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Thermoreversible Polymer Gels for Enhanced Oil Recovery

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Abstract

Thermally reversible polymeric gel forming systems based on polymer solutions with the lower critical temperature of dissolution – cellulose ethers – were developed to increase the oil recovery from highly heterogeneous strata. The reversible phase transition solution–gel occurs due to the thermal energy of a stratum or injected heat transfer agent. Temperature and time of gelatinization can be controlled by adding electrolytes and non-electrolytes. Laboratory studies of the gelatinization kinetics, rheological and filtration characteristics in the system cellulose ethers–aqueous phase–oil are presented. Results of experimental-industrial tests of the technologies of oil recovery enhancement involving thermally reversible polymeric gels for limitation of water inflow, increase in stratum coverage degree during flooding and thermal steam formation treatment are presented. Technologies are economically profitable and ecologically safe; the pay-back period is 5–9 months. The products of large-scale industrial production are used as reagents.

Key words: polymers, solutions, phase transition, gels, cellulose ethers, kinetics, rheology, oil recovery enhancement, water shutoff, experimental-industrial tests

INTRODUCTION

Today the majority of large-scale deposits in Russia, as well as around the world, entered a late stage of development. The current well stream watering exceeds 80 %. Newly entered fields, as a rule, are characterized by low permeability, increased oil viscosity and complex geology, *i. e.* these reserves belong to the category of stranded oil. The share of such oil reserves in Russia constantly increases. According to the experts, oil reserves difficult to recover in the world exceed 1 trillion t and they are considered not only as an oil production reserve, but also as the basis for its development for the next years in the developed industrial countries. The stocks of heavy and extra heavy oil are several times as much as those of easy and low viscosity oil [1–3]. Creation and large-scale application of new complex technologies of increase in oil recovery [4–6] is necessary for increase in oil production and effective development of hard to recover reserves. At the Institute of Petroleum Chemistry, SB RAS (Tomsk, Russia) basic and applied researches are carried out being the basis of creating a number of new knowledge-intensive and ecologically safe technologies of increase in oil recovery. Their large-scale industrial application allows to prolong profitable operation of the fields being at a late stage of development, and to involve in development the fields with difficult stocks of oil, including high-viscosity oil fields. The perspective concept of use of oil bed energy or the downloaded heat transfer agent for generation of oil displacement fluid, gels and sols directly in the oil bed is created. Physical and chemical bases of methods of enhanced oil recovery with application of gel forming systems (GFS) and compositions of the surface active substances maintaining and self-regulating in a layer for a long time a complex of properties optimum for oil displacement [7, 8] are developed.

The reservoir coverage problem during flooding is especially serious in case of the deposits consisting of hydrodynamically separated reservoirs in an oil zone, far from oil water contact, because the mechanism of alignment of the displacement front at the expense of capillary and hydrodynamic cross flows doesn't operate in this case. Producing wells water out too early already at the initiatory stage of development. In this case it is expedient to apply first of all methods of enhanced oil recovery increasing reservoir coverage by flooding, and only then to provide displacement efficiency increase. One of perspective ways of the solution of this problem is intrastratal gel generation [7–9].

PHYSICAL AND CHEMICAL BASES OF ENHANCED OIL RECOVERY METHOD

The new enhanced oil recovery method for highly heterogeneous strata based on regulation of filtrate flows and reservoir coverage increase by thermoreversible polymer gels [10–13] is developed. The latter are formed from solutions of polymers with the low critical solution temperature (LCST) [14, 15]. Gelatinization is directly connected with thermal energy of reservoir or downloaded heat transfer agent. Polymer solutions with LCST are capable to form gels directly in reservoir: at low temperatures solutions are low viscous, and at high they turn into gels. This is a reversible process: when cooling gel is diluted, becomes low viscous solution again, after reheating it gelatinizes again and so on repeatedly. The temperature and time of gelatinization in the range from 30 to 120 °C can be regulated by inorganic and organic additives, according to specific reservoir conditions (temperature and water mineralization). Gels can be used as an effective agent for water shutoff, prevention of gas breakthrough, elimination of gas cones *etc.*

Gels are generated from polymer solutions for which liquid–liquid phase equilibrium curve in polymer–water system is characterized by LCST value. At temperatures below LCST the system is homogeneous, and above – breaks up to two phases [14, 15]. The first phase is much diluted polymer solution, the second – is concentrated one. Owing to high viscosity of the second phase the break up is delayed and is nonequilibrium. Micro heterogeneous kinetically stable structure – thermoreversible polymer gel – appears, in which the concentrated phase forms a three-dimensional gel framework, and the polymer diluted phase is settled in its cells.

Thanks to the ability of systems LCST polymer–water to form gels with increasing temperature, they can be used in technologies of enhanced oil recovery, focused on increase in reservoir coverage by flooding *via* selective isolation of the washed out high permeability formation zones. The most perspective LCST polymers are cellulose ethers (CE) [10, 15, 16].

