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Multifunctional Composition Based on Surfactants and a Complex of Buffer Systems to Enhance Oil Recovery of High-Viscosity Oil Deposits

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Abstract. To enhance oil recovery of high-viscosity oil deposits in the temperature range of 20-210 °C, a multifunctional composition with adjustable viscosity and high oil-displacing ability has been developed based on surfactants, aluminum and ammonium salts, an adduct of inorganic acid, carbamide and polyol. High buffer capacity of the composition in a wide pH range, 2.5-10 units pH, is provided by a complex of buffer systems: in the acidic range of pH, 2.5-4.0, the system "polyolboric acid and its salt", in the alkaline range of pH – anammonia-borate buffer system. The composition has a low interfacial tension, a prolonged reaction with carbonate rocks, prevents the precipitation of insoluble reaction products, and increases the permeability of reservoirs. The composition is both oil-displacing and flow-diverting, it provides an enhance in the oil recovery factor, both due to the increase in the displacement factor and the the reservoir sweep by waterflooding or thermal steam stimulation.

Keywords: high-viscosity oil, enhanced oil recovery, physicochemical technologies, surfactant compositions, buffer systems, polyol, rheology, sols.

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Многофункциональная композиция на основе ПАВ и комплекса буферных систем для увеличения нефтеотдачи залежей высоковязких нефтей

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Аннотация. Для увеличения нефтеотдачи залежей высоковязких нефтей в области температур 20–210 °C создана многофункциональная композиция с регулируемой вязкостью и высокой нефтевытесняющей способностью на основе ПАВ, солей алюминия и аммония, аддукта неорганической кислоты, карбамида и полиола. Высокая буферная емкость композиции в широком диапазоне pH, 2.5–10 ед. pH обеспечивается комплексом буферных систем: в кислой области pH, 2.5–4.0 ед. pH, системой «полиолборная кислота и ее соль», в щелочной области pH – аммиачно-боратной буферной системой. Композиция имеет низкое межфазное натяжение, пролонгированную реакцию с карбонатными породами, предотвращает образование нерастворимых продуктов реакции, увеличивает проницаемость пластов-коллекторов. Композиция является и нефтевытесняющей, и потокоотклоняющей, обеспечивает увеличение коэффициента извлечения нефти (КИН) за счет как прироста коэффициента вытеснения, так и охвата пласта заводнением или паротепловым воздействием.

Ключевые слова: высоковязкая нефть, увеличение нефтеотдачи, физико-химические технологии, композиции ПАВ, буферные системы, полиол, реология, золи.

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Introduction

The share of heavy, high-viscosity oils in oil production is steadily increasing and they are currently regarded as the main reserve of world oil production. For their effective development and further increase in production, it seems promising to use large-scale new integrated technologies for enhanced oil recovery, combining the basic treatment of the reservoir by water or steam injection with physicochemical methods that increase the reservoir coverage and oil displacement ratio with simultaneous development intensification [1–4].

To increase the oil recovery of high-viscosity oil deposits, there is a promising tendency to create the most autonomous systems for enhancing oil recovery based on the use of «smart» compositions of chemical reagents that are unpretentious to the climatic conditions of transportation and storage, do not require additional preparation for use in the field and are capable of maintaining high oil-displacing activity for a long time after injection into the reservoir, as well as to increase the degree of reservoir coverage by waterflooding or other active treatments [5–9].

At the Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences (IPC SB RAS), this trend is implemented through the development of physicochemical methods based on the creation of gel-forming and oil-displacing «smart» compositions that generate thermotropic inorganic and polymer gels and sols with adjustable viscosity and density, as well as oil-displacing liquids directly in the reservoir, based on surfactants with adjustable viscosity and alkalinity for injection into oil reservoirs in order to enhance oil recovery, reduce water cut of production wells and intensify oil production in difficult operating conditions, including for high-viscosity oil fields developed with and without thermal methods [9–12].

At the Permian-Carboniferous high-viscosity oil reservoir of the Usinsk oilfield, Ltd. LUKOIL-Komi jointly with the IPC SB RAS, Ltd. LUKOIL-Engineering and Ltd. OSK, since 2002, have been conducting field tests of integrated technologies for thermal steam and physicochemical treatment in order to increase oil recovery, and industrial use of the developed technologies, as well as «cold» physical and chemical technologies for enhanced oil recovery and intensification of heavy oil production under natural conditions, without thermal effects using «smart» compositions [12–16].

