Enhanced Oil Recovery for Deposits of High Viscosity Oils Using Multifunctional Systems Based on Surfactants

L K Altunina, V A Kuvshinov, L A Stasieva and I V Kuvshinov
1Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences (IPC SB RAS), 4, Akademichesky Avenue, 634055, Tomsk, Russia
2National Research Tomsk State University, 634050 Tomsk, Lenin Avenue, 36

E-mail: alk@ipc.tsc.ru

Abstract. To enhance the oil recovery of high-viscosity oil deposits in the temperature range of 20-210 °C, the multifunctional composition based on surfactants, aluminum and ammonium salts, an adduct of inorganic acid, carbamide and polyol with an adjustable viscosity and high oil-displacing ability was created. The composition has a low interfacial tension, a high buffer capacity in a wide pH range, 2.5-10 units pH, a delayed reaction with carbonate rocks, prevents the precipitation of insoluble reaction products, increases the permeability of reservoirs. The composition is both oil-displacing and flow-diverting, provides an enhance in the oil recovery factor (ORF) due to the increase in the oil displacement and formation sweep by water or steam flooding. Practical recommendations are given on the application of the composition at the Permian-Carboniferous deposits of the Usinsk oilfield.

1. Introduction
Nowdays, heavy and highly viscous oils are considered as the main reserve of world oil production. For the effective development of hard-to-recover oil reserves, including highly viscous oil, and for further increase in its production, it seems promising the widespread use of new integrated technologies for enhancing oil recovery, combining the basic effect of water or steam injection with physicochemical methods that increase the formation sweep and the oil displacement coefficient with simultaneous intensification of production [1-7].

A promising trend is the creation of the most autonomous oil recovery enhancement systems based on the use of “smart” compositions of chemical reagents, unpretentious to the climatic conditions of transportation and storage, not requiring additional preparation for field application and capable of maintaining high oil displacing activity for a long time, as well as increase the reservoir sweep by flooding or other active treatment [8-10].

In the work of the Institute of Petroleum Chemistry of the SB RAS (IPC SB RAS), this approach is implemented by creating “smart” compositions based on thermotopic inorganic and polymer gel-forming and sol-forming compositions with adjustable viscosity and density directly generated in the formation, as well as oil-displacing compositions based on surfactants with adjustable viscosity and alkalinity for injection in oil reservoirs in order to enhance oil recovery, reduce water cut in producing wells and intensify oil production in difficult operating conditions, including fields of high-viscosity oils, both developed using thermal and non-thermal methods [8-11].

Since 2003, on the Permian-Carboniferous deposit of high-viscosity oil of the Usinsk oilfield, LLC “LUKOIL-Komi”, together with IPC SB RAS and enterprises of LLC “LUKOIL-Engineering” and LLC “OSK”, have been conducting field tests of complex technologies of steam-thermal and...
physicochemical treatment with the aim of increase oil recovery and performing full scale industrial application of the developed technologies, as well as “cold” physical and chemical technologies to enhance oil recovery and intensify the production of heavy oil under natural conditions, without heat treatment, with the use of such compositions [9-12].

2. Acid and alkaline compositions based on surfactants and buffer systems
To enhance oil recovery and intensify the development of highly viscous oil fields, a prolonged-action acidic oil-displacing composition based on surfactants, an adduct of inorganic acid and polyhydric alcohol (GBK composition) was created at the Institute of Petroleum Chemistry SB RAS [8, 9]. The composition has a high buffer capacity in the acidic pH range, 2÷4 units pH, compatible with saline formation waters, has a low freezing temperature (minus 20÷minus 60 °C), low interfacial tension at the contact with oil, is applicable in a wide temperature range, from 10 to 200 °C, is most effective in carbonate reservoirs, in particular Permian-Carboniferous deposits of the Usinsk oilfield. The composition has a delayed reaction with carbonate rocks. As a result of the interaction of the GBK composition with the carbonate reservoir, CO₂ is released, which dissolves in oil and reduces its viscosity by 1.2–2.7 times, which helps to increase the oil recovery factor.

The composition showed high efficiency in pilot tests on the Permian-Carboniferous deposits of heavy oil of Usinsk oilfield (Figure 1, a) and was recommended for full-scale industrial application to increase oil recovery and intensify oil production by increasing the permeability of reservoir rocks and productivity of oil wells.

