Eurasian ChemTech Journal 3 (2001) 179-190

EOR Technologies: Physico-Chemical Aspects

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Abstract

The application of self-regulating oil-displacing systems is considered to be a promising trend in the development of physico-chemical EOR methods. Technologies intended to increase conformance predominate. EOR technologies, where heat energy of the formation is used to generate alkaline buffer systems, CO_2 and gels increasing oil displacement and conformance, have wide potentialities. Such methods have been realized in the technologies developed at the Institute of Petroleum Chemistry SB RAS (IPC). Hydrolysis, hydrolytic polycondensation and coagulation in the system carbamide – aluminum salt – surfactant – water is the physico-chemical base for the technologies involving alkaline buffer systems, CO_2 and inorganic gels. To prepare thermoreversible polymer gels one uses change of phase from solution to gel in the system: cellulose ether with a lower critical dissolution point – water. Presented are the results obtained on the application of physico-chemical EOR methods and technologies developed at IPC in oil fields of Russia. The technologies proved to be economically effective and environmentally safe. The period of payback is 5-12 months.

Introduction

In recent decades the share of oil and gas in fuel and energy balance of our country accounts for three fourth of energy consumption - in fact it has converted into oil and gas balance. As a result one observes substantial increase both in oil and gas production and consumption. Now enterprises of fuel and energy complex manufacture more than 30 % of the industrial output of the country, form about 40 % of federal budget income and give about 50 % of all currency earnings. The major part in these figures falls to the share of oil, oil products and natural gas to give priority to oil and gas industry both in oil and energy complex and in Russian economy as a whole. Therefore in Government approved conception of energy policy overcoming of setback in production in oil and gas industry and assurance of further development in these base branches of Russian economy is considered as the primary objective.

In spite of setback in production Russia is a first-rate producer of energy resources. Our country has the opportunity to satisfy in full internal requirements in energy and at the same time Russia remains one of the primary oil and gas exporter. In 2000 the volume of oil production in Russia was 323 million tons, in other words it increased by 18 million tons as compared with 1999. In the first place it is concerned with rise in oil prices (to 34 $ per barrel). In 1999-2000 about 6 billion dollars were invested in extractive industry. It allowed one to develop more than 9600 inactive wells, including more than 6 thousand wells in 2000, which produced more than 12 million tons of oil and put into operation 3300 new wells, which produced about 11 million tons of oil.

Progressive growth of difficult to recover reserves, namely unrecovered oil after flooding in the regions, in the development of which great investments have been already made, predetermined great attention to novel EOR methods: physico-chemical, heat and gas. In 2000 due to application of such EOR methods about 42 million tons of oil were recovered in RF, a great portion – due to chemical methods. In many respects the reasons for widespread application of chemical methods in Russia is objectively related to the structure of residual oil reserves, a significant part of which is localised in water-flooded oil fields in low permeable reservoirs [1-4].

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Progress trends in EOR methods

Most of oil fields in Russia are commonly developed by flooding. Water is injected in reservoir through a system of injection wells. Water injection fills the loss of the formation pressure, caused by oil recovery through a system of production wells. Flooding is considered as oil displacement with water from fractured-porous medium under formation pressure maintenance at complete compensation of the recoverable oil by the injected water. Oil recovery factor (ORF) – ratio of the recovered oil amount to that occurring in the object under development. ORF is presented as the product of two values: oil displacement factor K_d and surface efficiency factor K_c for the object under operation by the used stimulation system:

$$ORF = K_d \times K_c \quad (1)$$

Even in the most favourable case when the water has passed through 70 % of reservoir volume (K_c = 0.7) and there where it has passed the water displaced 70 % of oil (K_d = 0.7), final ORF would not exceed 50 %:

$$ORF = K_d \times K_c = 0.7 \times 0.7 = 0.49 \quad (2)$$

Now computer modelling of the history of oil field development allows to refuse the evident application of K_d and K_c in design documents. Nevertheless they remain their usefulness, since they enable to differ two aspects in the problem of ORF increase – K_d and K_c increases.

There are many factors causing incomplete oil recovery at flooding [5-7]. One can divide them into two groups. The first group is related to capillary-porous structure of rock-reservoir and to large total oil-rock interface. There is always oil film on the rock surface that cannot be displaced with water. The volume of oil film can account for 10-20 % of the total volume in the reservoir. Besides about 10 % of oil remain in the formation in the form of drops stuck in the restrictions of capillary porous and rock cracks. Capillary gradient prevents oil displacement, which in hundred and thousand times exceeds really accessible pressure gradients for oil displacement with water. Therefore maximal oil displacement factor K_d usually does not exceed 0.7 and often lower. Thus, at a molecular level the first group of reasons is concerned with a negative behaviour of ionic-molecular forces on phase boundaries in the system oil – water - rock.

The second group of the reasons causing incomplete oil displacement is concerned with geological-physical heterogeneity of reservoir and appears in incomplete conformance, in other words conformance factor K_c is below 1. It is mainly heterogeneity of the construction and properties of rock-reservoir on macro- and microlevels, which in the long run intensifies dispersion of hydrodynamic, energy- and mass-exchanged processes in the formation.

Great EOR reserves occur in the use of physico-chemical methods for stimulation of oil formations, in particular, by injection of different chemical agents into production wells. Some of them – surfactants, solvents, carbon dioxide and etc. - partially or completely remove negative effect of capillary forces. The other agents change rheological properties and structure of filtration flows in the formation fluids and decrease hydrodynamic anisotropy of the formation (polymer solutions, gels, emulsions and foams).

The main conclusion following from the application of various EOR methods in oil fields of West Siberia is that the most successful proved to be EOR methods, which increase conformance by the injected water. It depends on the fact, that in many oil fields progressive flooding of the produced oil (water cut > 70 %) at the earlier stage of oil field development becomes an obstacle for design performance, because of a lower conformance factor (K_c~0.1-0.2). At the same time in the flushed high permeable zones of the formation oil displacement factor is close to maximal, oil displacement with water is close to frontal drive and K_d~0.6-0.7.