This paper presents the results of laboratory studies and field tests of acid and alkaline oil-displacing compositions based on surfactants and buffer systems to increase oil recovery of high-viscosity oil deposits under natural development and under thermal steam treatment, as well as laboratory studies of physicochemical, acid-base and rheological properties in the system «surfactant – polybasic acid – carbamide – polyol – aluminum salt – ammonium salt – water», which made it possible to create a multifunctional composition with adjustable viscosity and high oil-displacing ability.

Acid and alkaline compositions based on surfactants and buffer systems

Within the framework of a unified theoretical approach, acid and alkaline oil-displacing compositions based on surfactants and buffer systems have been created – an acidic composition named GBK and an alkaline composition named NINKA-Z.

The GBK composition based on surfactants, adduct of an inorganic acid and a polyhydric alcohol [9, 13, 15] has a high buffer capacity in the acidic pH range, 2–4 units pH, compatible with saline formation waters, has a low freezing point (minus 20 ÷ minus 60 °C), low interfacial tension at the boundary with oil, is applicable over a wide temperature range, from 10 to 200 °C, is most effective in carbonate reservoirs due to prolonged action on the rock. As a result of the GBK composition interaction with the carbonate reservoir, CO_2 is released, which dissolves in oil and reduces its viscosity by 1.2–2.7 times, this contributes to an increase in the degree of oil recovery. The composition showed high efficiency in field tests on the Permian-Carboniferous heavy oil reservoir of the Usinsk oilfield (Fig. 1A), and was recommended for industrial use to improve oil recovery and enhance oil production by increasing the permeability of reservoir rocks and the productivity of producing wells.

Composition NINKA-Z is a thickened oil-displacing composition based on surfactants, ammonium and aluminum salts and carbamide, which, as a result of chemical evolution in the reservoir, simultaneously becomes a flow-diverting and oil-displacing nanostructured system [9, 13, 14]. In the

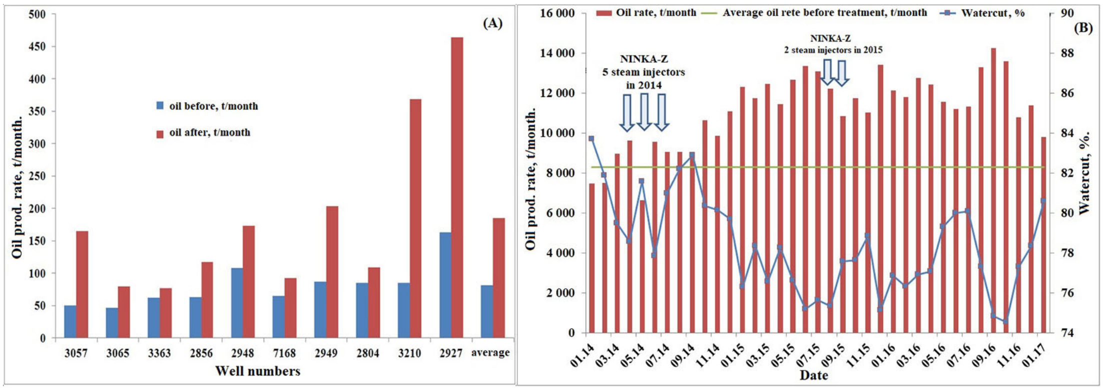

Fig. 1. Results of field tests on the Permian-Carboniferous deposit of the Usinskoilfield: A – acid composition GBK, the average value of monthly oil rates for producing wells for a period of 19 months, before and after processing; Б – an increase in oil production rates and a decrease in water cut before and after injection of the NINKA-Z composition in 2014–2015 in steam injection wells

reservoir under high temperature condition, the composition forms CO_2, an alkaline ammonia buffer system with a maximum buffer capacity in the alkaline pH range, 8 ÷ 10.5 units pH, and aluminum hydroxide sol. As a result, the reservoir coverage and oil recovery factors increase. In 2014–2015 field tests of the NINKA-Z composition were successfully carried out at the site of the continuous steam injection at the Permian-Carboniferous deposit of the Usinsk field (Fig. 1b). The composition was injected into 7 steam injection wells in an area with 75 production wells. Injection volume was 80–110 m^3 per well. The total effect on the site was 70 thousand tons of extra produced oil. The composition was recommended for application at industrial scale.