GELATINIZATION KINETICS AND RHEOLOGICAL PROPERTIES OF SOLUTIONS AND GELS

Gelatinization kinetics and rheological characteristics in CE–water phase system [10, 12] were investigated with the purpose to ascertain possibility of application of CE gels in various geological and physical reservoir characteristics. The type of CE with LCST is methylcellulose (MC). The properties and structure of MC solutions and gels are considered in works [7, 10, 13]. Temperature dependence of CE solution viscosity has extreme nature: when heating the gradual decrease in viscosity takes place (from 40–70 to 5–20 mPa · s, *i. e.* two to ten times), and when achieving the gelatinization temperature (phase transition) – sharp increase in viscosity up to 100–2000 mPa · s (5–100-fold) associated with gelatinization (Fig. 1). This is a reversible process, *i. e.* when cooling gel turns into liquid again. The temperature at which viscosity is minimal corresponds to LCST. The cyclic reversal of a temperature mode – alternation of heating and cooling – showed reproducibility of rheological parameters of gels.

The influence of electrolytes and non-electrolytes changing hydrophobic interactions in a system on phase balance and gelatinization kinetics in MC solutions (Fig. 2) is experimentally studied.

The greatest influence on the change of the temperature of EC solutions gelatinization exerts anions, their influence correlates with place

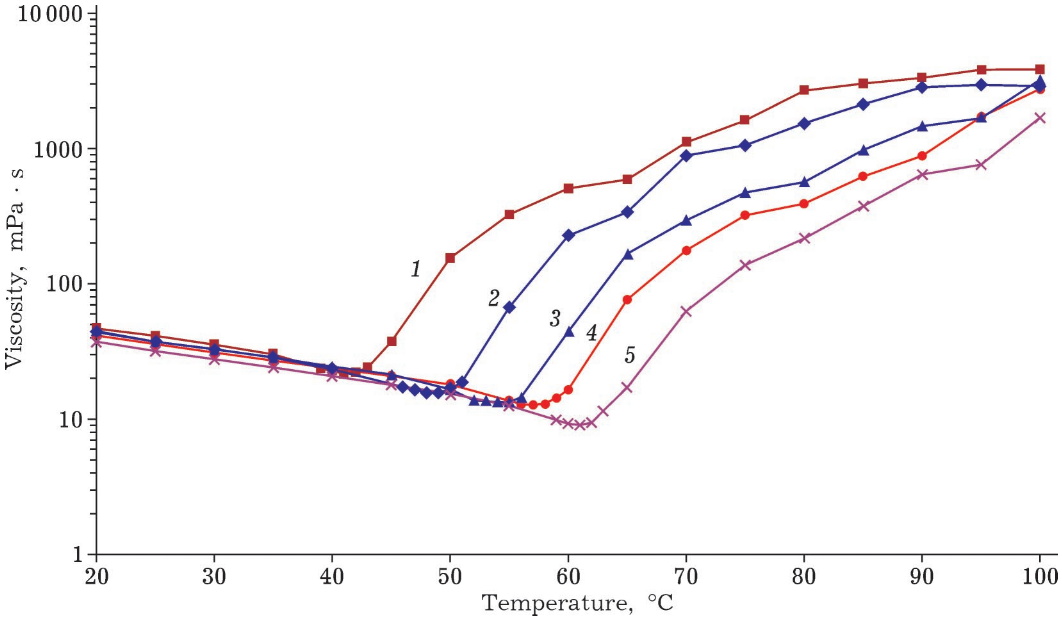

Fig. 1. Temperature dependence of viscosity of 1 % CE solutions with a various mineralization of reservoir water, g/L: 60 (*1*), 30 (*2*), 15 (*3*), 7.5 (*4*), 0 (*5*).

in lyotropic series [10]. The greatest decrease in LCST is caused by salts with Cl^- anion; the opposite action (increase in LCST) exert the salts with CNS^- anion. The influence of the salts with NO_3^- ion is intermediate: depending on a cation some increase or reduction of gelatinization temperature is observed. The influence of cations is far less. For example, for the salts with Cl^- or CNS^- anions the action of cations is appreciable, however it is incapable to change the nature of anion influence. The greatest decrease in temperature of gelatinization is observed at the action of electrolytes with a ratio of cation and anion charges equal to 1 : 1. The influence of electrolytes with a ratio of charges 2 : 1 and 3 : 1 is far smaller and almost the same. The exception to the rule is $ZnCl_2$, which promotes gelatinization temperature increase at concentration more than 5 mass % (see Fig. 2), as well also aluminum chloride with a mass fraction more than 10 %. The solutions of $ZnCl_2$ and $AlCl_3$ in such concentration acts as coordinating solvents. Thiourea, ethyl and isopropyl alcohols essentially raise LCST. It is established that the action of electrolytes and not electrolytes agents is additive. Taking into account geological and physical reservoir conditions, in particular reservoir temperature and mineralization of reservoir water and water blanket it is possible to select gel-forming compositions for regulation of filtration flows and increase in sweep efficiency optimum for specific conditions.

