) becomes the rate-limiting step.

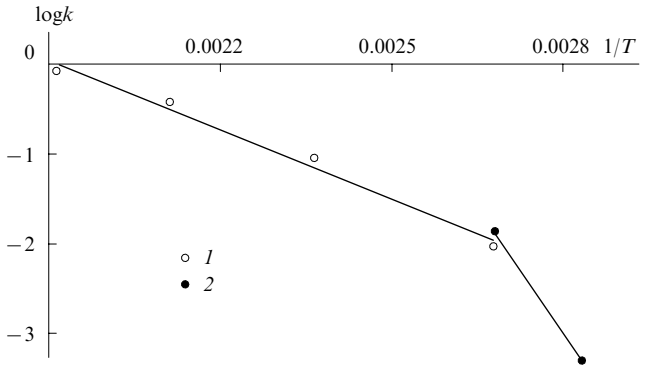


Figure 3. Temperature dependence of the rate constant for hydrolysis of carbamide in a surfactant-based composition at 80 – 250 °C.[95] Temperature range /°C: (*1*) 100 – 250, (*2*) 80 – 100.

As a result of carbamide hydrolysis at 80 – 250 °C, solutions of carbamide and oil-displacing compositions acquire high buffer capacity with a maximum at pH 9.0 – 10.5 (Fig. 4).[98] In water, the rate of carbamide hydrolysis is higher and the time it takes to attain the maximum pH is shorter than in solutions containing ammonium salt; however, the highest buffer capacity is observed only in the presence of the ammonium salt. Indeed, at 100 °C, the highest buffer capacity of the composition is 14.4 g-equiv. litre^{-1} (pH unit)$^{-1}$, while that of a carbamide solution is 5.3 g-equiv. litre^{-1} (pH unit)$^{-1}$. At 250 °C, the buffer capacities of the composition and carbamide solutions are 22.3 and 7.22 g-equiv. litre^{-1} (pH unit)$^{-1}$, respectively. The buffer capacity of compositions is 2 – 4

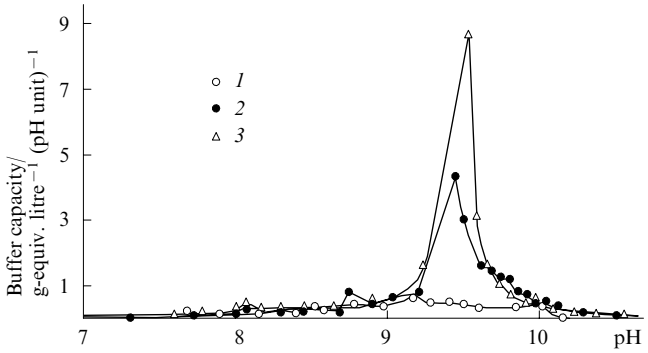


Figure 4. Buffer capacity of the surfactant-based composition *vs.* pH.[98] (*1*) Before heating; (*2*, *3*) after heating at 150 °C for 7 and 10 h, respectively.

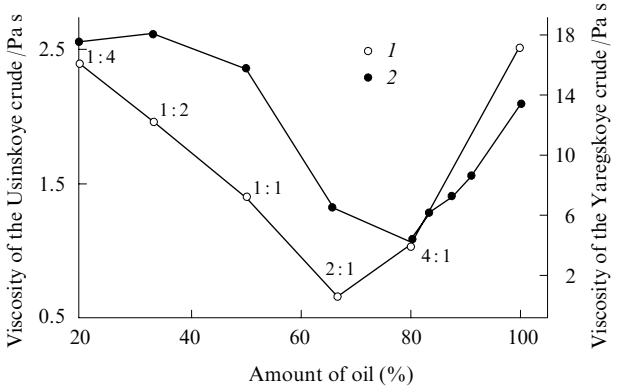


Figure 6. Viscosities of the oil from Usinskoye (*1*) and Yaregskoye (*2*) oil fields at 20 °C after maintenance at 150 °C *vs.* oil to surfactant composition ratio.[98]

times higher than that of carbamide solutions in water under the same conditions. Due to the high buffer capacity, 10–100-fold dilution of the hydrolysed composition with water results in only a slight change in pH (0.2–0.5 pH units).

2. Rheological and filtration properties of high-viscosity oil systems with various surfactant compositions generating carbon dioxide and an alkaline buffer system in the oil formation

The alternating thermal steam treatment and physicochemical treatment with surfactant compositions of a high-viscosity oil formation is based on the changes in the rheological properties and a decrease in the viscosity of oil.[28–30, 48] The features of such alternating treatment were revealed by rheokinetic studies of high-viscosity oils of the Usinskoye and Yaregskoye oil fields in Russia and the Liaohe and Fluarti oil fields in China. The effects of time and temperature of oil autoclaving with compositions on the temperature dependence of oil viscosity during the consecutive heating and cooling were investigated by vibrational and rotational viscometry[44, 45] in the temperature range of 150–250 °C. For oil : composition ratios varying from 4 : 1 to 1 : 1, heating at 150–250 °C for 4–24 h results in a 3–6-fold decrease in oil viscosity in the temperature range of 20–50 °C (Fig. 5). Moreover, the higher the autoclaving temperature the lower the oil viscosity and the broader the composition concentration range in which the viscosity drop takes place. For autoclaving temperature of >200 °C, the viscosity almost does not decrease. The most pronounced decrease in the viscosity of the oils from the Usinskoye and Yaregskoye fields occurs at the oil to composition ratio of 2 : 1 and 4 : 1, respectively (Fig. 6). As the fraction of the composition heated with oil increases further, the oil viscosity increases due to the formation of high-viscosity emulsions, which was confirmed by ^{1}H NMR.[95] These regularities hold most clearly for small shearing stresses corresponding to the filtration conditions of the formation fluids in the reservoir rock and are retained under thermobaric conditions similar to those in the formation, which was confirmed by studies of these systems with a high-pressure viscometer.[95]

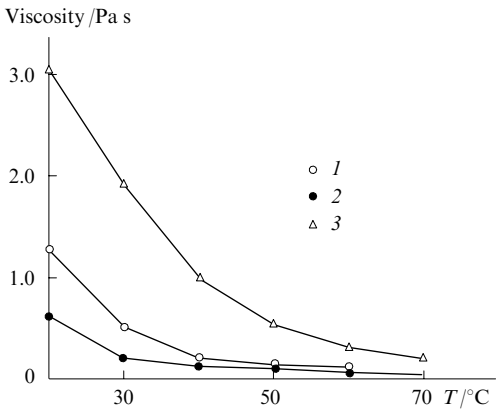


Figure 5. Temperature dependences of the oil viscosity of the Usinskoye field after maintenance at 200 °C for 6 h with the IHN-KA (*1*) and NINKA (*2*) compositions and water (*3*).[98]

Laboratory studies on a high-pressure filtration setup have shown that alternation of steam and composition slugs allows one to enhance oil displacement efficiency compared to thermal steam treatment. The major contribution to the gain in oil displacement efficiency comes from the injection of the first composition slug. A computer model for such process was designed.[99]

3. Pilot-plant testing of the technology using the NINKA compositions

The pilot tests of the technology using surfactant compositions generating *in situ* CO_2 and alkaline buffer system (the NINKA compositions) were carried out in the Permo-Carboniferous high-viscosity oil formation region of the Usinskoye field occurring at a late stage of development. The process was designed to increase the efficiency of thermal steam treatment.[100, 101] In 2002, injection of 264 m^3 of the NINKA composition into three steam injection wells was carried out. The use of this process in long-term steam injection decreases the water cut of the product by 10%–20% and increases the oil production rate by 40% on average with increasing the liquid production rate by 5%–10% on average. The total additional oil production from October 2002 to February 2004 in three pilot sites was 44.3 th t (Table 2) or 14.7 th t of additional oil production per treated well. The process was recommended for use in high-viscosity oil deposits developed using thermal steam treatment.

A promising way is the integrated use of gel-forming and oil-displacing compositions in the high-viscosity oil pool development by means of thermal steam treatment. As a result, it is possible to increase both the sweep efficiency and the oil displacement efficiency with simultaneous intensification of the development.

In 2003, pilot tests of the process involving alternating physicochemical treatment and cyclic steam treatment of the high-viscosity oil pool of the Liaohe field (China) using the NINKA composition were successfully carried out.[100] Thirty and forty tons of the composition and 2.5 th t of steam were injected into each of two wells as several slugs. This provided a

Table 2. Additional oil production from October 2002 to February 2004 for injection of the NINKA composition in the pilot sites of the Usinskoye field.[100]

Number of the injection well	Target	Additional oil production /th t	Gain in the month average oil production rate for producing wells (%)
4029	lower	11.2	31
4040	lower	14.0	41
4596	upper	19.1	49
Total		44.3	on average, by 40%

1.8 – 2.3-fold increase in oil production with respect to steam injection alone, the oil production time increased by 3 – 5 months; oil viscosity decreased three-fold and the oil pour point decreased from (6 – 10) to – (4 – 16) °C. For example, oil production from well 3-2 was 874 t between October 2003 and March 2005, while in the previous cycle with steam injection alone, this was 375 t (Fig. 7). In 2005, the works on using the NINKA composition were continued; injection into five cyclic steam wells was carried out, and monitoring of their operation was completed in 2006. Note that in 2005, repeated injection of the NINKA composition into well 3-2 was carried out (see Fig. 7). Oil production in this cycle was nearly the same as in previous cycle. The alternating injection of steam and the composition is more efficient than steam injection alone.