EOR methods increasing only K_d, showed to be unsuccessful under field conditions, e.g. the injection of weak concentrated solutions of surfactants and polymer. At the same time EOR methods increasing K_c or both factors had positive technological and economic effect independent on specific stimulation mechanism [8-15]. They are:

- Hydrodynamic methods intended to change filtration flow directions (nonstationary cyclic flooding in different variants);
- Physico-chemical methods intended to control filtration flows: injection of concentrated surfactant solutions, surfactant-based solutions and alkaline buffer systems (IKhN and IKhN-KA systems), cross-linked polymer (CPS) and polymer-dispersed systems (PDS), viscoelastic (VS) and gel forming systems (GFS), gas, emulsions, foams, as well as generating of similar systems *in situ* (inorganic gel-forming systems GALKA, GALKA-surfactant, thermoreversible polymer systems METKA and organosilicate systems).

From the point of view of reservoir hydrodynamics the problem of conformance is reduced to filtration flow control in the formation fluids [16]. At present EOR methods are considered as an effective controlling means for filtration flows increasing conformance by flooding or by any other active stimulation. For this purpose one uses hydraulic fracturing of the formation (HBF) and drills horizontal wells.

The oil remained in the reservoir after waterflooding is called as residual one. Based on expert judgement the residual resources are classified as follows:

1. Oil remaining in low permeable seams and areas not covered with water – 27 %;
2. Oil occurring in dead zones of homogeneous reservoirs – 19 %;
3. Oil remaining in lens and near impermeable screens of untapped wells – 24 %;
4. Capillary-retained and film oil – 30 %.

Thus, oil, which was not involved into the flooding process due to reservoir heterogeneity (items 1, 2 and 3), amounts to 70 % of the total residual resources presenting reserve for enhanced oil recovery. System approach to EOR technologies proved to be effective. It allows to organise the use of different kinds of stimulation for injection and production wells in certain order and in time [17].

Since 1981 Institute of Petroleum Chemistry is engaged in enhance oil recovery by physico-chemical methods. The research was initiated by academician Valentin A. Koptyug. At that time he headed Siberian Branch of the Russian Academy of Sciences. A novel scientific approach was proposed to develop effective oil-displacing solutions based on surfactants and alkaline buffer systems. A complex of original devices and methods has been developed to study physico-chemical and rheological properties of the surface and bulk phases in the system oil - rock – surfactant solution. A novel prospecting conception has been developed to utilise formation energy or that of a heat carrier to generate oil-displacing fluid, gels and sols *in situ.*

Physico-chemical basis for EOR methods has been developed employing gel forming and surfactant systems. The principles of surfactant systems selection for enhanced oil recovery realise a novel conception of oil-displacing fluids as physico-chemical systems with a negative feedback retaining and self-regulating a complex of properties in the formation for a long time; the properties being optimal for EOR purposes. Recently novel EOR technologies are being developed involving inorganic and polymer gel forming systems capable to generate gels *in situ*. Using these technologies one can create deflecting screen in the formation and regulate filtration flows aimed to enhance oil recovery and to decrease water cut. Due to ecological safety and harmlessness of chemical agents gel-technologies are widely used in oil fields of West Siberia.

Oil production is a process of geological scale, therefore any impact on the process will be successful only in case it is compatible by material and energy resources It is obvious, that chemical agents utilised in technological processes of oil recovery should be relatively cheap, large-tonnage and ecologically safe. Their application should not cause irreversible environmental changes in oil production areas. Search of new cheap sources of raw materials for EOR technologies is of special importance. From this point of view joint study of IPC SB RAS and Institute of Solid State and Mechanochemistry SB RAS is considered to be promising. The study is carried out to prepare soluble products from plant raw material (cellulose, rice husks) applying mechanochemical impact and coordinating solvents, as well as the products of domestic large-tonnage industry, waste of chemical, petrochemical and coal industries.

Seven EOR technologies have been developed and are used in oil fields of West Siberia and other regions. Additional oil recovery averages 1-3 thousand tons per 1 well-treatment, period of payback – 5-10 months. More than 1 million tons of oil has been recovered due to the application of EOR technologies in oil fields of West Siberia. Pilot tests of gel-technologies were successfully carried out in “White Tiger” oil field on the shelf of South China Sea (Vietnam).

EOR methods involving surfactants and alkaline buffer systems

In the course of development of physico-chemical EOR methods one clearly observes the tendency to endow an oil-displacing fluid with self-regulation elements, permitting it to function in the formation for a long time. One of the variants of this tendency has been realised at IPC SB RAS, according to which oil-displacing fluid is considered as a physico-chemical system with a negative feedback. These ideas formed the basis of the development of physico-chemical principles intended to select surfactant systems taking into account thermodynamic and kinetic parameters in the system oil – rock – aqueous phase promoting oil displacement from a porous medium. Alkaline buffer systems with maximum buffer capacity ranging from 9.0 to 10.5 pH units have been proposed to provide negative feedback in oil-displacing surfactant systems (IKhN systems). The feedback allows the systems to retain and self-regulate a complex of colloidal-chemical properties, being optimal for oil displacement purposes [6]. The choice of alkaline buffer systems is specified by important role of physico-chemical processes proceeding in the presence of hydroxyl-ions in oil displacement from capillary-porous formation medium by aqueous solutions of surfactants. Such interactions include the reactions of acid group neutralisation, saponification of ester bonds, deprotonation of donor heteroatoms of heteroatomic oil compounds, association of hydroxyl-ions containing aromatic fragments of oil component molecules, the effect on water structure and thereby on hydrophobic linking and on conformational mobility of hydrophobic surfactant parts. These interactions resulted in decreased interfacial tension and viscosity on oil-water boundary, increased wettability of reservoir rock with water and in reduced loss of surfactants due to rock adsorption.