The rheological researches carried out using a Haake RheoStress 600 rotational viscometer at the temperatures 20–150 °C and pressure up to 50 atm, showed that in case of joint addition of carbamide and ammonium thiocyanate to the CE solution it is possible to obtain the solutions with gelatinization temperature above 100 °C (Fig. 3) [13, 17]. The gels keep the rheological characteristics at high temperatures – up to 150–220 °C. In the range of high rate of shear 0.5–5 s^{-1} gel is a solid body, and the rheological dependence type indicates its viscoelastic properties. Thus gel-forming compositions can be applied for regulation of steam injection profile in cyclic steam soaking.

Characteristic of LCST polymer–water systems is a temperature hysteresis of phase transition from solution to gel. In MC–water phase system the hysteresis phenomenon was investigated by gelatinization test when heating and dilution of gel test when cooling [13, 17]. Influence of the additives increasing gelatiniza-

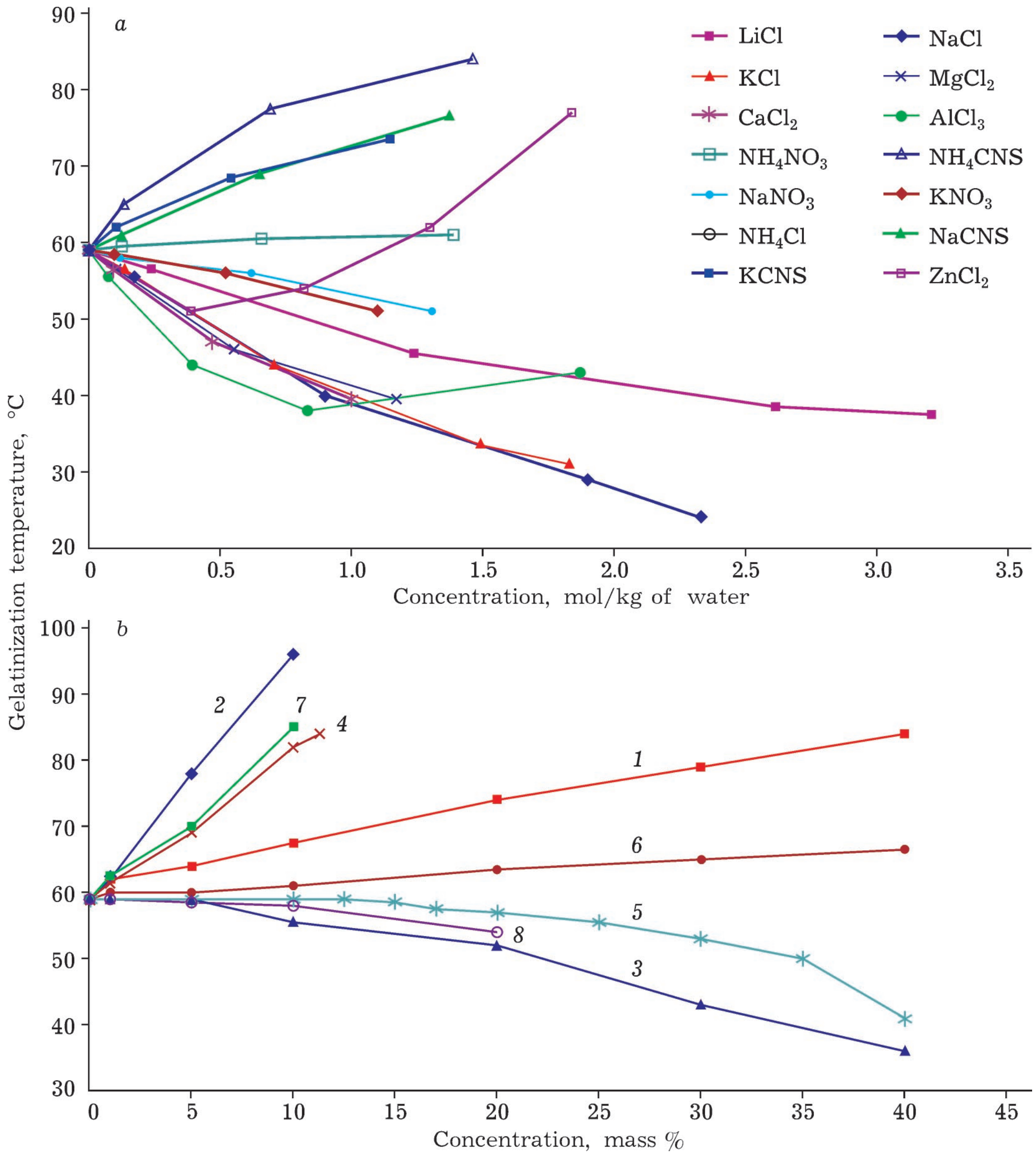

Fig. 2. Influence of electrolytes (*a*) and nonelectrolytes (*b*) on the gelatinization temperature of methylcellulose solutions with concentration 1 mass %: *b* – carbamide (*1*), thiourea (*2*), glycerin (*3*), ethyl alcohol (*4*), ethylene alcohol (*5*), triethanolamine (*6*), isopropyl alcohol (*7*), polyglycol (*8*).