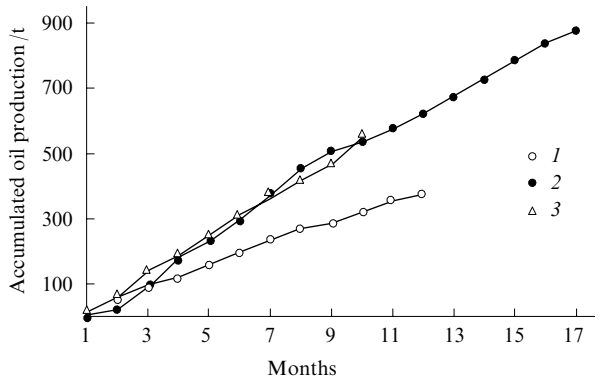


Figure 7. Dynamics of the accumulated oil production from well 3-2 of the Huanxiling region of the Liaohe field (China) in the steam injection cycle in 2001 (*1*) and the subsequent steam injection cycles with the NINKA composition in 2003 and 2005 (*2*, *3*).[101]

The pilot tests of using the NINKA composition with thermal steam and cyclic steam treatment of high-viscosity oil pools of Russian and Chinese fields demonstrated the engineering efficiency and environmental safety of the composition.

In China, industrial manufacture of the solid commercial form of the NINKA-1 oil-displacing composition was organised.

V. Thermotropic gel-forming systems for increasing sweep efficiency in water flooding and thermal steam treatment

The increase in the formation sweep efficiency in water flooding is especially topical for oil pools consisting of formations not connected hydrodynamically. In this case, the mechanism of alignment of the displacement front due to capillary and hydrodynamic cross-flows is not effective. The producing wells are water-flooded even at an early stage of development; it is desirable that the EOR methods that increase the sweep efficiency be used prior to the methods that increase the oil displacement efficiency.

A promising way of solving the problem is gel generation *in situ*. A number of methods for gel generation differing in the type of gel-formation reaction are known. The most widely used reactions are hydrolytic polycondensation ending in the formation of inorganic gels (for example, metal hydroxide and silicic acid gels),[4, 8] the formation of three-dimensional polymeric structures through cross-linking of the macromolecules of natural and synthetic polymers in solutions (polyacrylamide cross-linked by chromium salts, *etc.*),[8, 9, 12, 13] and solution – gel phase transitions in systems involving polymers with either upper or lower critical solution temperature and water (ethers, cellulose, polyvinyl alcohol, *etc.*).[102, 103]

In the IPC SB RAS, new methods were developed for enhancing oil recovery using thermotropic inorganic and polymeric gel-forming systems that generate gels *in situ* and are designed for increasing sweep efficiency of water flooding or thermal steam treatment.[95, 102 – 106]

Each oil deposit has its geological and physical characteristics. The composition of oil and the reservoir rock, the oil viscosity, water salinity and the formation temperature and pressure vary over broad ranges. Thus the formation temperature is 8 – 12 °C in Yakutia oil fields, 20 – 40 °C in Tatarstan fields, 50 – 100 °C in West Siberia and 110 – 170 °C in the South China sea offshore deposits in Vietnam. Water salinity can vary from 0 to 300 – 400 g litre^{-1}. Therefore, gel-forming systems with controllable properties should be used for enhancing oil recovery.

A study of the physicochemistry and hydrodynamics of the *in situ* gel generation has shown that gel-forming systems are low-viscosity aqueous solutions under surface conditions, while under reservoir conditions, they are converted into gels. Gelation is induced by the thermal energy of the formation or an injected heat carrier, or by the interaction of the injected system with the formation fluids and reservoir rock. The gel formation kinetics and the rheological and filtration characteristics of various types of gels for heterogeneous formations with permeability ranging from 0.01 to 10 μm^2 were studied. Gel-forming systems with different gel-generation times (ranging from several minutes to several days) in the temperature range of 30 – 320 °C were proposed. Using these systems, five gel processes for enhancing oil recovery of highly heterogeneous formations were developed at the IPC SB RAS; these processes are used at oil fields of West Siberia and the Komi Repiblic.[95, 102 – 107] The environmental safety of reagents accounts for the extensive use of gel processes at oil fields in Russia and abroad.

1. Thermally reversible polymeric gels

A new method for enhancing oil recovery from highly heterogeneous formations based on control of filtration flows and increase in the sweep efficiency by thermally reversible polymeric gels during water flooding has been developed. The gels are formed from polymer solutions with a lower critical solution temperature (LCST).[103, 108, 109] The gelation is induced by the thermal energy of the formation or injected heat carrier. Solutions of LCST polymers can form gel *in situ*: at low temperatures, the solutions have low viscosity, while at high temperatures they are converted into gels. The process is reversible: on cooling, the gel is liquefied and becomes again a low-viscosity solution and on repeated heating, the gel is restored. The gelation temperature in the range from 30 to 120 °C and the gelation time can be controlled by inorganic and organic additives, thus adjusting the systems to particular formation conditions, *viz.*, temperature and water salinity. The

gels can be used as effective means for controlling the water influx, preventing gas breakthrough, elimination of gas cones, *etc*.

At temperatures below LCST, an aqueous solution of the polymer represents a homogeneous system, which splits into two phases above LCST:[103–109] one phase is a highly dilute and the other phase is a concentrated polymer solution. Due to high viscosity of the latter, decomposition is hindered and non-equilibrium. This gives rise to a microheterogeneous kinetically stable structure, *viz*., a thermally reversible polymeric gel. In the concentrated phase, a three-dimensional framework is formed, the dilute polymer phase being situated in its cells.

The ability of LCST polymer–water systems to form gels with an increase in temperature allows one to use them in EOR processes aimed at increasing the formation sweep efficiency in water flooding by selective isolation of the swept highly permeable areas of the formation. Cellulose ethers (CE) are the LCST polymers of choice.

The gelation kinetics and rheological characteristics in the CE–aqueous phase system have been studied [102, 106] in order to establish the possibility of using CE gels under various geological deposit conditions. A typical example of LCST CE is methylcellulose (MC). The properties and structure of MC solutions and gels have been considered in the literature.[110–114] The temperature dependence of the viscosity of MC solutions passes through a minimum: on heating, the viscosity first gradually decreases from 40–70 to 5–20 MPa s, *i.e*., 2–14-fold and, after the gelation point has been reached, sharply increases to 100–2000 MPa s (20–100-fold), which is due to a phase transition (Fig. 8). The process is reversible: on cooling, the gel is converted again into a liquid. The temperature where the viscosity is minimum corresponds to the LCST. In cycling (alternation of heating and cooling processes), the rheological parameters of the gel are reproduced.

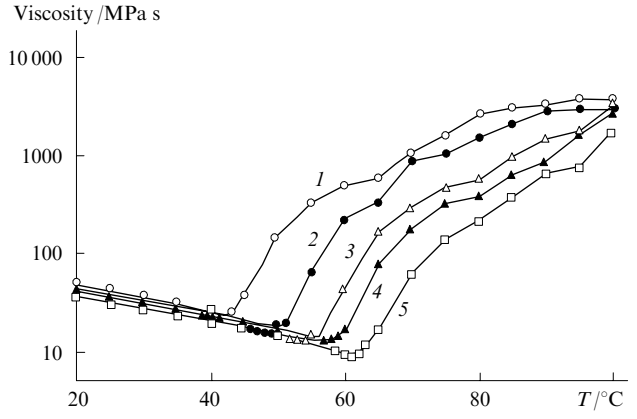


Figure 8. Viscosities of the aqueous solutions of methylcellulose (1 mass %) *vs*. temperature at different formation water salinity.[95]
Salinity /g litre^{-1}: (*1*) 60, (*2*) 30, (*3*) 15, (*4*) 7.5, (*5*) 0.

The effect of electrolytes and non-electrolytes that change the hydrophobic interactions in the system on phase equilibria and gelation kinetics in MC solutions has been studied experimentally (Fig. 9 and 10). The change in the gelation point of CE solutions is affected most appreciably by anions, the effect being correlated with positions of the anions in the lyotropic series.[95] The greatest decrease in the LCST is induced by chlorides. The opposite effect, *i.e*., an increase in the LCST, is exerted by salts with the CNS^- anion, and the effect of salts with NO_3^- is intermediate: the LCST somewhat increases on a decrease in the gelation point depending on the cation nature. The effect of cations is much less pronounced. For salts with

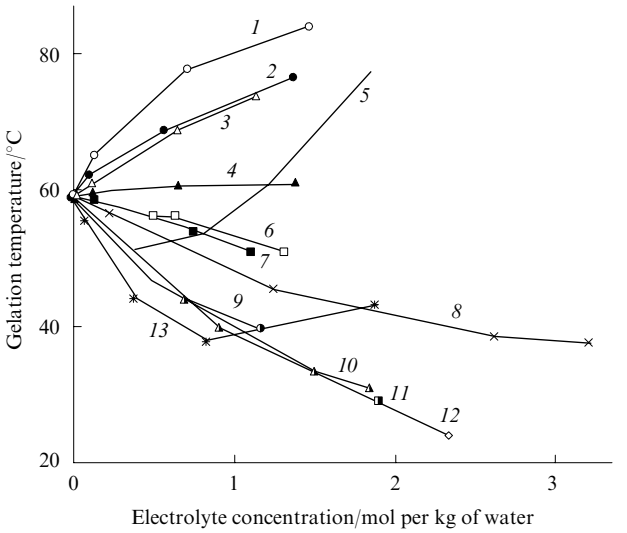


Figure 9. Effect of the electrolyte nature on the gelation temperature of solutions with a methylcellulose concentration of 1 mass %.[95]
(*1*) NH_4CNS, (*2*) NaCNS, (*3*) KCNS, (*4*) NH_4NO_3, (*5*) $ZnCl_2$, (*6*) $NaNO_3$, (*7*) KNO_3, (*8*) LiCl, (*9*) $MgCl_2$, (*10*) $CaCl_2$, (*11*) KCl, (*12*) NaCl, (*13*) $AlCl_3$.