Multifunctional composition based on surfactants and complex buffer systems

In the development of these works, as a result of experimental studies, a multifunctional composition (MFC) was created based on the system «surfactant – polybasic acid – carbamide – polyol – aluminum salt – ammonium salt – water» with adjustable viscosity and high oil-displacing ability in the temperature range of 20–210 °C. Boric acid was used as the polybasic acid, and glycerol was used as the polyol. The composition has a high buffer capacity in a wide pH range, 2.5 ÷ 10.5 units pH, which is provided by a complex of buffer systems: in the acidic pH range, 2.5 ÷ 4.0, a buffer system formed by polyolboric acid and its salt works, in the alkaline pH range – an ammonia-borate buffer system. MFC has a low interfacial tension and a low freezing point (minus 20 ÷ minus 50 °C), a prolonged reaction with carbonate rocks, is compatible with saline formation waters, prevents the precipitation of insoluble reaction products, and increases the permeability of reservoirs. Three MFC compositions were identified as the base ones: MFC-1, MFC-2 and MFC-3. MFK-2 contains an increased amount of polyol and is recommended for low reservoir temperatures, MFK-3 – an increased amount of carbamide and is recommended for high temperatures, MFK-1 is the universal (basic) one.

At low temperatures, 20–70 °C, MFC is acidic, similar to the GBK composition, but more effective, since it has a lower pH value due to the influence of the Al salt. High buffering capacity in the acidic pH range, Fig. 2, and adjustable viscosity are provided by the presence of complexes of the polyol and Al salt with polybasic acid ions, in particular, borate ions.

In the temperature range of 70 °C and above, where the viscosity of the polyol decreases, the controlled viscosity of the composition and a high buffer capacity in the alkaline pH range are provided by a different mechanism. Carbamide, which is part of the composition, hydrolyzes under thermal condition to form CO_2, which dissolves in oil and reduces its viscosity, and ammonia NH_3, which with polyolboric acid and ammonium salt gives an alkaline borate-ammonium buffer system, Fig. 2, optimal for oil displacement purposes. This provides maximum oil displacement and minimum adsorption of surfactants on the formation rock.

An increase in pH also causes hydrolysis of the aluminum salt with the generation of an Al hydroxide sol, as in the thickened NINKA-Z composition, while the viscosity of the MFC will increase by 1–2 orders of magnitude, but the composition remains mobile. The viscosity of the composition is controlled by the concentration of the Al salt. An increase in the viscosity of the MFC leads to an increase in the sweep of the reservoir by thermal treatment, the connection to production of low-permeability interlayers, a decrease in the viscosity of oil and its additional washing.

The study of the rheological properties of MFC before and after thermostating at various temperatures was carried out by the method of rotational viscometry using a rotational viscometer Rheometer HAAKE Viscotester iQ (measuring system of CC25 DIN / Ti coaxial cylinders). The required amount of the composition or sol (gel) obtained 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}, the rheological curves of the composition flow were obtained and the values of the viscosities before and after thermostating were determined, Fig. 3.

As can be seen from the figure, before thermostating, the compositions are classical Newtonian liquids, after the formation of a sol (gel) at a temperature of 90–150 °C, they become either pseudoplastic or visco-plastic liquids, with an increase in viscosity from 3.7–47.6 to 132.4–344.3 mPa · s.

It has been experimentally established that after thermostating oil at 90–250 °C with the composition, its pour point decreases by 11–16 degrees and the oil viscosity decreases by 2–5 times, Fig. 4.

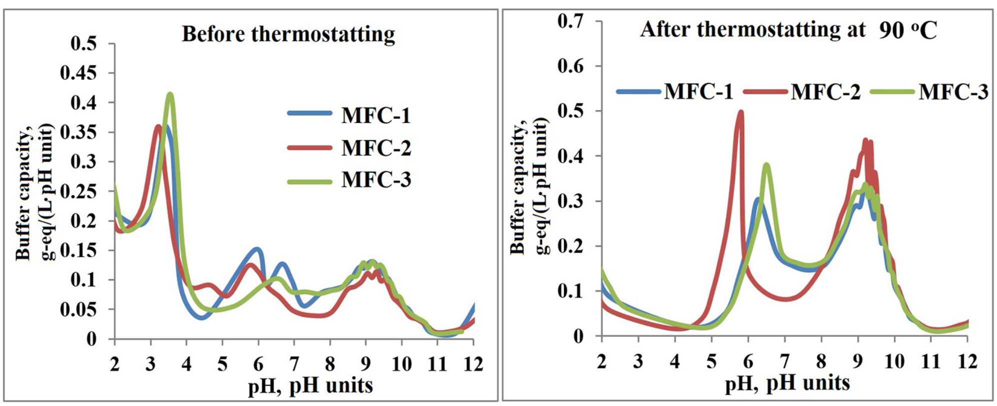

Fig. 2. Dependence of the buffer capacity of the MFC compositions on pH before and after thermostating at 90 °C for 24 hours