tion temperature (ethyl alcohol, ammonium thiocyanate, thiourea and carbamide) on a hysteresis was studied. It is found that in these systems of gelatinization temperature practically coincide with LCST of polymers which were obtained by oscillatory viscometry [8]. The dilution temperature is 30–50 °C lower than the gelatinization one (Fig. 4). Gelatinization and dilution temperatures increase almost linearly with increase in reagents concentration, and for all studied reagents, except carbamide, these dependencies are symbate.

FILTRATE CHARACTERISTICS AND OIL DISPLACEMENT CAPACITY

Convertibility of phase transition solution–gel was found experimentally *via* research of a water filtration through heterogeneous reservoir model under conditions simulating those of reservoir. Researches were carried out with the help of plant for studying filtration with a constant flow rate through the reservoir model consisting of two parallel columns with different permeability being a model of heterogeneous oil reservoir rock. In the tests the cores

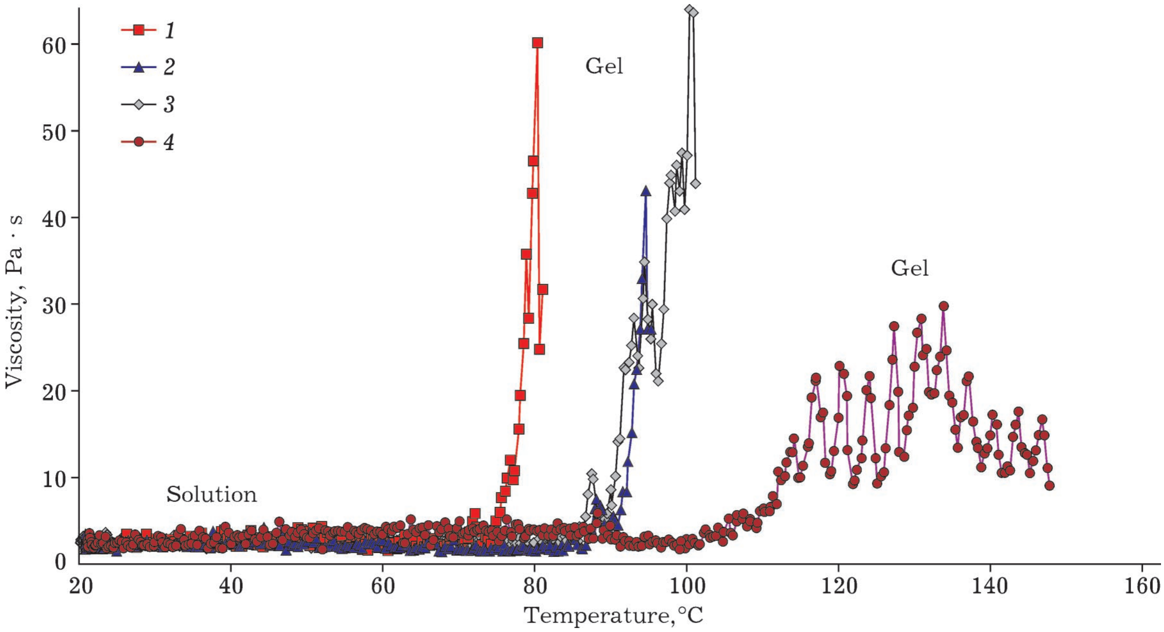

Fig. 3. Viscosity change upon phase transition solution–gel for polymer with LCST (cellulose ether, CE): *1* – CE solution, *2* – CE solution + NH_4CNS, *3* – CE solution + carbamide, *4* – CE solution + NH_4CNS + carbamide.

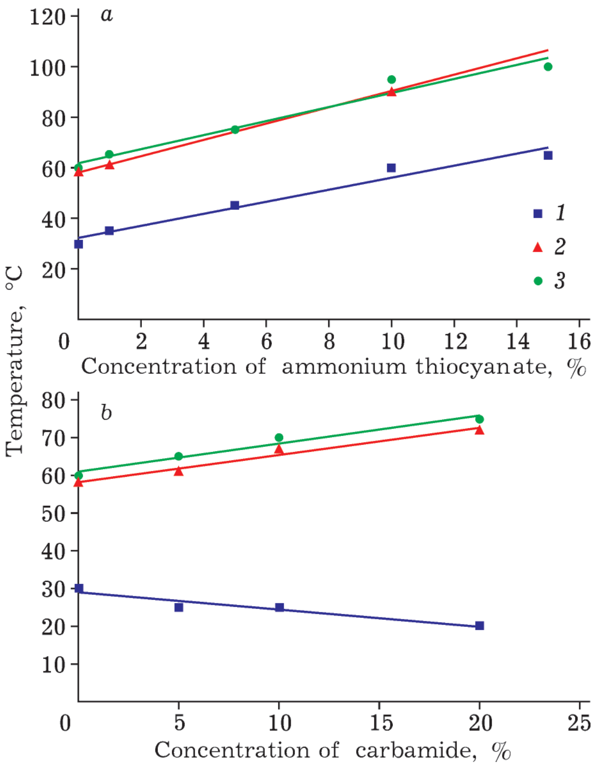

Fig. 4. Influence of ammonium thiocyanate (*a*) and carbamide (*b*) on the temperatures of gelatinization and gel dilution in the CE solutions: *1* – gel dilution temperature, *2* – LCST, *3* – gelatinization temperature.