Systematic investigations carried out on the effects of pH and ionic force of aqueous electrolyte solutions on interfacial tension of oils and their fractions promoted the development of an electrocapillary model of interfacial phase. According to the model interfacial phase has the properties of ion-exchange membrane, which represents an amorphous adsorption layer of natural surfactants. The model explains extremal character of the dependence of oil interfacial tension on pH of aqueous phase by the existence of a double electric layer initiated by ionisation of ionogenic groups of natural surfactants – heteroatomic compounds being a part of resins and asphaltenes. The model enables one to connect component composition of oil with physico-chemical parameters of the interfacial phase. These parameters define a mechanism of oil displacement by aqueous solutions: interfacial tension, adsorption of natural surfactants, composition and concentration of electrolytes in aqueous phase. Within the framework of this model the dependence of oil interfacial tension σ on pH of aqueous phase is expressed by the following equation:

$$\sigma = \sigma_i - b\cdot\vartheta^2\cdot[lg(a_{H+} - K\cdot I)\,) - pH_i]^2 - \\ + c\cdot\vartheta^4\cdot[-\,lg(a_{H+} - K\cdot I) - pH_i]^4 - \\ - \Gamma_0\cdot R\cdot T\cdot ln(1 + K_a\cdot I) \qquad (3)$$

where pH_i – isoionic point of interfacial phase (pH of peak curve $\sigma - pH$); σ_i – interfacial tension in isoionic point; b – integral capacity of double electric layer (DEL); c – parameter, characterising the dependence of DEL integral capacity on its potential; a_{H+} – activity of hydrogen ions in aqueous phase; K – constant of ion-exchange equilibrium for interfacial membrane; I – ionic force of aqueous phase; K_a –constant of electrolyte ions adsorption in the interfacial phase; Γ_0 – limiting adsorption of electrolyte ions in the interfacial layer; R – absolute gas constant; T – temperature; $\vartheta = 2.303\cdot R\cdot T/F$; F – Faraday constant.

Figure 1 presents, as an example, calculated (line) and experimental (dots) dependences of interfacial tension to pH for oil recovered from Sovetskoye oil field, formation AV_{1-2}, on the boundary with aqueous electrolytic solution with a constant ionic force.

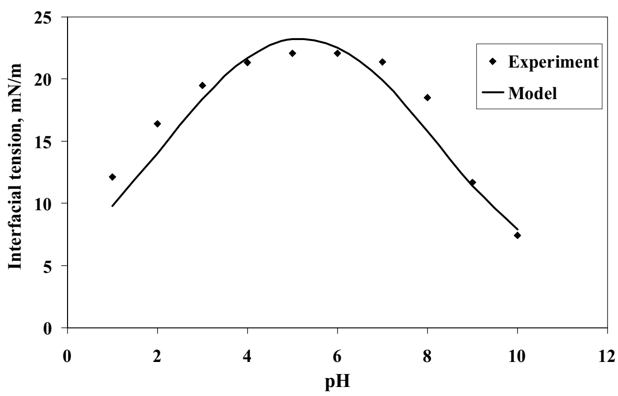

Fig. 1. Dependence of interfacial tension on pH for oil from Sovetskoye oil field, formation AV_{1-2} on the boundary with an aqueous solution 1-1 electrolyte with constant ionic force I=0.1 mole/kg of water.

The systems containing surfactants and an alkaline buffer system combine the advantages of alkaline flooding with that performed by surfactant solutions. Alkalinity pH ranging from 9.0 to 10.5 is considered to be optimal, since just in this pH range surfactants are chemically stable and exhibit maximum washing power, and suspensions of clay minerals have the lowest viscosity and adhesion that is important at flooding of low permeable collectors. In this pH range one observes no perceptible dissolution of rock minerals and precipitation of hydroxides of alkaline earth metals from the formation and injected waters. For pH ranging from 9 to 10.5 only some buffer systems, i.e. phosphate (tripoliphosphate), silicate, ammonia and borate systems are really suitable. Ammonia buffer system is the most promising.

Among all surfactants nonionic ones are the most suitable for the purposes of enhanced oil recovery, since one can use them in a wide salinity range of the formation and injected waters. In order to use the systems, consisting of nonionic surfactants and an alkaline reagent, at high formation temperatures the systems should include anion-active surfactants, which increase cloud point of nonionic surfactants.

Thus based on the studies of thermodynamic and kinetic factors in the system oil – rock – water – surfactants IKhN systems were proposed for commercial use in oil fields of West Siberia. The systems are based on surfactants and ammonia buffer system formed by ammonia and ammonium nitrate – cheap commercial products having practically unlimited source of raw material. A distinctive feature of IKhN systems consists in that their components are a constituent of geochemical cycles of nitrogen, carbon and oxygen. It provides their ecological acceptability and multifunctionality. Components serve as nutrition source for the formation microflora, natural indicator-tracers of filtration flows in reservoir and etc.

Low cold-test IKhN-60 and IKhN-100 systems are proposed for winter injections in the northern regions. The systems are low viscous fire-safe liquids, a freezing point of which ranges from –33 to –55°C. The injections of IKhN systems increase a displacement factor by 10 – 20 %. One can use the systems in a wide range of the formation temperatures and formation waters at the development of low permeable and heterogeneous formations. In the process of oil displacement with IKhN systems the mobility of filtered liquid increases 3-7 times indicating possible significant increase in injectivity of the injection wells at the treatment of bottomhole formation zone. Specific surfactant loss (adsorption) on a core material at oil displacement is 0.2-0.6 mg/g.

Using IKhN systems two EOR technologies have been developed:

- treatment of bottomhole formation zones by small amounts of the systems
- injection of large amounts of system slugs (portions) to affect crosswell space.

In 1984-2000 bottomhole formation zones of more than 150 injection wells were treated in oil fields of Tomsk and Tyumen regions under different geological-physical conditions. Treatment of bottomhole formation zones increases well injectivity 1.5 – 2.5 times, decreases injection pressure by 30 – 40 % and improve the efficiency of the production wells, which are hydrodynamically connected with the injection wells. The effect is in progress from 6 to 16 months. Additional oil production amounts for 20–30 tons per a ton of the injected system. The technology is economically effective. The period of payback is 4-9 months. One can use the technology for the formations with the formation temperature of 10 – 130°C and permeability - 0.005 – 0.500 μm^2, the greatest effect is achieved in low permeable reservoirs of Jurassic and Cretaceous deposits being typical for West Siberia.