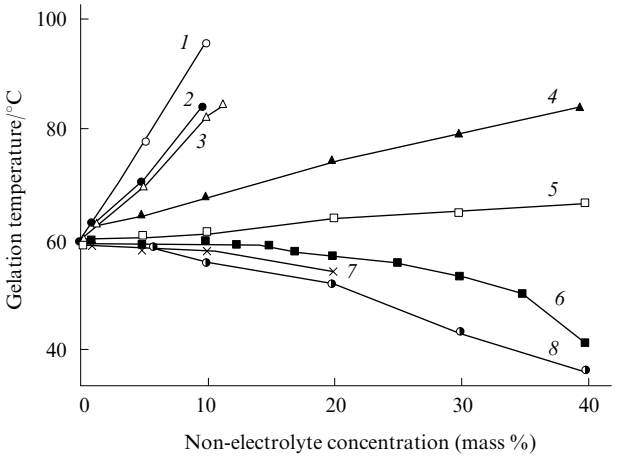


Figure 10. Effect of the electrolyte nature on the gelation temperature of methylcellulose solutions (1 mass %).[95]
(*1*) Thiourea, (*2*) isopropyl alcohol, (*3*) ethyl alcohol, (*4*) carbamide, (*5*) triethanolamine, (*6*) ethylene glycol, (*7*) polyglycol, (*8*) glycerol.

Cl^- or CNS^- anions, cations play a noticeable role but are unable to change the pattern of anion effect. The most pronounced decrease in the gelation point is induced by 1 : 1 electrolytes, while the action of 2 : 1 or 3 : 1 electrolytes is weaker and almost equivalent. An exception is provided by zinc chloride [a $ZnCl_2$ concentration above 0.4 mol per kg of water changes the character of effect on the gelation point, which increases (see Fig. 9)] and aluminium chloride (when present in a concentration of >0.8 mol per kg of water). At these concentration, solutions of these chlorides are coordinating solvents. Thiourea, ethyl alcohol and isopropyl alcohol also substantially increase the LCST. The action of electrolyte and non-electrolyte agents is additive.

In view of geological parameters of oil fields, in particular, the formation temperature, salinity of the formation and injected water, it is possible to select gel-forming compositions

optimal for particular conditions to control the filtration flows and increase the sweep efficiency during water flooding.

The rheological measurements carried out using a Haake RheoStress 600 rotational viscometer at temperatures from 20 to 150 °C and pressures of up to 50 atm have shown that joint addition of carbamide and ammonium thiocyanate into CE solutions may give solutions with gelation points of >100 °C (Fig. 11).[100] The gels retain their rheological characteristics at high temperatures, up to 150–220 °C. In the range of shear rates of 0.5–5 s^{-1}, the gel is a solid-like body exhibiting (judging by the rheological curves) viscoelastic properties. Therefore, gel-forming compositions can be used to control the steam injection profile in cyclic steam wells.

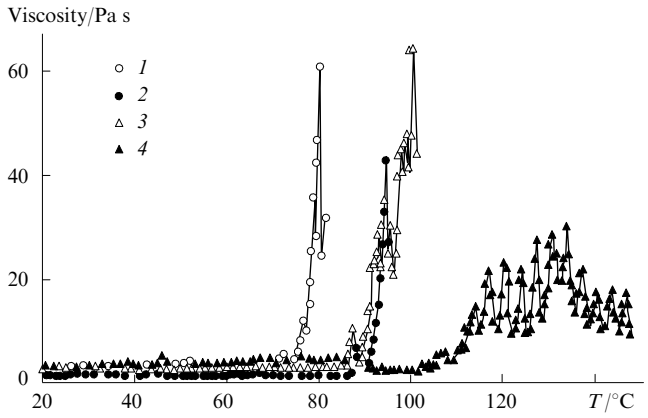


Figure 11. Change in the gelation point of an MC solution upon the addition of ammonium thiocyanate and carbamide (viscosity measurement at a shear rate of 3 s^{-1}).[100]
Solution: (*1*) 1 mass % MC; (*2*) 1 mass % MC + 5 mass % NH_4CNS; (*3*) 1 mass % MC + 20 mass % carbamide; (*4*) 1 mass % MC + 5 mass % NH_4CNS + 20 mass % carbamide.

The LCST polymer–water systems typically exhibit a temperature hysteresis for the solution–gel phase transition. The hysteresis in the MC–aqueous phase system was studied by determining the gelation point during heating and the liquefaction point during cooling.[100] The effect of additives increasing the gelation point (ethanol, ammonium thiocyanate, thiourea and carbamide) on the hysteresis was studied. The gelation points in these systems were found to almost coincide with the LCST values of polymers found by vibrational viscometry.[95] The liquefaction point was 30–50° below the gelation point (Fig. 12). The gelation and liquefaction points increase almost linearly with the reagent concentrations, these dependences being parallel for all reagents studied except for carbamide.

The reversibility of the solution–gel phase transition was established experimentally in a study of water filtration through a heterogeneous reservoir model under simulated formation conditions. The studies were carried out in a setup for filtration measurements at a constant water flow rate through the model, which consisted of two parallel columns with different permeabilities to simulate a heterogeneous reservoir. Reservoir rock cores from oil field, various crude oils and formation waters were used in the experiments. After injection of the gel-forming solution into the reservoir model and heating to 60 °C, redistribution of the filtration flows took place and was retained on temperature increase up to 220 °C. As the temperature was decreased from 220 to 20 °C and during the subsequent water filtration, the initial flow distribution was restored.

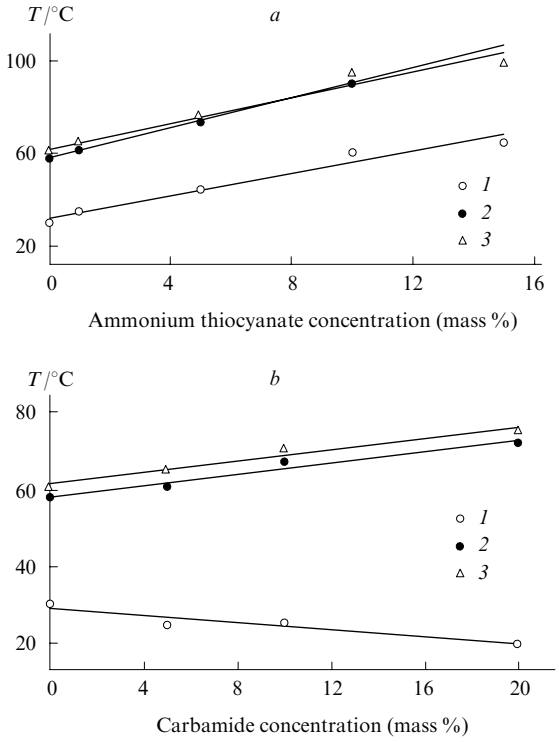


Figure 12. Effect of ammonium thiocyanate (*a*) and carbamide (*b*) on gel formation and liquefaction temperatures in solutions with MC concentration of 1 mass %.
T/°C: (*1*) liquefaction, (*2*) LCST, (*3*) gelation.

The gel formation in the reservoir rock results in a selective decrease in the phase permeability of the rock with respect to water (Fig. 13): the pressure gradient for water filtration through the gel is 2–3 times higher than that for oil filtration.[100]

The filtration characteristics and the oil-displacing properties of gel-forming compositions based on MC were studied experimentally as applied to heterogeneous reservoirs of West Siberia oil fields.[115, 116] It was found that injection of a slug of the gel-forming solution into a heterogeneous reservoir model results in redistribution of the filtration flows where the liquid mobility in the highly permeable part sharply decreases, while

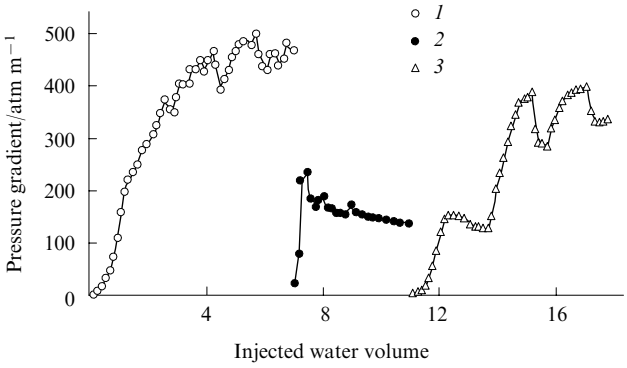


Figure 13. Selective increase in the phase permeability for water after the formation of the MC gel in the reservoir rock with a permeability of 11 μm².
(*1*) Water injection, (*2*) oil injection, (*3*) repeated water injection. The volume of the injected water is determined by the number of pore volumes.

that in the low- permeability part most often remains the same. The redistribution of filtration flows is accompanied by after-sweeping of the residual oil, which is especially pronounced in the case of low-permeability model. Gel-forming compositions have shown high efficiency in increasing the sweep efficiency on heterogeneous reservoir models with interlayer permeability differing by factors of 3 – 20. Therefore, these compositions were recommended for the control of filtration flows of formation fluids and water shutoff in highly heterogeneous reservoirs. Ammonium thiocyanate and carbamide present in gel-forming compositions are simultaneously trace indicators.