of oil reservoir rock, oil and reservoir waters were used. After loading the gel-forming solution into the reservoir model and heating up to 60 °C a redistribution of filtrate flows takes place which remains during temperature increase up to 220 °C. Temperature decrease from 220 to 20 °C and subsequent filtration of water results in initial distribution of flows [18].

The gelatinization in reservoir rock results in selective decrease in phase permeability of the rock by water (Fig. 5): a pressure gradient of water during filtration through the gel is 2–3 times as great as that of oil [13].

Filtrate characteristics and oil displacement capacity of CE based gel-forming compositions according to the conditions of heterogeneous reservoirs of West Siberia [18] are experimentally investigated. It is found that the gel-forming solution bank pumping to the heterogeneous reservoir model leads to redistribution of filtrate flows. And the mobility of liquid in a high permeability reservoir part sharply decreases, and as a rule it remains at the same level in a low permeability part. Redistribution of filtrate flows is attended by residual oil recovery, especially considerable in low permeability model. Gel-forming compositions demonstrate high efficiency in increasing reservoir coverage on

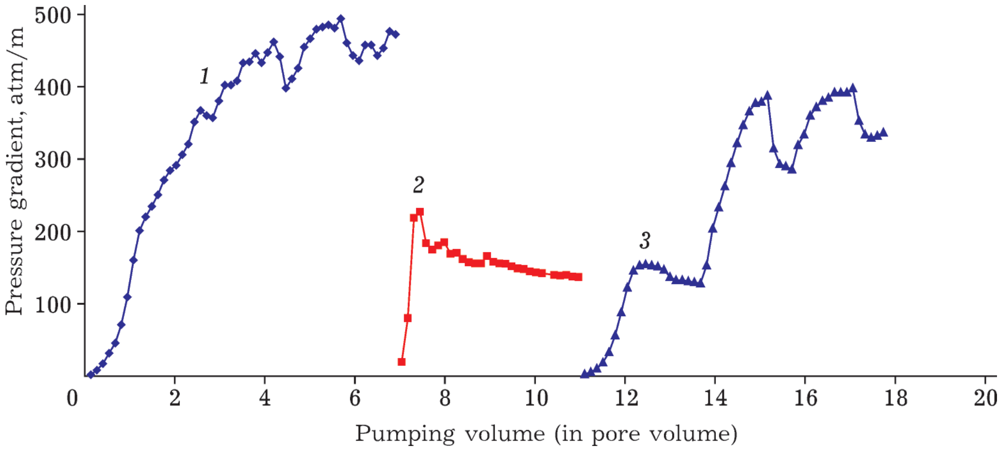

Fig. 5. Selective increase in phase rock permeability for water after CE gel forming in reservoir rock (initial permeability is 11 μm^2) using a model core as an example: *1*, *3* – water injection, *2* – oil injection.

the models of the heterogeneous reservoir with permeability of intercalations differing as much as 3–20 times. As a result they can be used for regulation of filtrate flows of formation fluids and restriction of a water production of highly heterogeneous reservoirs. Ammonium thiocyanate and carbamide being a part of gel-forming compositions are the tracers as well.

In the conditions modelling reservoir at the temperature of 200 °C filtrate characteristics and oil displacement ratio are investigated during physical and chemical impact of gel-forming composition on high-viscosity oil fields. It is