In 1985-1989 pilot tests were carried out in 12 test areas of West Siberian oil fields. Large amounts of IKhN system slugs with regulating alkalinity were injected under different geological-physical conditions into the following formations: AV_1 Sovetskoye, YuV_1 Vakhskoye, AV_{1-3}, AV_{2-3}, BV_{10} Samotlorskoye, BV_{10} Lor-Yeganskoye, YuV_1 Malo-Chernogorskoye and AS_4 Mamontovskoye oil fields (Table 1). The systems were also injected in Komi Republic in test areas of B_3 formation, Severo-Savinoborskoye oil field. More than 30 thousand tons of IKhN systems were injected. The volume of slugs accounted to 0.2–0.4 % from oil-saturated porous volume of the formation in the test areas.

Taking into account the results of geophysical, hydrodynamic and physico-chemical investigations, the analysis of test area development revealed that IKhN systems improve flooding process in the following way: decrease and stabilise water cut or reduce its growth rate; improve parameters of injection wells and formation bottomholes (productivity, water permeability, piezoconductivity and permeability); increase dynamic levels; reduce residual oil saturation; improve oil displacement characteristics and increase or retain coefficient of the effective formation thickness. Injectivity of the injection wells increases to intensify the development. IKhN systems advance in the formation as a single whole at gradual dilution. Frontal advance is accompanied by decreased water cut, to the maximum by 30 – 40 %, and increased pH value of the product ranging from 6–7 to 8–10. Separate components of IKhN system are detected (0.001 – 0.1 %) in the products recovered from the production wells for a long time, i.e. from two to three years. Maximal concentration of surfactants and ammonium nitrate is 0.2 – 1.0 %. The yields of components from different wells proceed in comparable amounts indicating the conformance of the whole test area. Surfactant-oil ratios in the recovered product are similar – the highest yield of surfactants is accompanied with the enhanced specific production of oil.

On coming out of IKhN systems the recovered

Table 1

The data obtained on oil production in pilot areas of West Siberian oil fields, where IKhN systems were injected

Oil field, formation, number of injection well	Reserve, thou. t	Volume of injected IKhN system, thou. t	Increase in oil recoveryfactor, %	Additional production	
				thou. t	t/t of IKhN system
Samotlorskoye, A_{1-3}, 4110	1576.0	5.0	12.8	201.7	40.3
Samotlorskoye, B_{10}, 12168	369.0	2.3	27.5	101.5	44.1
Samotlorskoye, B_{10}, 12162	403.9	1.6	3.9	15.8	9.9
Samotlorskoye, A_1^{1+2}, 15930	582.9	1.7	5.3	30.9	18.2
Samotlorskoye, A_1^3, 15618	589.0	1.5	2.8	16.5	11.0
Lor-Yeganskoye, B_{10}, Pilot area 1 (129, 132, 133, 134)	706.9	2.1	2.9	20.5	9.8
Lor-Yeganskoye, B_{10}, Pilot area 3 (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, A_1, 644	2458.0	5.8	7.5	184.4	31.8
Mamontovskoye, AS_4, 2054	768.0	0.8	7.1	54.5	68.1

waters become less corrosion-active as compared with the injected water. Thus, corrosion rate of reference-specimen, installed in oil-gathering line in test areas of Lor-Yeganskoye oil field, was 0.1 mm/year. It has been determined that both the process of preliminary discharge and that of complete oil dehydration are improved if the content of IKhN system in the recovered water is up to 0.5 %.

Technological and economic efficiency of IKhN system application in oil fields of West Siberia has been estimated. Oil recovery increased by 3 – 14 % (see table). The technology enables one to produce in addition 20 – 30 tons of oil per a ton of the system or 140 – 200 tons of oil counting on a ton of surfactant.

Pilot tests revealed stimulating effect of IKhN systems on the development of the formation microflora. Components of ammonia buffer system are a constituent of geochemical cycle of nitrogen. Besides they serve as additional nitrous nutrition for anaerobic and aerobic microorganisms in trophic chains of microbial biocenosis in oil formation. The studies of microbiological processes, carried out in the areas where IKhN-60 and IKhN-100 systems were injected into formations AV_1 Sovetskoye, AV_1, AV_{2-3}, BV_{10} Samotlorskoye, YuV_1 Vakhskoye and BV_{10} Lor-Yeganskoye oil fields, demonstrated that the amount of denitrifying and heterotrophic microorganisms, including Pseudomonas and Actinomices, is noticeably higher as compared with that determined in the test areas. The number of sulphate-reducing bacteria occurring in waters recovered from test areas is substantially lower than that determined in the injected waters and waters recovered from test areas.

EOR methods utilising the formation heat energy

Physico-chemical principles used to prepare IKhN systems were later realised in the development of physico-chemical methods intended to stimulate the formation, in which heat energy or that of the injected heat carrier was utilised to generate alkaline buffer systems and CO_2, as well as to form free- and bonded dispersions (inorganic gels and sols). IKhN systems increase oil displacement and conformance. The result obtained on the study of hydrolysis kinetics and gelation in the system aluminium salt – carbamide – surfactant – water – rock served as scientific basis for these methods.

IKhN-KA systems with controlled alkalinity and viscosity have been developed for high temperature formations [6, 15]. The systems are aqueous solutions of nonionic and anion-active surfactants, carbamide and ammonium nitrate. In the formation carbamide undergoes hydrolyzation due to high temperature to yield carbon dioxide and ammonia (Fig. 2).