![Average oil production rate per month before and after GBK injection](image1.png)

Figure 1. Results of field tests on the Permian-Carboniferous deposits of the Usinsk oilfield: (a) – acid composition GBK, average value of monthly oil production rates for production wells for a period of 19 months. before and after treatment; (b) – an increase in il production rates and a decrease in water cut before and after injection of the NINKA-Z composition in 2014-2015 to steam injection wells

To increase the oil recovery of highly viscous oil fields by heat and steam, a thickened oil-displacing composition based on surfactants, ammonium salts, aluminum and carbamide (a thickened composition NINKA-Z) was created at the Institute of Petroleum Chemistry SB RAS. The composition, as a result of chemical evolution in the formation, becomes both a flow-diverting and oil-displacing nanostructured system [8, 9, 11]. In the formation, when exposed to heat, the composition generates CO₂, an alkaline ammonia buffer system with a maximum buffer capacity in the alkaline pH range, 8–10.5 units pH, and sol of aluminum hydroxide. As a result, the coefficients of reservoir coverage and oil recovery increase. In 2014-2015 field tests of the NINKA-Z composition were successfully carried out in the steam-thermal section of the Permian-Carboniferous deposit of the Usinsk oilfield (Figure 1, b). The composition was injected into 7 steam injection wells in a section with 75 production wells. The injection volume is 80-110 m³ per well. The total effect on the site amounted to 70 thousand tons of additional oil. The composition was recommended for industrial use.
3. Multifunctional composition based on surfactants and complex buffer systems

In development of the above work, as a result of experimental studies, a multifunctional composition (MFC) was created on the basis of the surfactants – polybasic acid – carbamide – polyol – aluminum salt – ammonium salt – water system with adjustable viscosity and high oil displacement ability at the temperature range 20–210 °C. The composition has a high buffer capacity in a wide pH range, 2.5÷10.5 units pH, low interfacial tension and low freezing point (minus 20÷minus 50 °C), a delayed reaction with carbonate rocks, is compatible with mineralized formation waters, prevents the precipitation of insoluble reaction products, increases the permeability of reservoirs. As the base, three MFC compositions were created: MFC-1, MFC-2 and MFC-3. MFC-2 contains an increased amount of polyol and is recommended for low formation temperatures, MFC-3 contains an increased amount of carbamide and is recommended for high temperatures, MFC-1 is the most universal.

At low temperatures, 20-70 °C, MFC is acidic, similar to the composition of GBK, but more effective, since it has a lower pH due to the influence of the Al salt. High buffer capacity in the acidic pH region, Figure 2, and adjustable viscosity are ensured by the presence of a polyol and complexes of Al salt with polybasic acid ions, in particular, borate ions. In the temperature range of 70 °C and above, where the polyol viscosity decreases, the adjustable viscosity of the composition and the high buffer capacity in the alkaline pH range are provided by a different mechanism. The carbamide, included in the composition, is hydrolyzed by heat exposure to generate CO$_2$, which dissolves in oil and reduces its viscosity, and ammonia NH$_3$, which, with boric acid and ammonium salt, gives an alkaline borate-ammonia buffer system, Figure 2, that is optimal for oil displacement. This ensures maximum oil displacement and minimal adsorption of surfactants on the formation rock.

![Figure 2](image_url). The pH dependence of the composition solution buffer capacity before and after thermostating at a temperature of 90 °C for 24 hours

An increase in pH also causes hydrolysis of the aluminum salt to form an Al hydroxide sol, as in the thickened NINKA-3 composition, while the viscosity of the composition will increase by 1-2 orders of magnitude. The viscosity of the compositions is controlled by the concentration of Al salt. The increase in viscosity of multifunctional compositions leads to an increase in the formation sweep by thermal exposures, the inclusion of low-permeability layers, a decrease in the viscosity of the oil and its washing out.

The study of the rheological properties of MFCs before and after thermostating at various temperatures was carried out by the method of rotational viscometry using rotational viscometer of the HAAKE Viscotester iQ Rheometer (measuring system of coaxial cylinders CC25 DIN/Ti). The required amount of the composition solution or sol (gel) obtained from the composition solution after thermostating at temperatures of 90 and 150 °C was placed in the cell of the rheometer. Then, at a temperature of 20 °C and various shear rates from 1 to 1200 s$^{-1}$, rheological curves of the flow of solutions were obtained and viscosity values were determined before and after thermostating, Figure 3. As can be seen from the Figure 3, before thermostating, the composition solutions are classical
Newtonian liquids, after the formation of sol (gel) at a temperature of 90-150 °C become either pseudoplastic or visco-plastic fluids, with an increase in viscosity from 3.7-47.6 to 132.4-344.3 mPa·s.