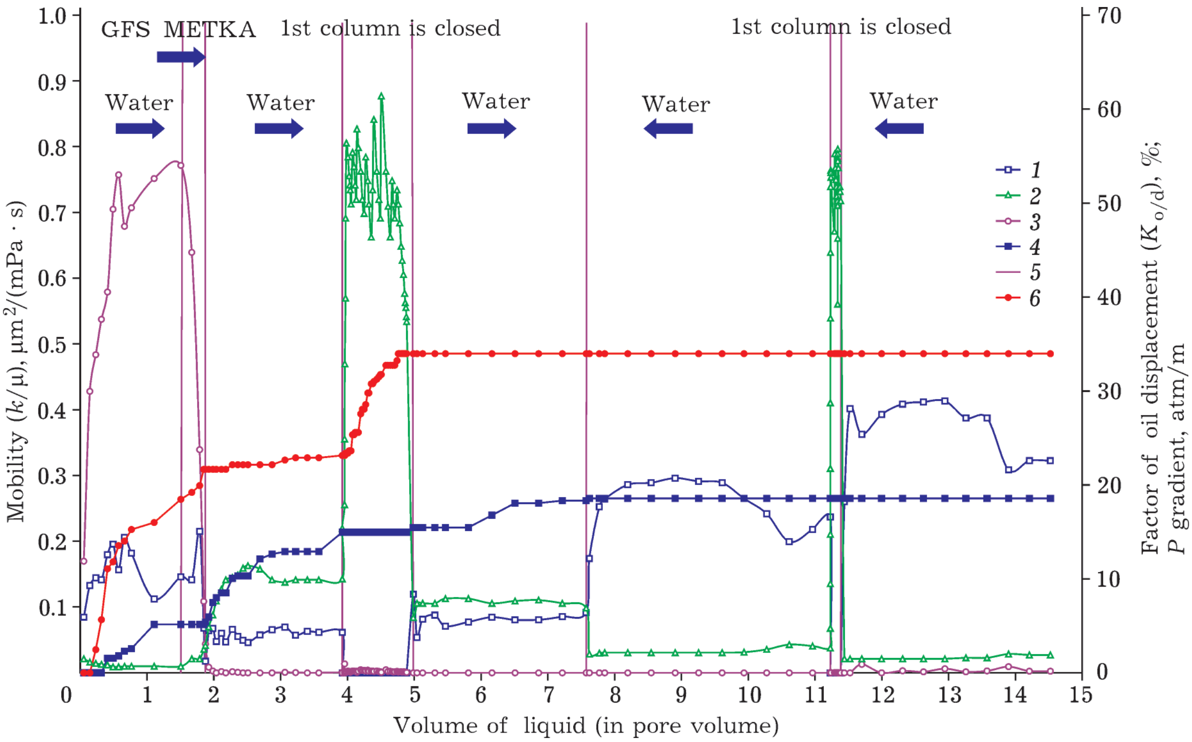

Fig. 6. Redistribution of filtration flows and washout of high-viscosity oil from model reservoir at 200 °C in the conditions modelling cyclic steam treatment. Permeability, μm^2: 1st column – 0.397, 2nd column – 2.123; *1*– 1st column, mobility; *2* – pressure gradient; *3* – 2nd column, mobility; *4* – 1st column, oil displacement ratio; *5* – injection; *6* – 2nd column, oil displacement ratio.

established that application of gel-forming compositions provides alignment of filtrate flows because of decrease in mobility in high permeability intercalations that is accompanied by oil recovering both from low- and high-permeability zones of reservoir model. For example, after composition pumping into heterogeneous reservoir model with permeability of columns differing in 5.4 times (0.397 and 2.123 μm^2) (Fig. 6), there was a redistribution of filtrate flows. At the same time the liquid mobility ratio in the reservoir model changed from 1 : 4.3 to 50 : 1. During the reverse water pumping modelling cyclic steam soak well, the character of a filtration is the same. The gain of oil displacement ratio was 12–13 % [17].

EXPERIMENTAL-INDUSTRIAL TESTS OF ENHANCED RECOVERY METHODS

The researches carried out allowed to find the optimum gel-forming compositions for enhanced recovery method based on water shutoff during flooding and thermal impact on reservoir. Gel-forming METKA system and the technologies employing it for reservoir coverage increase and water shutoff are developed. The low-viscous water solution capable to gel forming in reservoir conditions is injected to the reservoir at 30–120 °C. The main quantity of composition gets into a high-permeability part of a layer and the gel screen is formed there; as result filtration flows are redistributed. Injecting of METKA system to the injection wells results in alignment of their intake capacity profiles, low water influx and increase in well yields of the producing oil wells hydrodynamically connected with the injection wells. METKA system is practically feasible; the best water solubility of polymer is reached at 0–10 °C. These are cost effective and environmentally safe technologies using of the standard oil field equipment.

In 1996–1997 large-scale industrial tests of technologies using thermoreversible gels were carried out successfully in oil fields of West Siberia. In 1996 METKA system was injected into 11 delivery wells, and in 1997 – into 47 ones, 50–100 m^3 into each well. In 2–3 months after injecting the extracting wells hydrodynamically connected with the delivery ones show de-