Several useful effects are observed. The dissolution of carbon dioxide reduces oil viscosity. Carbon dioxide and ammonia suppress the swelling of clay minerals in rock-reservoir and thereby preserve the

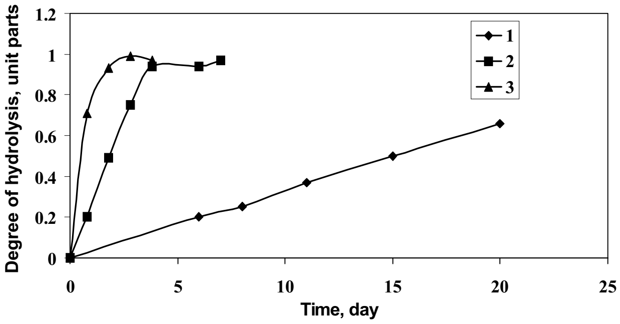

Fig. 2. Temperature effect on the kinetics of carbamide hydrolysis in IKhN-KA system. 1 - 80°C; 2 - 100°C; 3 - 120°C.

initial permeability of the formation. Ammonium buffer system performs the same function. It is formed at the dissolution of ammonia in aqueous solution of ammonium nitrate (Fig. 3). Besides due to its alkalinity, pH = 9-10, and the presence of surfactants buffer system intensifies return-flow impregnation and oil displacement.

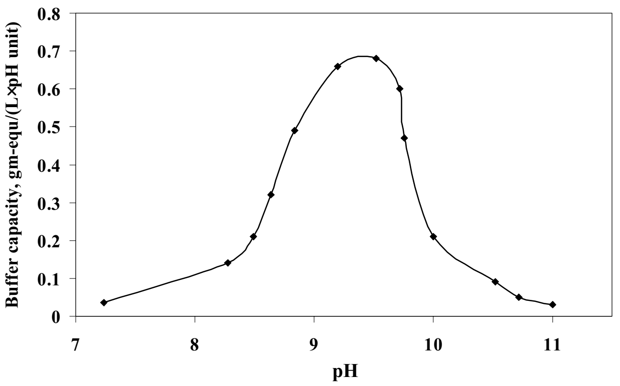

Fig. 3. The dependence of buffer capacity on pH for IKhN-KA system, subjected to thermostatting during 15 days at 100°C.

The effects of temperature, component concentration and formation rock on the kinetics of carbamide hydrolysis have been studied to optimise the composition of IKhN-KA system. It has been determined that temperature and concentration of ammonium nitrate produce the greatest effect on hydrolysis rate. The influence of surfactants is less noticeable. The presence of surfactants and especially of ammonium nitrate retards the rate of carbamide hydrolysis. The temperature rise significantly reduces braking effect of surfactants and ammonium nitrate. Maximal pH value is fixed, when hydrolysis degree is equal to 10-20 %. Maximal buffer capacity is achieved in the presence of ammonium nitrate only. At 353 K the formation rock does not affect the rate of hydrolysis and at 373 K and higher it significantly reduces the rate.

Kinetics of the summary reaction of hydrolysis carbamide, proceeding in the solutions of IKhN-KA system at the temperature ranging from 353 to 373 K at carbamide concentration ranging from 0.5 to 20 wt. %, follows reaction equation of the first order:

$$ln(1-\alpha) = -k\cdot\tau \qquad (4)$$

where k – hydrolysis rate constant, s^{-1}; τ - time, s.

At 373 K the order of the reaction is higher. The rate constant for carbamide hydrolysis increases from $1.4\cdot10^{-7}$ s^{-1} at 353 K to $140\cdot10^{-7}$ s^{-1} at 353 K. The following parameters of Arrhenius equation: E – activation energy and A – preexponential factor (E = 134 kJ/mol, A = $1.51\cdot10^{-13}$ s^{-1}) were calculated based on temperature - rate constant dependence in the reaction of carbamide hydrolysis.

Thus, CO_2 and oil-displacing fluids of IKhN system type with a high buffer capacity in pH region 9.0 – 10.5 are generated *in situ*. The technology of physico-chemical stimulation with IKhN-KA system combines the advantage of flooding by the solutions of alkalis and surfactants with the stimulation by CO_2.

Carbamide and ammonium nitrate are not sorbed by the rocks of oil fields. It promoted their application as indicator-tracers of filtration flows in the formation. Adsorption of surfactants from the solutions of IKhN-KA systems on the cores of West Siberian oil fields is lower as compared with that from surfactant solutions in water. At oil displacement with IKhN-KA systems mobility of filtrated fluid increased substantially. Core permeability increased by 6 – 60 %. Displacement efficiency increased by 13.2 – 21.9 % at rewashing, at the initial displacement it increased by 17.2 – 23.2 %.

In 1990—1992 pilot tests of EOR technologies involving IKhN-KA systems were carried out in oil fields of West Siberia with a high formation temperature. In Nivagalskoye oil field (formation Yu_1) IKhN-KA system slugs were injected into three injection wells. Bottomhole zones of the production wells in the test area were treated to increase well productivity due to disclaying of the bottomhole zone and removal of remains of drilling fluid filtrate. In Talinskoye oil field (formation YuK_{10-11}) bottomhole zones of six injection wells were treated. More than 2.5 thousand tons of IKhN-KA system was injected. Field tests proved the efficiency of IKhN-KA systems with respect to low permeable formations with a high temperature, their technological effectiveness and ecological safety. In 1991–1992 additional oil recovery was more than 40 thousand tons, oil recovery increased by 4.8–10.6 %.

EOR methods involving inorganic gel-forming systems

Conformance at flooding is an urgent problem for multilayer deposits consisted of hydrodynamically disconnected formations in oil zone, far from water-oil contact, since in this case a mechanism of displacement front levelling fails to work because of capillary and hydrodynamic cross-flows. Production wells are subjected to premature flooding at an earlier stage of their development. In this case it is desirable EOR methods increasing conformance to anticipate the methods increasing displacement factor.

Step curve of watering against accumulated oil withdrawal is a commercial indicator of hydrodynamically isolated layers. In the areas, where there are wells of such behaviour, it is advisable to use first EOR methods increasing conformance and then those ones increasing displacement factor.