At a temperature of 200 °C under simulated formation conditions, the filtration characteristics and oil displacement efficiency upon physicochemical action of a gel-forming composition on the high-viscosity oil pool were studied. The use of gel-forming composition ensured equalisation of filtration flows due to a decrease in the liquid phase mobility in high-permeability interlayers, which is accompanied by oil after-sweeping from both low- and high-permeability zones of the reservoir model. For example, after injection of the composition into the heterogeneous reservoir model with permeabilities of the columns differing by a factor of 5.4 (0.397 and 2.123 μm^2), redistribution of the filtration flows took place and the ratio of liquid mobilities in the reservoir model changed from 1 : 4.3 to 50 : 1. When water was pumped in the opposite direction (simulation of the operation conditions of a cyclic steam well), the filtration pattern was retained. The oil displacement efficiency increased by 12% – 13% compared to that observed with steam injection.[115]

The investigations resulted in the selection of the optimal gel-forming blends for enhancing oil recovery by water influx control during water flooding or thermal treatment of the formation. In particular, gel-forming METKA compositions were developed. A low-viscosity aqueous solution capable of forming gels under formation conditions is injected into the formation at 30 – 120 °C. A gel screen is formed in the high-permeability formation part into which the main bulk of the composition gets; this results in redistribution of filtration flows. Upon pumping of the METKA composition into injection wells, their input profiles are equalised, water production decreases and the oil production rates of the producing wells that are hydrodynamically connected to injection wells increase. The METKA compositions are easy to handle; the best water solubility of the polymer is attained in the temperature range of 0 – 10 °C. The processes are cost effective and environmentally safe and are implemented by means of standard oil field equipment.

Successive large-scale pilot tests of EOR processes based on the use of thermally reversible gels in the West Siberia oil fields were carried out from 1996 to 1997. In 1996, the METKA composition was injected into 11 wells and in 1997, into 47 injection wells (50 – 100 m^3 per well). In 2 – 3 months after injection, the producing wells hydrodynamically connected to injection wells showed lower water production and higher oil production rates. This process has been used on an industrial scale at the West Siberia oil fields since 1998 (Lukoil company). An industrial mobile unit for the preparation and injection of the composition was designed (designer the OJSC OTO). Between 1998 and 2003, the METKA composition was injected into 382 wells. The additional oil production amounted to 480 th t; the payback period was 5 – 9 months; the process efficiency was on average 1300 t of additionally produced oil per treated well. All reagents are large-scale commercial chemicals.

On combined treatment of both hydrodynamically connected injection wells and producing wells, the process efficiency increases. In 2001, pilot testing of the water shutoff process by simultaneous treatment of the bottomhole zones of the injection and producing wells with gel-forming compositions was carried out in two pilot sites of the AB_1 formation of the Urievskoye oil field.[107, 117] The injected volume of the composition per well was from 50 to 200 m^3; altogether 620 m^3 were injected. This resulted in redistribution of the filtration flows and decrease in water influx, which was manifested in lower water production and higher oil production rates of the producing wells (Fig. 14). The additional oil production was 6542 t over 7 months.

Thermally reversible polymer gels are used in a number of technologies.

A technology for elimination of the behind-the-casing water flow was tested in gas wells of the Myldzhinskoye gas condensate field.[118] For example, well No. 133 produced gas

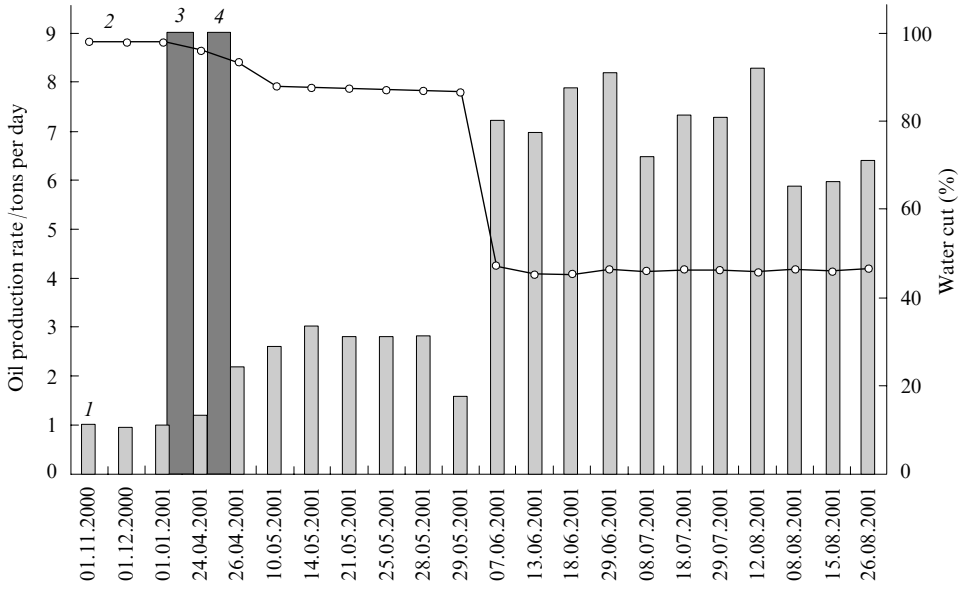


Figure 14. Increase in the oil production (*1*) and decrease in the water cut (*2*) for the producing well 1438 after pumping of the gel-forming composition into injection well 1810 (*3*) and producing well 1438 (*4*) in the Urievskoye field, formation AV_1.[117]

containing formation water; at a gas production rate of 300 th m^3 per day, water content was 30 t, which is much higher than the allowable value. After injection of the METKA gel-forming composition together with the installation of a cement bridging, the gas production rate was 430 th m^3 per day with only traces of water; the well has operated at such production rate for three years.

In 2002–2003, the Institute of Petroleum Chemistry of the Siberian Branch of the RAS, together with the Institute of Mining of the Siberian Branch of the RAS carried out successful pilot testing of integrated vibroseismic and physicochemical treatment of the BV_8 formation of the Pokachevskoye oil field using the METKA composition.[107]

In 2005–2006, processes of increasing the efficiency of cyclic steam treatment of a high-viscosity oil pool using the METKA composition for water shutoff were successfully tested at two wells of the Liaohe deposit (China).[100] After injection of the gel-forming composition, the oil water cut in producing wells decreased and oil production rate increased.

2. Methods for enhancing oil recovery using inorganic gel-forming systems

The ability of the aluminium salt–carbamide–water–surfactant system to generate inorganic gel and CO_2 *in situ* at temperatures 40–320 °C underlies the technology where inorganic gel-forming compositions are used to increase the sweep efficiency of water or steam injection.[105, 107, 119–121]

The free or bound disperse systems (sols and gels) may be generated in the oil formation by the condensation mechanism, in particular, based on the 'arising reactants' (homogeneous precipitation) principle known in analytical chemistry.[5] Within the framework of this principle, a new physicochemical method for enhancing oil recovery was proposed. A homogeneous aqueous solution containing a gel-forming system is injected into the oil formation. Due to the thermal energy of the formation or an injected heat carrier, one component of the system is gradually hydrolysed, the hydrolysis products inducing a shift of the protolytic equilibrium of another component. This triggers hydrolytic polycondensation of monomer units, and, after a definite period of time, a gel is formed almost instantaneously throughout the whole solution volume. The 'arising reactants' principle was implemented in the development of the reported physicochemical EOR method.[122, 123]

Liquid aluminium salt–carbamide–water–surfactant gel-forming systems are low-viscosity solutions with pH 2.5–3.5. They are able to dissolve carbonate minerals in the reservoir rock and decrease (suppress) clay swelling. The solutions can be prepared using water with any salinity. They are injected into the oil-bearing formation through injection wells using standard equipment.