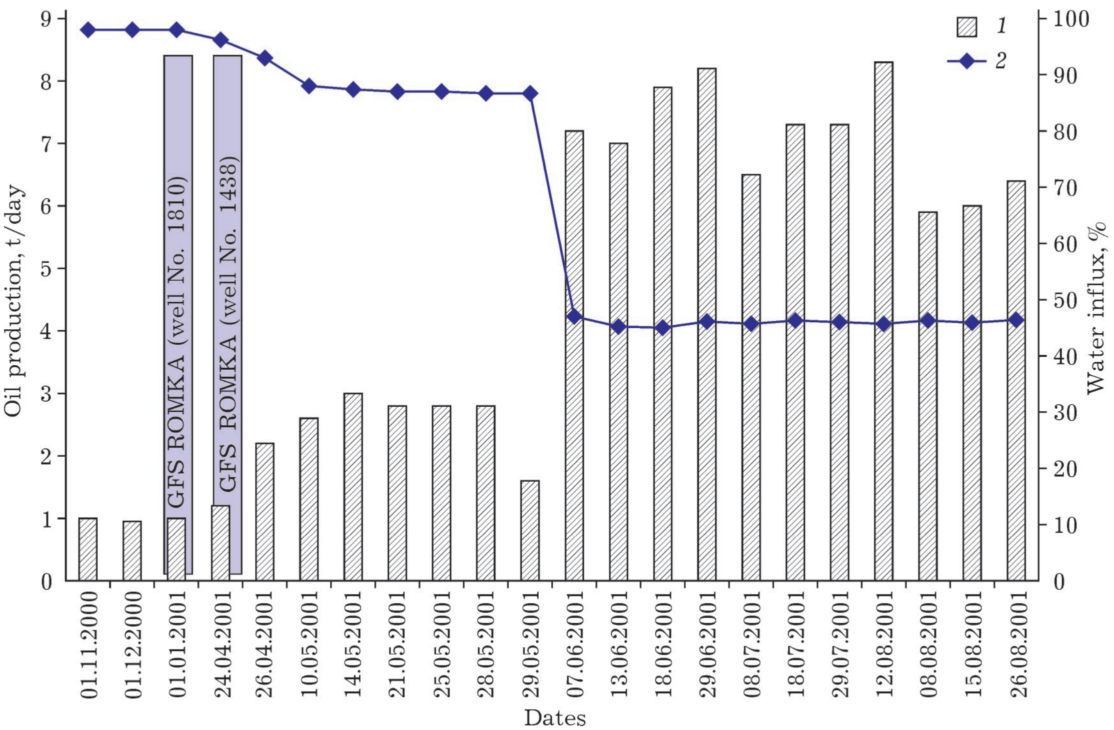

Fig. 7. Oil production increase (*1*) and water influx decrease (*2*) after downloading ROMKA system at the Uryevskoye field, AV_1 layer (extracting well No. 1438, injection well No. 1810).

crease in water production and increase in well yields. Since 1998 at the oil fields of West Siberia Lukoil Oil OJSC used the technology on a commercial scale.

The commercial mobile unit for preparing and injecting the systems was created by OTO enterprise. In 1998–2003 the METKA system was injected into 382 wells, as result an additional oil production was 480 000 t. The payback period is 5–9 months. Technology efficiency was on average 1300 t of extra oil production per well treatment. All the reagents area the products of large tonnage commercial manufacture.

The efficiency of technology increases in the case of complex impact on hydrodynamically connected delivery and extracting wells. In 2001 the experimental industrial tests of technology of water shutoff by simultaneous effect of gel-forming systems to the well bottom zones of delivery and extracting wells [12, 19] were carried out at two pilot regions of AV_1 reservoir of the Uryevskoye field. The system injection into a well was 50–200 m^3, totally 620 m^3. This resulted in redistribution of filtration flows and water shutoff observed in decrease in water influx and increase in well yields of extracting wells (Fig. 7). Extra oil production in 7 months was 6542 t.

Thermoreversible polymeric gels are widely used in a number of technologies.

The technology of elimination of water cross flow behind casing was tested in the gas producers of Myldzhinskiy gas condensate field [20]. So, during the well tests (well No. 133) the gas inflow with produced water was obtained; while the gas output was 300 000 m^3/day, the content of water was 30 t, *i. e.* far exceeded the permissible level. After injecting the gel-forming METKA system to the well together with cement bridging the commercial operations commenced with gas rate of 430 000 m^3/day being the same for four years and with the trace level content of water.

In 2002–2003 at the BV_8 reservoir of the Pokachevskiy field (West Siberia) the trial tests