In the course of several years physico-chemical and hydrodynamic aspects of gelation *in situ* are being studied at the Institute of Petroleum Chemistry SB RAS. Gel-forming systems are low viscous aqueous solutions under surface conditions, while under the formation conditions they convert into gels. Gelation proceeds under the influence of the formation heat energy or that of the injected heat carrier, as well as the result of interaction of the injected system with the formation fluids and rock-reservoir. Kinetics of gelation, rheological and filtration characteristics of various gels have been studied for heterogeneous formations with permeability ranging from 0.01 to 10 μm^2. Proposed are gel-forming systems with different time of getation – from some minutes to several days – in temperature range from 40 to 200°C. Based on these systems three gel-technologies have been developed to enhance oil recovery from highly heterogeneous formations. The technologies are commercially used in oil fields of West Siberia [6, 18-20].

Technologies involving inorganic gel-forming systems are effective to increase conformance at the injection of water or steam at 0 – 300°C. The capacity of the system aluminium salt – carbamide – water – surfactants to generate inorganic gel and CO_2 *in situ* is used. Gel-forming solutions based on this system are low viscous liquids with pH ranging from 2.5 to 3.5. They are not mixed with oil and form no stable emulsions. One can prepare them using water of any salinity. The solutions cause no clay swelling, but are capable, due to their acidity, to dissolve carbonate minerals of oil-reservoir rock. Gel-forming systems are environmentally appropriate. The products of national industry are used for their preparation. To realize the technology homogeneous aqueous solution containing gel-forming system is injected into the formation. Due to heat energy of the formation or that of the injected heat carrier carbamide is gradually hydrolysed to yield CO_2 and ammonia, pH of the solution increases and hydrolysis of aluminium ions occur. When pH value reaches 3.8-4.2, the gelation of aluminium hydroxide proceeds practically instantly in the whole volume of the solution (Fig. 4). Time of gelation depends on the formation temperature and component ratio being independent of dilution ratio. Based on kinetic studies of carbamide hydrolysis and that of gelation in a gel-forming solution at 70 - 120°C it has been determined that kinetics of gelation in the system is defined by kinetics of carbamide hydrolysis, the rate of which is much lower as that of coagulation process of aluminium hydroxide gelation. The latter is carried out as a cooperative process similar to a change of phase. The effect of temperature on gelation time is subject to Vant-Hoff rule: at temperature rise each 10 degrees time of gelation increases 3.5 times. Thus for a definite system it is 6 hours at 100°C, 1, 3, 6 and 30 days at 90, 80, 70 and 60°C, respectively. Besides temperature the ratio of carbamide content to aliminium salt in the solution produces noticeable effect on the time of gelation. Thus at increased carbamide content at a given concentration of aluminium salt the time of gelation decreases. Specifing carbamide-aliminium salt ratio one can regulate the time of gelation.

Capillary rotary and vibration viscosimetries were used to study rheological properties of gels and sols, formed in the system aluminium salt – carbamide – surfactant – water within 70–120°C. Aluminium hydroxide gel has been determined to be a thixotropic pseudoplastic solid-like body of a coagulation structure. Due to gelation formation permeability for water decreases. A degree of permeability decrease is as higher as higher is the initial water saturation and permeability of the formation rock. The effect of gel on filtration characteristics of solid samples from collector polymictic rock has been studied for oil fields of West Siberia. Under reservoir simulated conditions gel decreases water mobility 4—35 times. Static shear stress for gel in the formation model depends on the concentration of gel-forming solution and ranges from

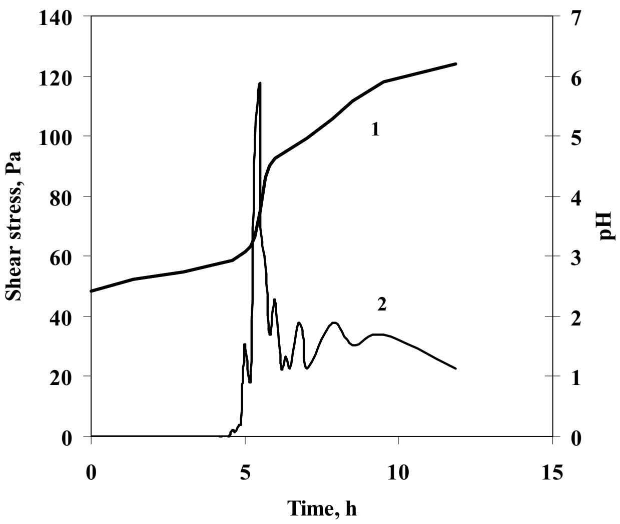

Fig. 4. pH (1) and shear stress (2) changes occurring in gel-forming solution during thermostatting at 97°C.

3 to 8 Pa for gels containing no surfactant and from 10 to 40 Pa – for gels containing surfactants.

A principle of interformational gelation was used to develop thickened IKhN-KA and gel-forming GALKA and GALKA – surfactant systems. By injection of additional components it is possible to control their surfactant, rheological and kinetic parameters for the purpose of adapting to concrete geological-physical conditions.

In 1989-1995 pilot tests of EOR technology were successfully carried out in oil fields of West Siberia. Inorganic gel-forming GALKA systems were injected into high-temperature formations (above 70°C) to increase conformance. As a result of EOR technology employment one can observe rearrangement of filtration flows, and conformance increase resulting in the enhancement of oil recovery by 3-8 items. Additional oil recovery ranges from 400 to 3000 t per 1 well/treatment.

GALKA system includes aluminium chloride and carbamide, the products of large-scale manufacture. Besides GALKA systems have been developed, where industrial alumo-containing waste was used instead of aluminium chloride. It reduced the price of the system 3-5 times. In 1996-1997 pilot tests of water-shutoff GALKA systems based on alumo-containing industrial waste were successfully carried out in oil fields of West Siberia. GALKA system was injected in 14 injection wells in the volume of 13-46 m^3 per well. In 2-3 months after injection production wells, which are hydrodynamically connected with the injection ones, reacted by a decreased volume of the produced water and by increased oil flow rate (Fig. 5). Pilot production of GALKA system concentrate is launched from alumo-containing waste. It is delivered by tank wagons. Concentrate freezing point is minus 20 - 25°C. It enables to work all year round. In 2000 IPC SD RAS jointly with Joint-Stock Company «Khimeko-GANG» arranged the production of GALKA system in solid granules.