Carbamide is hydrolysed in the formation to give ammonia and carbon dioxide, which leads to gradual increase in the solution pH. When pH becomes 3.8–4.2, hydrolysis of aluminium ions takes place, and, as a consequence, after some period of time, aluminium hydroxide gel is formed almost instantaneously throughout the whole solution bulk (Figs 15, 16). The time required for gelation depends on the formation temperature and the component ratio in the gel-forming system. After gel generation, the reservoir rock permeability for water decreases 4–35-fold. The greater the initial water saturation and permeability of the reservoir rock the higher the degree of permeability decrease. The static shear stress of the gel is within 3–40 Pa. In the presence of surfactants, wetting of the oil reservoir rock by the gel-forming solution is enhanced and the penetrating and oil-displacing ability of the solution increases. In addition, the surfactant exerts a plasticising action on the aluminium hydroxide gel and can form a foam with carbon dioxide and ammonia evolved upon carbamide hydrolysis.[5]

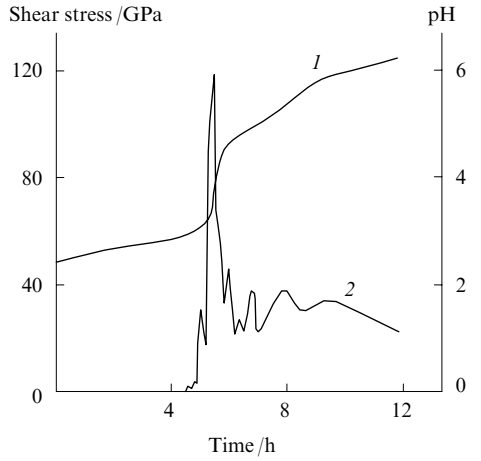


Figure 15. Change in the pH (*1*) and shear stress (*2*) in the aluminium salt–carbamide–water system upon gel formation during maintenance at 97 °C.[107]

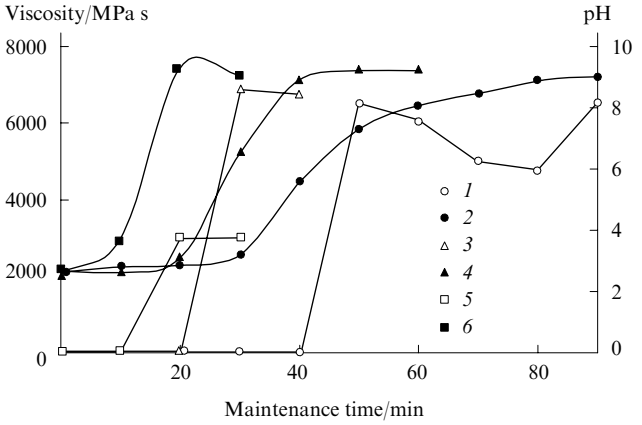


Figure 16. Viscosity (*1–5*) and pH (*6*) change in the aluminium salt–carbamide–water system upon gel formation during maintenance at 150 (*1*, *2*), 200 (*3*, *4*) and 250 °C (*5*, *6*).[106]

The rheological properties of the gel correspond to the properties of a thixotropic pseudoplastic body with the coagulation structure. A distinctive feature of the gel is the permeability for the aqueous phase at shear stresses lower than the static shear stress of the gel itself. Gelation results in redistribution of filtration flows, equalisation of input profiles of injection wells, and a decrease in water cut of the oil from producing wells. Gel-forming systems are designed for the development of oil pools with high formation temperature and heterogeneity, which is typical of West Siberia oil fields and high-viscosity oil pools developed by thermal methods.

In the temperature range of 70–100 °C, the gelation kinetics is determined by the hydrolysis of carbamide, which is much slower than the formation of aluminium hydroxide gel by the coagulation mechanism representing is a cooperative process. The pre-exponential factor (1.1×10^{12} s^{-1}) in the Arrhenius equation and the activation energy (115 kJ mol^{-1}) for carbamide hydrolysis in the gel-forming solution were estimated. The results are consistent with published values.[96] However, the activation energy found is lower than the activation energy for carbamide hydrolysis in the absence of aluminium salt (134 kJ mol^{-1}), which is indicative of catalysis by the acid resulting from hydrolysis of the aluminium salt. The effect of temperature on the gelation time (t_g) obeys the Van't

Hoff rule: upon temperature increase by each 10°, the gelation time increases 3.5-fold.

In the temperature range of 100–250 °C the Arrhenius dependence for the solution–gel transition is described analytically by the following regression:

$$\log\frac{1}{t_g} = 0.8322 - 3999.9\frac{1}{T}.$$

The activation energy and the pre-exponential factor in the Arrhenius equation for the solution–gel transition are equal to 33.3 kJ mol^{-1} and 2.3 s^{-1}, respectively, which is much lower than for the temperature below 100 °C. In addition, in the 100–250 °C range, the effect of temperature on the gelation time does not obey the Van't Hoff rule: an increase in temperature by each 10° results in a 1.2-fold increase in the gelation time. These results provide the conclusion that in the temperature range of 100–250 °C the gelation kinetics in the aluminium salt–carbamide–water system is determined by the coagulation type formation of the aluminium hydroxide gel. The S-shape of the curves shown in Fig. 16 and the low activation energy attest to a cooperative mechanism of the coagulation process similar to the mechanism of phase transition or branching chain reaction.

At 70–100 °C, the gelation time depends on the concentrations and the concentration ratio of aluminium chloride and carbamide in solution; at a temperature above 150 °C this dependence is smoothened down. The lower the carbamide concentration the longer the gel formation. By varying the ratio of the aluminium salt and carbamide, one can control the gelation time, thus adjusting it to a particular formation temperature.[119, 120]

In the range of 100–250 °C, the gel viscosity depends most appreciably on the aluminium chloride concentration. The effect of the component ratio and temperature is insignificant. The viscosity of solutions with aluminium chloride concentration of 4.0 mass % and 8.0 mass % increases during gel formation by the coagulation mechanism from 1.2–1.6 to 300–3500 MPa s and from 1.8–2.5 to 1800–7500 MPa s, respectively.

On the basis of the results of studies on the gelation kinetics and the rheological characteristics of the aluminium salt–carbamide–water–surfactant systems, gel-forming GALKA compositions and GALKA–surfactant systems were designed. During the period from 1989 to 1995, pilot testing of the EOR technology using inorganic gel-forming GALKA compositions was successfully carried out at West Siberia oil fields; since 1996, this method has been industrially used. This results in redistribution of filtration flows, an increase in the sweep efficiency of water flooding, and, hence, an increase in the ultimate oil recovery by 5%–8%. The additional oil production was 400 to 3000 t per treated well. The pilot testing of gel-processes was successfully carried out at the White Tiger oil field (Vietnam).

In 1996, the IPC SB RAS organised, in cooperation with the OJSC Nefteotdacha, the manufacture of the GALKA composition as a liquid commercial product using aluminium-containing industrial wastes. In 2000, the IPC SB RAS organised, in cooperation with the OJSC AURAT, the manufacture of solid commercial products including the GALKA composition, *viz*., GALKA–thermogel-S for formation temperatures of 70–320 °C, GALKA–thermogel-U for temperatures of 40–70 °C, GALKA–thermogel-NT for temperatures of 20–40 °C. The advantages of the GALKA–thermogel systems include: controlled gelation temperature, homogeneity and low viscosity of aqueous solutions, low pour points of solutions, and availability of a solid commercial product. This allows them to be used over a broad temperature range (from 20 to 320 °C); they are applicable to low-permeability reservoirs; the composition can be injected into a well by batching directly into the water pipe without preliminary dissolution (this process can be used in the winter season).

The inorganic gels GALKA withstand the temperatures of 300–320 °C; hence, they can be used to increase the sweep efficiency in the thermal steam treatment for the development of high-viscosity oil pools.[107] In 2002, pilot testing of the process using the composition as the commercial solid product was carried out on the thermal steam treatment site PTV-3 of the Permo-Carboniferous pool of the Usinskoye field; 600 m^3 of the GALKA–thermogel-S composition were injected into four steam injection wells. The composition showed good field

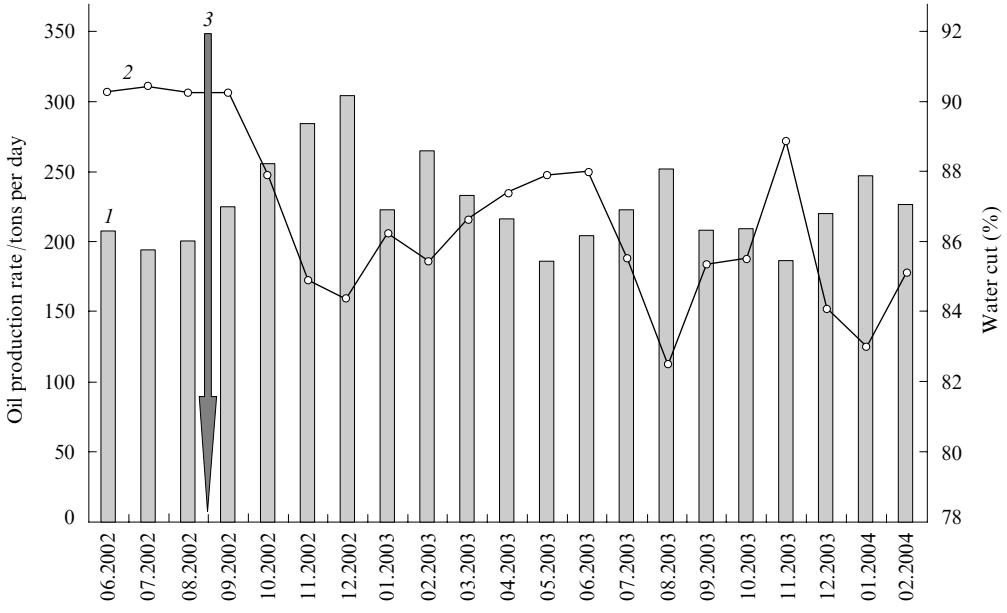


Figure 17. Monthly oil production (*1*) and water cut (*2*) dynamics for 29 wells of the pilot site after injection of the GALKA–thermogel-S composition (*3*) in the Usinskoye field (observation period from June 2002 to February 2004).[107]