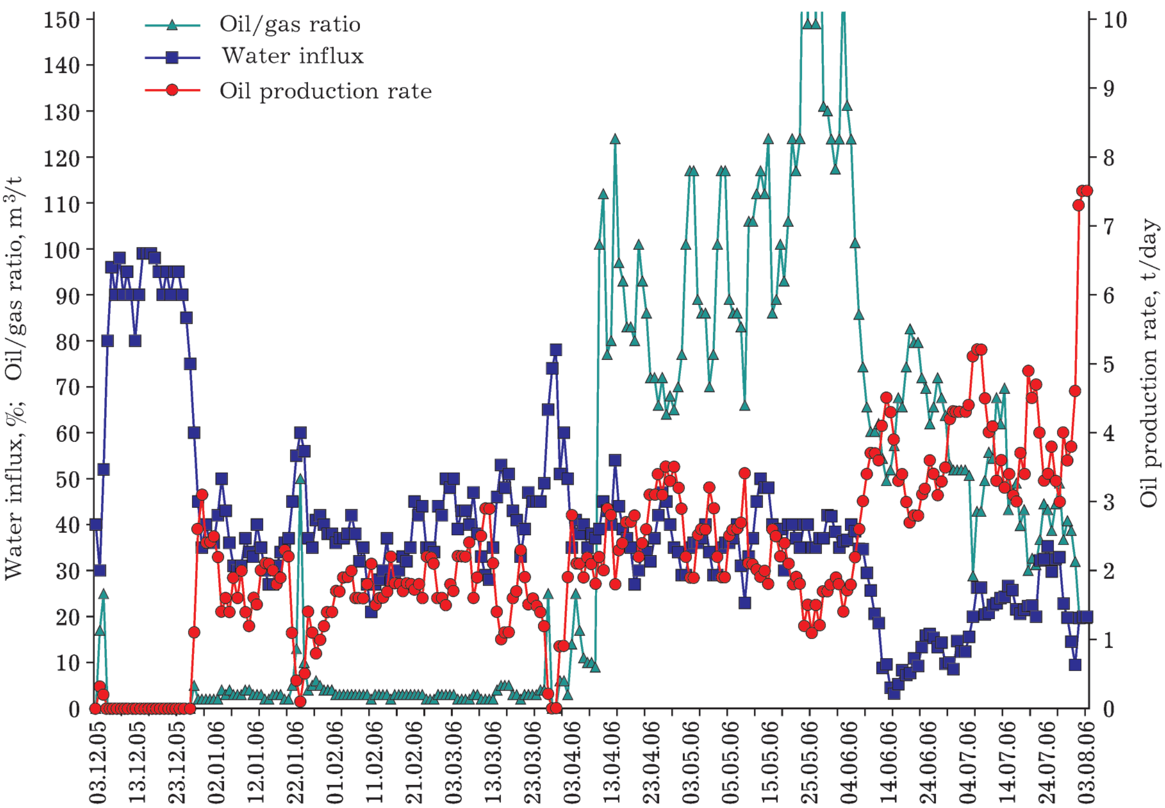

Fig. 8. Characteristics of the work of a cyclic steam well Gao3-6-0155, the high-viscosity oil deposit, Gaoshen field after injection of METKA system and steam in November, 2005.

of complex vibroseismic and physicochemical effect to the reservoir with application of LABEL system together with Institute of Mining, SB RAS (Novosibirsk, Russia) were carried out successfully [12].

The trial tests of technology increasing the efficiency of cyclic steam stimulation of high-viscosity oil deposits with applying the LABEL system for water shut off [13] (Fig. 8) were successfully carried out at two wells of Gaosheng field (Liaohe, China) in 2005–2006. In 2006–2007 at 24 wells of RussNeft OJSC fields the works for water shutoff and elimination of behind the casing flows were carried out. In 2007 the trial tests of the technology were also carried out successfully at 9 wells of fields Liqaer, Jabal and Delilah in Oman. After injection of gel-forming composition the water flooding decreases and oil output increases.

Complex technologies applying thermoreversible polymer gels in water flooding and cyclic steam techniques are the additional reserve for enhanced oil recovery of hard to recover reserves, including high-viscosity oil fields.

CONCLUSIONS

1. For enhanced oil recovery of high heterogeneous strata based on the polymer solutions with low critical solution temperature – cellulose ethers – the thermoreversible gel-forming systems are created, capable to form gels directly in the reservoir under the effect of its thermal energy or that of the injected heat transfer agent.

2. Research of kinetics of a gelatinization and rheological characteristics in CE–water phase system showed that at the attainment of gelatinization temperature (solution–gel phase transition) sharp increase in viscosity (5–100 times) occurs. In the rate of shear 0.5–5 s^{-1} gel is a solid body with viscoelastic properties. Gels maintain the rheological characteristics at high temperatures, up to 150–220 °C. The temperature hysteresis of solution–gel phase transition is established: the dilution temperature is 30–50 °C lower than gelatinization one.

3. Pilot studies of electrolyte and non-electrolyte additives influence on the temperature and time of CE solutions gelatinization showed that anions have the most important effect, and that of the agents is additive.

4. During the research of water and oil filtration from a natural core material through the reservoir model it is established that gelatinization in the deposit rock leads to selective decrease in phase permeability of the rock by water: a pressure gradient of water filtration through gel is 2–3 times higher, than that of oil.

5. Gel-forming systems demonstrate high efficiency in increase of reservoir coverage at the model of heterogeneous reservoir with the intercalations permeability differing 3–20 times, that allowed to recommend them for regulation of filtration flows of formation fluids, restriction of water production of high heterogeneous reservoirs, including high-viscosity oil fields.

6. At applying thermoreversible polymer gels the new technologies for water production restriction in oil and gas wells, increases in reservoir coverage under flooding and cyclic steam technique are developed. The results of trial tests of technologies at the fields of Russia, China and Oman testify to their economic efficiency and ecological safety. The payback period of expenses is 5–9 months. All reagents are the products of large-scale industrial production.

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