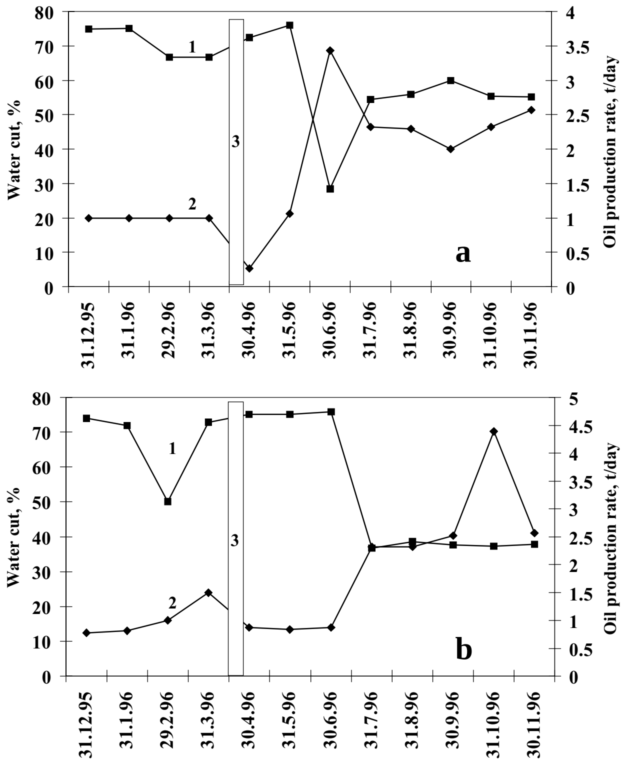

Fig. 5. The results obtained on the injection of GALKA system in injection well 1119 in the pilot area of formation Yu_1, Pokachevskoye oil field. Production wells 1120 (a), 1130 (b): 1 – overflooding, 2 – oil production, 3 – injection of GALKA system.

In 1997-2000 GALKA system was commercially used in oil fields of West Siberia. For example, in 1999 GALKA system was injected into 41 injection wells in 8 oil fields of West Siberia, i.e. Yuzhno-Surgutskoye, Pravdinskoye, Severo-Salymskoye, Sredne-Asomkinskoye, Vostochno-Surgutskoye, Petelinskoye and Maiskoye. In Maiskoye oil field the injection was performed by means of group pumping station (GPS) into 26 wells. 225.5 thousand tons of oil were recovered in addition. Specific technological effect amounted for 3.4 thousand tons per one well-treatment. The duration of the effect was more than 12 months. Period of payback was 5-9 months. In 2000 the technology based on GALKA system was applied in 5 oil fields of Joint Stock «Yuganskneftegaz» in the network of investment projects. During the first 6 months 50 wells were treated, including 1 well in Maiskoye oil field, which was treated twice. About 12 thou m^3 of the working solution (1184 t of commercial reagent) were injected. Additional oil production amounted for 31.3 thousand tons as of October 1, 2000; specific technological effect was 1.6 thousand tons per one well-treatment. The effect is still in progress. Good results were obtained for high-temperature formation of Yu group in Yuzhno-Surgutskoye and Vostochno-Surgutskoye oil fields, where specific technological effect amounted for 1.6-2.2 thou.t/well-treatment. Thus the treatment of four wells in Vostochno-Surgutskoye oil field was performed in the zones of the greatest withdrawals in June 2000. It reduced water cut up to 7 % and as a consequence enhanced oil recovery. Additional oil recovery amounted for 9.0 thousand tons. Oil production increase by 30 % and stimulation effect is still in progress. Total technological effect with respect to well treatment in Sredne-Asomkinskoye oil field will be estimated later, since major wells were treated only in September 2000 and stimulation effect is still under way.

EOR methods involving thermoreversible polymer gels

A novel method has been developed to enhance oil recovery from highly heterogeneous formations via regulation of filtration flows and conformance increase by thermoreversible polymer gels [21-23], which are formed from the solutions with lower critical solution temperature. Formation heat energy is a factor causing gelation. The main feature of the method is as follow: at low temperatures the solutions are low viscous and at high temperatures they convert into gels. It is a reversible process – at cooling gel becomes again low viscous and at reheating it converts into gel. One can repeat the process many times. Cellulose ethers (CE) are considered as the most promising polymers. CE viscosity dependence within 20 - 95°C is of extreme character – at the beginning of heating viscosity decreases and then at further heating viscosity increases (Fig. 6). As a result the solution is converted into gel. One can regulate temperature and time of gelation ranged from 40 to 120°C by inorganic and organic additives, adapting temperature and water salinity to the concrete formation conditions (Figs. 7, 8). Gels are stable up to 200 - 250°C and may be effectively used to decrease water cut, to prevent gas breakthrough and to liquidate gas cones.

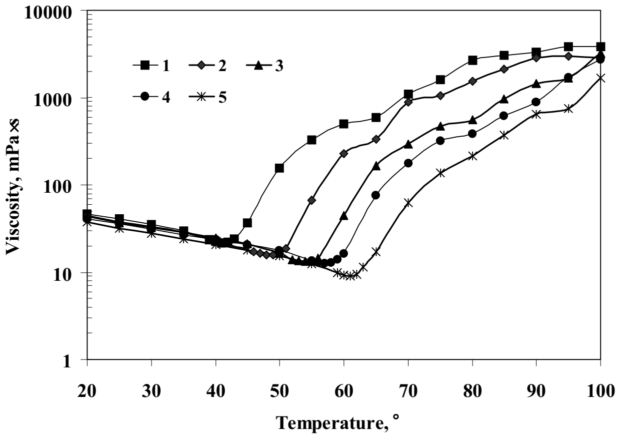

Fig. 6. Viscosity dependence of 1 % solutions of cellulose ether on the temperature at different salinity of the formation waters. Salinity, g/L: 1 – 60, 2 – 30, 3 – 15, 4 – 7.5, 5 – 0.