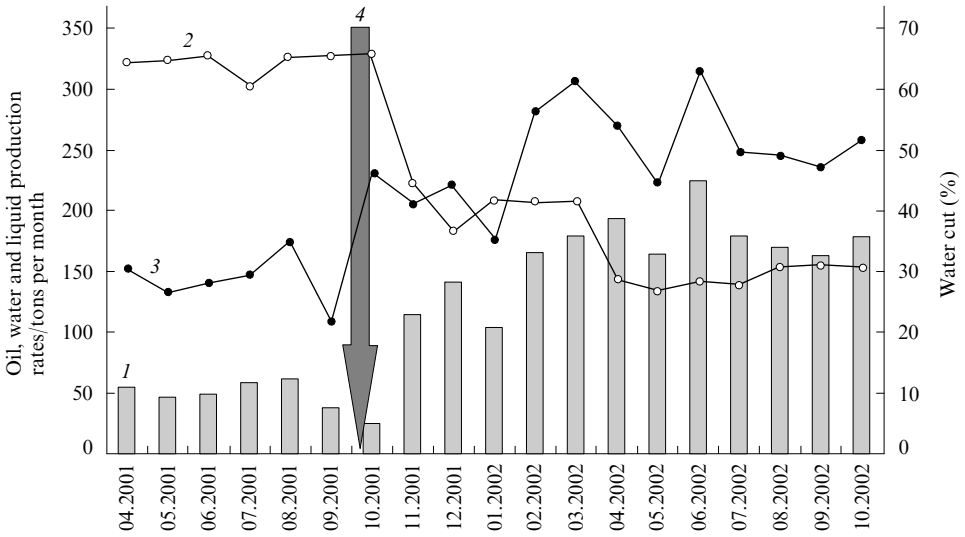


Figure 18. Results of the use of the integrated EOR technology including injection of the gel-forming GALKA composition and an oil-displacing composition IHN-100 on the pilot site of the YuV_1 formation of the Las-Yeganskoye field (injection well 9066, producing well 152p).[107]
(*1*) Oil production rate, (*2*) water cut (%), (3) liquid production rate, (4) injection of compositions.

handling properties and environmental safety. The 29 producing wells of the pilot site produced additionally 33 th t of oil from October 2002 to February 2004. The engineering efficiency amounts to 275 t of additional oil production per t of the solid commercial GALKA – thermogel-S composition. The water production of the producing wells decreased by 3% – 45% and the oil production rate increased by 23% on average (Fig. 17); the decrease of the monthly liquid production rate was 19.8% on average.

3. Integrated EOR process using gel-forming and oil-displacing compositions

For enhancing the oil recovery of fields with highly heterogeneous reservoirs at a later stage of development, the isolation of high-permeability watered formations by their blocking should be followed by intensification of liquid filtration in low-permeability formations. This requires an integrated technology: first, a gel-forming composition is used to increase the sweep efficiency of water flooding and then an oil-displacing composition is employed to intensify the development of a low-permeability formation. This combined action on the oil pool allows one to efficiently redistribute the filtration flows of formation fluids and to develop the formations not swept previously by water flooding; this method is efficient for enhancing the oil recovery of low-permeability highly heterogeneous oil pools at both early and late stages of field development.

For the development of oil reserves difficult to recover of the Jurassic deposits of West Siberia, an integrated process was proposed wherein GALKA – thermogel was used as the gel-forming composition and IHN-100 was used as the oil-displacing composition. Unlike the known compositions, these gel-forming and oil-displacing compositions possess complementary physicochemical properties, resulting in synergistic action.

In 2001, pilot testing of the integrated process was carried out in the Las-Yeganskoye field (YuV_1 formation). The GALKA – thermogel-U composition (6, 10 and 18 t) and IHN-100 composition (30, 50 and 48 t) were pumped into injection wells. Analysis of the field data showed that the combined action of these compositions resulted in redistribution of the filtration flows in the formation, involvement of low-permeability interlayers and intensification of their development, which is manifested in lower water cut of the products and higher oil and liquid production rates from the producing wells hydrodynamically connected to the injection wells (Fig. 18). The additional oil production over the site from January 2001 to October 2002 was 4.4 th t.[107] The process was recommended for industrial use in West Siberia fields.

Currently, development of other integrated methods is in progress, for example, the pulse explosive stimulation of the formation combined with using oil-displacing and gel-forming compositions, physicochemical and microbiological EOR methods.

The development of the physicochemical methods for enhancing oil recovery and increase in the extent of their application may provide, even in the near future, a significant gain in the recoverable reserves and current oil production both on operating and newly explored oil fields in Russia.

References

1. A Varlamov *Nef. Rossii* **1** 106 (2007)
2. A Bokserman, I Mishchenko *Tekhnol. TEK* **8** 30 (2006)
3. Kh Kh Gumerskii, S A Zhdanov, V K Gomzikov *Neftyanoe Khozyaistvo* **5** 38 (2000)
4. M L Surguchev, A T Gorbunov, D P Zabrodin, E A Ziskin, G S Malyutina *Metody Izvlecheniya Ostatochnoi Nefti* (The Methods of Residual Oil Recovery) (Moscow: Nedra, 1991)
5. L K Altunina, V A Kuvshinov *Uvelichenie Nefteotdachi Plastov Kompozitsiyami PAV* (Enhancing Oil Recovery by Surfactant Blends) (Novosibirsk: Nauka, 1995)
6. V D Lysenko *Geol. Geofiz. Razrab. Nef. Gaz. Mestorozh.* **6** 37 (1996)
7. L W Lake *Enhanced Oil Recovery* (New York: Prentice-Hall, 1996)
8. V N Manyrin, I A Shvetsov *Fiziko-khimicheskie Metody Uvelicheniya Nefteotdachi pri Zavodnenii* (Physicochemical Methods for Enhanced Oil Recovery using Water Flooding) (Samara: Samarskii Dom Pechati, 2002)
9. A A Gazizov *Uvelichenie Nefteotdachi Neodnorodnykh Plastov na Pozdnei Stadii Razrabotki* (Enhanced Oil Recovery from Heterogeneous Formations in Late Stages of Development) (Moscow: Nedra-Biznestsentr, 2002)
10. A Ya Khavkin *Geologo-fizicheskie Faktory Effektivnoi Razrabotki Mestorozhdenii Uglevodorodov* (Geological and Physical Factors of Effective Hydrocarbon Field Development) (Moscow: Sputnik + , 2005)