Figure 3. Rheological flow curves and viscosity of solutions of the MFC-1 composition before and after temperature control at a temperature of 90 °C

It was experimentally established that after thermostating of oil at 90-250 °C with the compositions, oil pour point decreases by 11-16 degrees and the viscosity of oil decreases by a factor of 2-5, Figure 4.

Figure 4. Temperature dependences of Usinsk oilfield oil viscosity before and after thermostating at 90-250 °C with water and MFC-3 (vibrational viscometry method)

A series of experiments on studying the filtration characteristics of heterogeneous reservoir models and assessing the oil-displacing ability of MFCs for the conditions of the Permian-Carboniferous deposit of the Usinsk oilfield at 20-210 °C showed that there is an equalization of filtration flows and an increase in the oil displacement coefficient (5.4 – 43.4 %), which depends on the ratio of permeabilities patterns and volume of composition injected.

4. Conclusions
A multifunctional composition based on surfactants, aluminum and ammonium salts, an adduct of inorganic acid, carbamide and polyol with an adjustable viscosity and high oil displacing ability in the temperature range of 20–210 °C was created. The composition has a low interfacial tension, a high buffer capacity in a wide pH range, 2.5–10 units pH, a delayed reaction with carbonate rocks, prevents the precipitation of insoluble reaction products, increases the permeability of reservoirs.
The composition is both oil-displacing and flow-diverting, provides an increase in oil recovery factor due to an increase in the displacement and coverage factors of the formation by water flooding or heat and steam. It is recommended for pilot tests with the aim of increasing the recovery factor in combination with the injection of hot water for the conditions of the Permian-Carboniferous deposit of the Usinsk oilfield. The composition includes available on the Russian market and environmentally friendly common industrial products.

Acknowledgments
This work was carried out as part of the state assignment of the Institute of Petroleum Chemistry of the SB RAS (project V.46.2.3 of the Program for Basic Scientific Research of State Academies of Sciences “Physical chemistry and rheology of oil and polydisperse oil-containing systems in the processes of enhanced oil recovery and transportation”), funded by the Ministry of Science and Higher Education of the Russian Federation.

References
[1] Donga X, Liua H, Chen Z, Wua K, Lua N and Zhanga Q 2019 Applied Energy 239 1190–1211
[2] Wang Y, Hou J, Song Z, Yuan D, Zhang J and Zhao T 2018 SPE Reservoir Evaluation & Engineering 21(01) 109–121
[3] Romero-Zeron L 2016 Chemical Enhanced Oil Recovery (cEOR). A Practical Overview (InTech) 191 DOI: 10.5772/61394.
[4] Raffan P, Broekhuis A A and Picchioni F 2016 Journal of Petroleum Science and Engineering 145 723–733
[5] Abass A 2014 Olajire Energy 77 963–982
[6] Ruzin L M, Morozyuk O A and Durkin S M 2013 Oil industry 8 51–53
[7] Hascakir B 2017 Journal of Petroleum Science and Engineering 154 438–441
[8] Altunina L, Kuvshinov V, Stasieva L, Kuvshinov I 2018 Chemistry for Sustainable Development 26 (3) 261–277
[9] Altunina L, Kuvshinov V, Kuvshinov I, Stasieva L, Chertenkov M, Shkrabyuk L and Andreev D 2017 Oil industry 7 26–29
[10] Altunina L K, Kuvshinov V A, Kuvshinov I V, Chertenkov M V and Ursegov S O 2015 Proc. SPE Russian Petroleum Conference, Moscow, Paper 176703–MS
[11] Altunina L K, Kuvshinov V A, Kuvshinov I V, Stasieva L A, Chertenkov M V, Andreev D V and Karmanov A Yu 2018 Journal of Siberian Federal University. Chemistry 11 (4) 462–476
[12] Kuvshinov I V, Altunina L K and Kuvshinov V A 2019 Journal of Siberian Federal University. Chemistry 12 (4) 473–482 DOI: 10.17516/1998-2836-0143