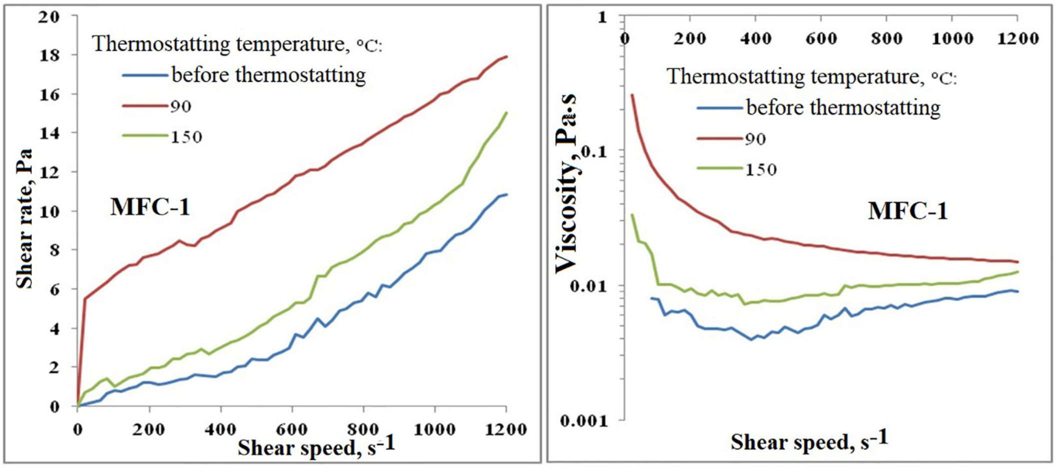

Fig. 3. Rheological flow curves and viscosity of the MFC-1 composition before and after thermostating at a temperature of 90 °C

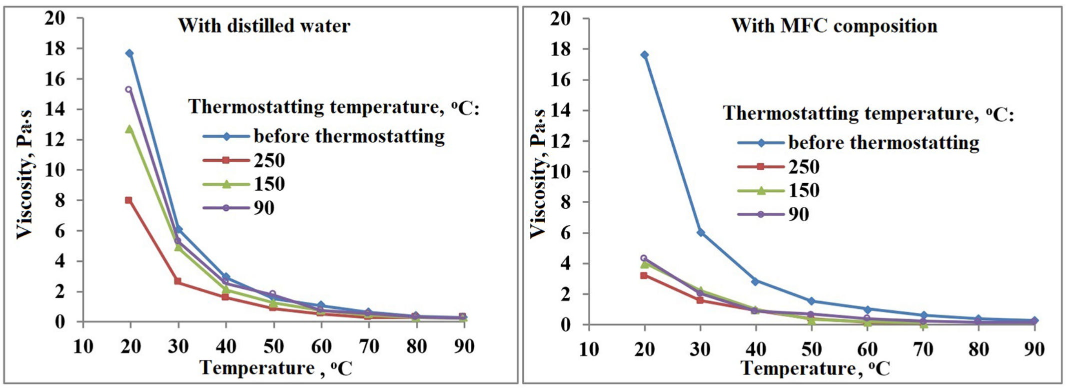

Fig. 4. Temperature dependences of the viscosity of oil from the Usinsk oilfield before and after thermostating at 90–250 °C with water and MFC (vibrational viscometry method)

A series of experiments on studying the filtration characteristics of heterogeneous reservoir models and assessing the oil-displacing capacity of the MFC for the conditions of the Permian-Carboniferous reservoir of the Usinsk field 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 models and the size of the composition slug.

Conclusions

A multifunctional MFC composition based on surfactants, aluminum and ammonium salts, adduct of inorganic acid, carbamide and polyol with adjustable viscosity and high oil-displacing ability in the temperature range of 20–210 °C has been created. The composition is both oil-displacing and flow-diverting, provides an increase in oil recovery factor due to an increase in displacement coefficients and formation sweep by waterflooding or steam injection. It is planned to carry out pilot tests to increase the oil recovery factor by combination of the MFC with hot water injection for the conditions of the Permian-Carboniferous reservoir of the Usinsk field.

The composition includes environmentally friendly industrial products available on the Russian market.

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