11. A I Shvetsov, G N Bakaev, V Ya Kabo, V V Perunov, Yu V Solyakov *Neftyanoe Khozyaistvo* (4) 37 (1994)
12. A Sh Gazizov, L A Galaktionova, V S Adagymov, A A Gazizov *Neftyanoe Khozyaistvo* (2) 12 (1998)
13. V V Devyatov, R Kh Almaev, P I Pastukh, V M Sankin *Primenenie Vodoizoliruyushchikh Khimreagentov na Obvodnennykh Mestorozhdeniyakh Shaimskogo Raiona* (The Use of Water-Shutoff Agents in the Flooded Fields of the Shaimsky Region) (Moscow: VNIIOENG, 1995)
14. A G Dyabin, A Ya Sorkin, V E Stupochenko, V A Kan, I A Sidorov, A B Pogosyan, Yu M Smirnov *Neftyanoe Khozyaistvo* (12) 16 (2000)
15. S V Ivanov, L S Brilliant *Neftyanoe Khozyaistvo* (9) 47 (2000)
16. E V Lozin, O G Gafurov, Ya G Mukhtarov, R G Shirgazin *Neftyanoe khozyaistvo* (2) 39 (1996)
17. N A Lebedev *Neftyanoe Khozyaistvo* (7) 16 (1997)
18. L K Altunina, V A Kuvshinov *Ros. Khim. Zh.* (5) 16 (1994) [a]
19. O E Tsinkova, N A Myasnikova, B T Baishev *Gidrodinamicheskie Metody Uvelicheniya Nefteotdachi* (Hydrodynamic Methods of Enhanced Oil Recovery) (Moscow: Nedra, 1993)
20. R R Ibatullin, N G Ibragimov, Sh F Takhautdinov, R S Khisamov *Uvelichenie Nefteotdachi na Pozdnei Stadii Razrabotki Mestorozhdenii* (Enhanced Oil Recovery in the Late Stages of Oil Field Development) (Moscow: Nedra, 2004)
21. V N Martos, T M Umariev *Geol. Geofiz. Razrab. Nef. Gaz. Mestorozh.* **2** 37 (1994)
22. R D Kanevskaya *Matematicheskoe Modelirovanie Razrabotki Mestorozhdenii Nefti i Gaza s Primeneniem Gidravlicheskogo Razryva Plasta* (Mathematical Modelling of Oil and Gas Field Development using Hydrofracturing) (Moscow: Nedra-Biznest-sentr, 1999)
23. B M Suchkov *Gorizontal'nye Skvazhiny* (Horizontal Wells) (Izhevsk: RKhD, 2006)
24. M M Khasanov *Neftyanoe Khozyaistvo* (3) 43 (2007)
25. Kh Kh Gumerskii, A T Gorbunov, S A Zhdanov, A M Petrakov *Neftyanoe Khozyaistvo* (12) 12 (2000)
26. S A Zhdanov, D Yu Kryanev, A M Petrakov *Neftyanoe Khozyaistvo* (5) 39 (2005)
27. R Maksutov, G Orlov, A Osipov *Tekhnologii TEK* (6) 23 (2005)
28. Zh Burzhe, P Surio, M Kombarnu *Termicheskie Metody Povysheniya Nefteotdachi Plastov* (Thermal Methods of Enhanced Oil Recovery) (Moscow: Nedra, 1988)
29. N K Baibakov, A R Garushev, D G Antoniadi, V G Ishkhanov *Termicheskie Metody Dobychi Nefti v Rossii i za Rubezhom* (Thermal Methods of Oil Production in Russia and Abroad) (Moscow: VNIIOENG, 1995)
30. D G Antoniadi *Uvelichenie Nefteotdachi Plastov Gazovymi i Parogazovymi Metodami* (Enhanced Oil Recovery by Gas and Steam-and-Gas Methods) (Moscow: Nedra, 1998)
31. L K Altunina, L P Gossen, L DTikhonova, E G Yarmukhametova *Zh. Prikl. Khim.* **75** 166 (2002) [b]
32. L K Altunina, V A Kuvshinov, A I Gyngazov, V P Dorokhov *Ekonomicheskaya Nauka na Sluzhbe Proizvodstva (Tezisy Dokladov Nauchno-prakticheskoi Konferentsii MINIEKO TEK), Perm', 1998* [Economical Science for Production (Abstracts of Reports of the Scientific and Practic Conference MINIEKO TEK), Perm, 1998] p. 51
33. S S Sergienko, B A Taimova, E I Talalaev *Vysokomolekulyarnye Neuglevodorodnye Soedineniya Nefti* (High-molecular Non-hydrocarbon Oil Compounds) (Moscow: Nauka, 1979)
34. V F Kam'yanov, V S Aksenov, V I Titov *Geteroatomnye Komponenty Neftei* (Heteroatomic Oil Components) (Novosibirsk: Nauka, 1983)
35. O K Kimbler, R L Reed, I H Silberberg *Soc. Petrol. Eng. J.* **6** 153 (1966)
36. D D Eley, V L Hey, M A Lee *Colloids Surf.* **24** 173 (1987)
37. I L Markhasin *Fiziko-khimicheskaya Mekhanika Neftyanogo Plasta* (Physicochemical Mechanics of Oil Formation) (Moscow: Nedra, 1977)
38. N M Baikov, G N Pozdnyshev, R I Mansurov *Sbor i Promyslovaya Podgotovka Nefti, Gaza i Vody* (Collection and Field Treatment of Oil, Gas and Water) (Moscow: Nedra, 1981)
39. B P Singh, B P Pandey *Indian J. Technol.* **29** 443 (1991)
40. S Acevedo, G Escobar, L Gutierrez, H Rivas *Fuel* **71** 619 (1992)
41. E J Shen, M M De Tar, D Storm *Fuel* **71** 1277 (1992)
42. S Acevedo, M A Ranaudo, G Escobar, G Gutierrez *Fuel* **78** 308 (1999)
43. V N Izmailova, G P Yampol'skaya *Uspekhi Kolloidnoi Khimii i Fiziko-khimicheskoi Mekhaniki* (Progress in Colloid Chemistry and Physicochemical Mechanics) (Moscow: Nauka, 1992) p. 103
44. A V Bogoslovskii, L K Altunina *Molekulyarnye Vzaimodeistviya i Elektronnye Protsessy v Rastvorakh* (Molecular Interactions and Electronic Processes in Solutions) (Novosibirsk: Nauka, 1987) p. 55
45. Russ. P. 1229647; *Byull. Izobret.* (17) 179 (1985)
46. N Aske, R Orr, J Sjoblom, H Kallevik, G pye *J. Dispersion Sci. Technol.* **25** 263 (2004)
47. G A Babalyan, I I Kravchenko, I L Markhasin, G V Rudakov *Fiziko-khimicheskie Osnovy Primeneniya Poverkhnostno-aktivnykh Veshchestv pri Razrabotke Neftyanykh Plastov* (Physicochemical Foundations of Application of Surfactants for Oil Formation Development) (Moscow: Nedra, 1962)
48. M L Surguchev *Vtorichnye i Tretichnye Metody Uvelicheniya Nefteotdachi Plastov* (Secondary and Tertiary Methods of Enhancing Oil Recovery) (Moscow: Nedra, 1985)
49. R M Giordano, J C Slattery *AIChE J.* **33** 1592 (1987)
50. M Li, M Xu, Y Ma, Z Wu, A A Christy *Fuel* **81** 1847 (2002)
51. L K Altunina, V A Kuvshinov, I F Efremov, V V Novgorodov *Proceedings of the Third Symposium on Mining Chemistry, Siofok, Hungary, 1990* p. 211
52. V V Nauchitel', I V Golovanov, M V Vol'kenshtein *Dokl. Akad. Nauk SSSR* **392** 1144 (1988) [c]
53. A L Nicholls, L R Pratt *J. Chem. Phys.* **81** 579 (1984)
54. J Monin, A Vignat *Rev. Inst. Fr. Petrol.* **39** 821 (1984)
55. J Murgich *Petrol. Sci. Technol.* **20** 983 (2002)
56. N Siddiqui *Petrol. Sci. Technol.* **21** 1601 (2003)
57. L K Altunina, V A Kuvshinov *Problemy i Dostizheniya v Issledovanii Nefti* (The Problems and Achievements in Oil Investigation) (Tomsk: Tomsk Scientific Centre, Siberian Branch of Academy of Sciences of the USSR, 1990) p. 221
58. J Reisberg, T M Doscher *Producers Mon.* **21** 43 (1956)
59. V A Kuvshinov, L K Altunina, L F Genkina *Zh. Prikl. Khim.* **63** 926 (1990) [b]
60. L K Altunina, V A Kuvshinov *Eurasian Chem.-Technol. J., Kazakhstan* **3** (3) 179 (2001)
61. A Watanabe *Surface Coll. Sci.* **13** 1 (1984)
62. M I Gugeshashvili, A V Indenbom, L I Boguslavskii *Elektrokhimiya (Itogi Nauki i Tekhniki. Ser.)* [Electrochemistry (Advances in Science and Engineering Series)] (Moscow: Izd. VINITI, 1988) No. 28, p. 172
63. M Senda, T Kakiushi, T Osakai, T Kakutani *Elektrokhimiya (Itogi Nauki i Tekhniki. Ser.)* [Electrochemistry (Advances in Science and Engineering Series)] (Moscow: Izd. VINITI, 1988) No. 28, p. 248
64. I V Pisareva, A V Bogoslovskii, L K Altunina *Fiziko-khimicheskie Svoistva Rastvorov i Dispersii* (Physicochemical Properties of Solutions and Dispersions) (Novosibirsk: Nauka, 1992) p. 30
65. V A Kuvshinov, L K Altunina, L F Genkina *Kolloid. Zh.* **47** 279 (1985) [d]
66. B V Deryagin, N V Churaev *Smachivanie Plenki* (Watering Film) (Moscow: Nauka, 1984)
67. N P Tantsura, O G Us'yarov *Kolloid. Zh.* **43** 375 (1981) [d]
68. N R Morrow *J. Petrol. Technol.* **42** 1476 (1990)
69. S Y Yang, G J Hirasaki, S Basu, R Vaidya *J. Petrol. Sci. Eng.* **33** 203 (2002)
70. V A Kuvshinov, L K Altunina, N A Marchenko *Kolloid. Zh.* **50** 1184 (1987) [d]
71. V V Pushkarev, D I Trofimov *Fiziko-khimicheskie Osobennosti Ochistki Stochnykh Vod ot Poverkhnostno-aktivnykh Veshchestv* (Physicochemical Features of Waste Water Purification from Surfactants) (Moscow: Khimiya, 1975)
72. I V Sheveleva, A V Voit, A V Zryanina *Zh. Fiz. Khim.* **67** 1654 (1993) [e]