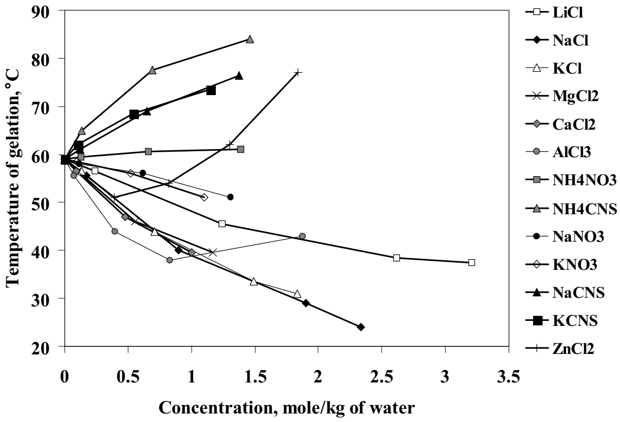

Fig. 7. The effect of electrolytes on the temperature of gelation for the solutions of cellulose ether.

The effect of complex-forming electrolytes and non-electrolytes on phase equilibrium and kinetics of gelation has been studied for thermoreversible polymer gels, which are formed in the system cellulose ether with a lower critical solution temperature (LCST) – aqueous phase (Figs. 7, 8). Anions exert the greatest influence upon the change of gelation temperature for CE solutions. Their influence correlates with the position in lyotropic series. The influence of cations is essentially smaller. The position of ions in lyotropic series is concerned with hydration, the formation of liquid hydrates (aqua-complexes) and with the values of their instability constants. It has been determined that large monovalent ions of K^+, Rb^+, Cs^+, Ag^+, NO_3^- and $H_2PO_4^-$ types are not able to form liquid

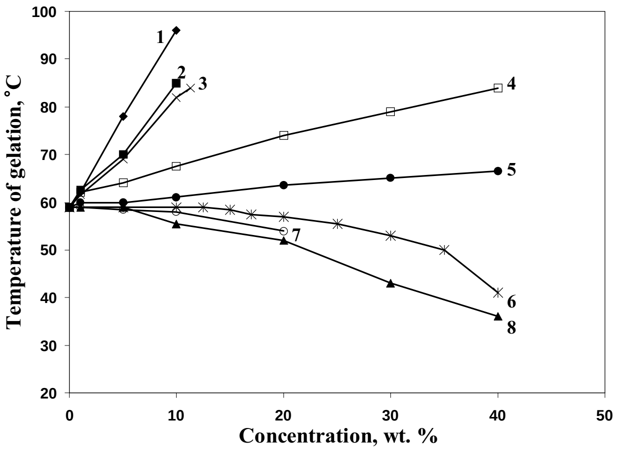

Fig. 8. The effect of non-electrolytes on the temperature of gelation for the solutions of cellulose ether: 1 – thiourea, 2 – isopropyl alcohol, 3 - ethyl alcohol, 4 - carbamide, 5 – triethanolamine, 6 – ethylene glycol, 7 – polyglycol, 8 – glycerin.

hydrates of certain stereochemical composition, while $(H_3O)^+$, Li^+, Na^+, Cl^-, Br^-, I^- and others form such liquid hydrates. Thus, in the range 1-10.8 m at 25°C liquid hydrate $[Na(H_2O)_4]^+$ has instability constant K = 0.34, whereas under similar conditions hydrate $[Li(H_2O)_4]^+$ has K = 0.022, which speaks about high stability of this hydrate. Anions Cl^- or CNS^- are located at the opposite ends of lyotropic series, ion NO_3^- – in the middle. The salts containing anion Cl^- cause the greatest LCST decrease. The salts containing CNS^- on the contrary increase LCST. NaCl, the both ions of which form hydrates, cause the greatest LCST decrease. Thiourea, ethyl and isopropyl alcohols significantly increase LCST. The effect of electrolytes and non-electrolytes has been determined to be additive.

The researches enabled us to select optimal gel-forming systems for EOR technologies due to decreased water cut at flooding and at heat stimulation of the formation. Gel-forming METKA systems and technologies involving these systems have been developed to increase conformance and to reduce water cut. Low viscous aqueous solution, capable to generate gel under the formation conditions at 40-120°C, is injected into the formation. Gel screen is formed in a highly permeable part of the formation, in which the main portion of the system falls, causing rearrangement of filtration flows. The injection of METKA system into injection wells equalises their injectivity profiles, decreases water cut and thereby increases oil flow rate of the production wells, which are hydrodynamically connected with the injection ones. METKA systems are easy to manufacture, the best polymer solubility in water is achieved at 0-10°C. The technologies are economically effective and ecologically safe. The technologies require standard oil field equipment. One can use the technologies to regulate filtration flows in heterogeneous oil formations, to reduce water cut at the injection of water or steam and to eliminate gas breakthrough. Due to ecological safety of agents and their absolute harmlessness for people one can employ the technology at mining oil production.

In 1996-1997 EOR technologies involving thermoreversible gels were successfully tested in oil fields of West Siberia. In 1996 METKA systems were injected into 11 and in 1997 - into 47 injection wells with a volume of 50-100 m^3 per well. In 2-3 months after injection the production wells, which are hydrodynamically connected with the injection wells, respond by decreased volumes of the produced water and increased oil production rate. Since 1998 Oil Company «LUKOIL» employs the technology in oil fields of West Siberia. During 1998-2000 gel forming systems were injected into 158 wells. Additional oil production was 194.5 thousand tons. Period of payback was 5-9 months. All agents are the products of large-tonnage commercial production. The efficiency averages 1630 tons per one well-treatment. Period of payback is 5-9 months.

Now novel complex methods and technologies are being developed to enhance oil recovery from low permeable highly heterogeneous reservoirs, as well as from oil fields at a later stage of their development and from oil fields of high viscosity oils via sequential influence of gel forming systems increasing conformance and oil-displacing systems, which intensify the development.

Thus, taking into account tendencies in oil producing industry mentioned above and high oil prices one can predict strong growth of the interest in physico-chemical EOR methods and in expansion of their application.

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Received 28 June 2001.