73. A M Koganovskii, N A Klimenko, T M Levchenko, I G Roda *Adsorbtsiya Organicheskikh Veshchestv iz Vody* (Adsorption of Organic Substances from Water) (Leningrad: Khimiya, 1990)
74. L K Altunina, V A Kuvshinov, I F Efremov *Sovremennye Metody Uvelicheniya Nefteotdachi Plastov* (Modern Methods for Enhancing Oil Recovery) (Moscow: Nauka, 1992) p. 121
75. T S Ramakrishnan, D T Wasan *AIChE J.* **36** 725 (1990)
76. V A Kuvshinov, L K Altunina, L F Genkina *Instrumental'nye Metody Issledovaniya Neftei* (Instrumental Methods of Investigation of Oil) (Novosibirsk: Nauka, 1987) p. 116
77. V A Kuvshinov, L K Altunina, N A Marchenko *Izuchenie Sostava i Svoistv Neftei Nizhnevartovskogo Svoda* (Study of the Composition and Properties of Nizhnevartovsk Oil Field) (Tomsk: TF SO RAN SSSR, 1984) p. 132
78. N V Churaev *Uspekhi Kolloidnoi Khimii* (Progress in Colloid Chemistry) (Kiev: Naukova Dumka, 1983) p. 24
79. G Shtyupel' *Sinteticheskie Moyushchie i Ochishchayushchie Sredstva* (Synthetic Detergents) (Moscow: Goskhimizdat, 1960)
80. M I Shakhparonov, V V Devlikamov, A B Tumasyan, A L Shtangeev, E V Lozin, T N Maksimova, T M Usacheva *Issledovaniya Stroeniya, Teplovogo Dvizheniya i Svoistv Zhidkostei* (Investigation of the Structure, Thermal Motion and Properties of Liquids) (Moscow: Moscow State University, 1986) p. 5
81. A T Gorbunov, L N Buchenkov *Shchelochnoe Zavodnenie* (Alkaline Water Flooding) (Moscow: Nedra, 1989)
82. R V Smith *Petrol. Eng. Int.* **61** 44 (1989)
83. G I Fuks, Ya Buribaev *Issledovaniya po Fizikokhimii Kontaktnykh Vzaimodeistvii* (Investigations in the Physical Chemistry of Contact Interactions) (Ufa: Bashkirskoe Knizhnoe Izd., 1971)
84. A A Bugaevskii *Matematicheskie Zadachi Khimicheskoi Termodinamiki* (Mathematical Problems in Chemical Thermodynamics) (Novosibirsk: Nauka, 1985) p. 42
85. Yu A Kokotov *Matematicheskie Zadachi Khimicheskoi Termodinamiki* (Mathematical Problems in Chemical Thermodynamics) (Novosibirsk: Nauka, 1985) p. 49
86. R Beits *Opredelenie pH. Teoriya i Praktika* (Determination of pH. Theory and Practice) (Leningrad: Khimiya, 1968)
87. S Outubuddin, C A Miller, T Fort *J. Colloid Interface Sci.* **101** 46 (1984)
88. L K Altunina, V A Kuvshinov *Proceedings of EUROPEC European Petroleum Conference Integrated Reservoir Management, Paris, 2000* p. 515
89. L K Altunina, V A Kuvshinov *Fiziko-khimicheskie Svoistva Rastvorov i Dispersii* (Physicochemical Properties of Solutions and Dispersions) (Novosibirsk: Nauka, 1992) p. 3
90. L Altunina, V Kuvshinov *Vestn. Inzhiniring. Tsentra YuKOS* **4** 49 (2002)
91. L I Svarovskaya, L K Altunina *Neftekhimiya* **39** 148 (1999) [f]
92. V S Ovsyannikova, L K Altunina, L I Svarovskaya, G S Pevneva, L D Stakhina *Trudy 12 Evropeiskogo Simpoziuma 'Povyshenie Nefteotdachi Plastov', Kazan', 2003* (Proceedings of the 12th European Symposium 'Enhancing Oil Recovery', Kazan, 2003) p. 169
93. L K Altunina, L I Svarovskaya, O P Boeva *Sovremennye Metody Uvelicheniya Nefteotdachi Plastov* (Modern Methods for Enhancing Oil Recovery) (Moscow: Nauka, 1992) p. 124
94. M Metwally *J. Can. Petrol. Technol.* **29** 26 (1990)
95. L K Altunina, V A Kuvshinov *Khim. Inter. Ustoich. Razvitiya* **9** 331 (2001) [g]
96. V I Kucheryavyi, V V Lebedev *Sintez i Primenenie Karbamida* (Synthesis and Applications of Carbamide) (Leningrad: Khimiya, 1970)
97. D M Gorlovskii, L N Al'tshuler, V I Kucheryavyi *Tekhnologiya Karbamida* (Technology of Carbamide) (Leningrad: Khimiya, 1981)
98. L K Altunina, V A Kuvshinov, L A Stasyeva *Progress in Mining and Oilfield Chemistry. Novelties in Enhanced Oil and Gas Recovery* Vol. 5 (Ed. I Lakatos) (Budapest: Akademiai Kiado, 2003) p. 123
99. V A Kuvshinov, V V Kuvshinov, L K Altunina *Proceeding of the 11th Symposium on Improved Oil Recovery, Amsterdam, 2001*
100. L K Altunina, V A Kuvshinov *Tekhnol. TEK* **2** 41 (2007)
101. L K Altunina, V A Kuvshinov, L A Stasyeva *Progress in Oilfield Chemistry. Managing Matured Fields and Wells* Vol. 6 (Ed I Lakatos) (Budapest: Akademiai Kiado, 2005) p. 81
102. L K Altunina, V A Kuvshinov, L A Stas'eva, V V Gusev *Neftekhimiya* **39** 42 (1999) [f]
103. I Yu Galaev *Usp. Khim.* **64** 505 (1995) [*Russ. Chem. Rev.* **64** 471 (1995)]
104. L K Altunina, V A Kuvshinov *Nefteotdacha* **5** 28 (2002)
105. L K Altunina, A A Bokserman, V A Kuvshinov, V V Polkovnikov *Geol. Soc. Spec. Publ.* **84** 219 (1995)
106. L K Altunina, V A Kuvshinov *Progress in Mining and Oilfield Chemistry. Novelties in Enhanced Oil and Gas Recovery* Vol. 5 (Ed. I Lakatos) (Budapest: Akademiai Kiado, 2003) p. 115
107. L K Altunina, V A Kuvshinov *Tekhnologii TEK* (6) 44 (2004)
108. R A Rehbinder *Izbrannye Trudy. Poverkhnostnye Yavleniya v Dispersnykh Sistemakh. Kolloidnaya Khimiya* (Selected Works. Surface Effects in Dispersion Systems. Colloid Chemistry) (Moscow: Nauka, 1978)
109. S P Papkov *Fiziko-khimicheskie Osnovy Pererabotki Rastvorov Polimerov* (Physicochemical Foundations of Processing of Polymer Solutions) (Moscow: Khimiya, 1971)
110. G A Petropavlovskii *Gidrofil'nye Chastichno Zameshchennye Efiry Tsellyulozy i ikh Modifikatsiya Putem Khimicheskogo Sshivaniya* (Hydrophilic Partially Substituted Cellulose Esters and Their Modification by Chemical Cross-linking) (Leningrad: Nauka, 1988)
111. A M Bochek, G A Petropavlovskii, O V Kallistov *Zh. Prikl. Khim.* **69** 1363 (1996) [b]
112. O V Alekseev, O V Rozhkova, A N Prusov, V A Padokhin, Ya A Anikin *Zh. Prikl. Khim.* **77** 483 (2004) [b]
113. M A V Axelos, J Desbrieres, M Rinaudo, M Hirrien, C Chevillard *Polymer* **39** 6251 (1998)
114. S B Ross-Murphy, M Hirrien, J Desbrieres *Polymer* **41** 2451 (2000)
115. L K Altunina, V A Kuvshinov, L A Stas'eva *Bashk. Khim. Zh.* **8** 53 (2001)
116. L K Altunina, V A Kuvshinov, L A Stasyeva *Progress in Mining and Oilfield Chemistry. Recent Advances in Enhanced Oil and Gas Recovery* Vol. 3 (Ed. I Lakatos) (Budapest: Akademiai Kiado, 2001) p. 67
117. L K Altunina, V A Kuvshinov, L A Stasyeva *Progress in Mining and Oilfield Chemistry. Focus on Remaining Oil and Gas Reserves* Vol. 4 (Ed. I Lakatos) (Budapest: Akademiai Kiado, 2003) p. 117
118. V A Kuvshinov, L K Altunina, V V Shevlyuk, V V Varaksin, S L Legeza, O A Ostapenko *Interval. Peredovye Neftegaz. Tekhnol.* **2** 72 (2003)
119. L K Altunina, A A Bokserman, V A Kuvshinov, V V Polkovnikov *Neftyanoe Khozyaistvo* (4) 45 (1994)
120. L K Altunina, V A Kuvshinov *Neftyanoe Khozyaistvo* (4) 36 (1995)
121. L K Altunina, V A Kuvshinov, A A Bokserman, V V Polkovnikov *Povyshenie Effektivnosti Razrabotki Trudnoizvlekaemykh Zapasov Nefti* (Increase in the Efficiency of the Development of Hard-to-Recover Oil Reserves) (Moscow: All-Russian Oil and Gas Research Institute, 1997) p. 222
122. L K Altunina, V A Kuvshinov, L A Stas'eva *Fiziko-khimicheskie Svoistva Rastvorov i Dispersii* (Physicochemical Properties of Solutions and Dispersions) (Novosibirsk: Nauka, 1992) p. 18
123. V A Kuvshinov, V N Manzhai, L K Altunina *Fiziko-khimicheskie Svoistva Rastvorov i Dispersii* (Physicochemical Properties of Solutions and Dispersions) (Novosibirsk: Nauka, 1992) p. 24

[a] — *Mendeleev Chem. J. (Engl. Transl.)*
[b] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[c] — *Dokl. Chem. (Engl. Transl.)*
[d] — *Colloid. J. (Engl. Transl.)*
[e] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[f] — *Petrol. Chem. (Engl. Transl.)*
[g] — *Chem. Sust. Develop. (Engl. Transl.)*