Technology for Enhanced Oil Recovery using an Oil-Displacing Acidic System of Prolonged Action

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Abstract. An oil-displacing system of prolonged action with adjustable viscosity based on surfactant inorganic acid adduct and polyol is created with the purpose to increase the efficiency of flooding or thermal steam formation treatment and to enhance oil recovery. The laboratory studies of physicochemical, rheological, and filtration characteristics of the system under natural exploitation conditions and thermal-steam treatment are presented. In 2014-2018 the field tests of the technology for enhanced oil recovery were successfully carried out using an acid oil-displacing system at the experimental sites of the Permain-Carboniferous reservoir of the high-viscosity oil of the Usinsk oilfield.

1. Introduction

As oil resources are depleted, technologies aimed at involvement into the development of deposits of hard-to-recover heavy and highly viscous oils have particular relevance [1-5]. The increase in oil recovery of heavy oil deposits can be realized using new physicochemical technologies, in particular, by injection of various compositions of chemical reagents into productive formations. In this regard chemically evolving systems including compositions capable of chemically reacting with the formation rock and fluids show promise. These systems change their composition and properties successively in the course of their motion through the formation. For example, being initially acidic and rock-dissolving, they become neutral or alkaline oil-displacing sol-forming systems after interacting with the rock.

Traditionally, chemically evolving systems develop as the acid composition by the complication with an increase of useful functions. Along with the known acids, complex acids formed by the donor-acceptor interaction of the components of the systems come into use. The composition and properties of complex acids are regulated by the concentrations and ratios of donor and acceptor. The acids have surface-active properties; they can enhance the oil recovery of a low-permeability matrix of the reservoir both due to the dissolution and contra-flow capillary imbibitions of the matrix. Complex acids, much stronger than the initial acid are formed in the ‘inorganic polyacid – polyol’ systems due to donor-acceptor interaction. The interaction allows increasing the acidity of oil-displacing systems and the duration of their action in the reservoir by increasing the buffer capacity and expanding the range of the buffer action in the acidic pH region. In Figure 1 is shown a scheme for the formation of complex acid and its dissociation into ions by the example of the interaction of boric acid and glycerin.
The oxygen atom of the hydroxyl group in the molecule of glycerol is the donor; it transfers its lone electron pair to the free orbital of the acceptor that is the boron atom in the boric acid molecule. As a result, one molecule of boric acid and two molecules of glycerol form a molecule of coordination compound, which is glycerol boric acid, four orders of magnitude stronger than boric acid.

To enhance oil recovery in low temperature (20–40 °C) reservoirs, cooled by water injection, and high viscosity oil pools in natural development mode, and in the mode of thermal-steam stimulation, an oil-displacing system based on surfactant, inorganic buffer system, carbamide and polyol with adjustable viscosity or a system of prolonged action based on adduct of inorganic acid was developed at the Institute of Petroleum Chemistry of the Siberian Branch of the Russian Academy of Sciences (IPC SB RAS) in Tomsk. The system has a freezing point of minus 20 ÷ minus 60 °C, low interfacial tension at the boundary with oil, density adjustable in the range from 1.1 to 1.3 kg/m³, and viscosity from tens to hundreds of mPa·s. The acid system is especially effective in carbonate reservoirs, since it slowly react with carbonate rocks without formation of any insoluble products and promotes the return of the original reservoir permeability. As a result of interaction of the system with the carbonate reservoir, CO₂ is released, which dissolves in oil reducing its viscosity and contributes to an increase in the oil recovery ratio. In addition, as a result of interaction with the carbonate reservoir and hydrolysis of carbamide, which is a part of the composition, its pH rises from 2.8–3.1 to 8.8–10.0 promoting its chemical evolution. The composition is converted into an alkaline oil-displacing system providing prolonged impact on the formation. After thermostatting with the system and carbonate reservoir at 70-120 °C, the viscosity of the oil decreases 1.2-2.7 times.

The paper presents the results of physicochemical studies and laboratory tests of an acid oil-displacing system developed at the Institute of Petroleum Chemistry of the Siberian Branch of the Russian Academy of Sciences.

2. Experimental

The solvent ability relative to carbonate rocks for the oil-displacing acid compositions based on surfactants, inorganic buffer systems (inorganic acid adduct) and polyol with adjustable viscosity was determined by the gravimetric method from the rate of reaction of solutions with marble. To establish the effect of concentration, the mass and surface area of pieces of marble were determined. For this purpose they were placed in bottles with the compositions and kept in an air thermostat at temperatures of 23, 50 and 90 °C for 20 hours. After the experiment, pieces of marble were washed, dried and weighed. The reaction rate of the composition with marble was calculated by the formula:

\[ V_p = \frac{(m_0 - m)}{(S \cdot \tau)}, \]  

where \( V_p \) is the reaction rate, g/m²·h; \( m_0 \) is the mass of a piece of marble before the experiment, g; \( m \) is the mass of a piece of marble after the experiment, g; \( S \) is the area of the piece, m²; \( \tau \) is the time of experience, h.

The rheological characteristics were investigated by the method of vibration viscometry using a ‘Rheokinetics’ vibration viscometer with a tuning fork sensor under heating from 20 to 90 °C and at different shear stresses. The pH values of solutions were obtained by potentiometric method using a glass electrode and a laboratory microprocessor pH meter manufactured by HANNA Instruments. Laboratory filtration tests of an acid system for enhanced oil recovery were carried out using an
installation for investigation of filtration characteristics (manufactured by CATACON LLC, Russia), consisting of two parallel columns, each 125 cm² in volume.

The filtration characteristics and oil-displacing capacity of the systems were studied using bulk reservoir models made of the disintegrated core material of the Permian-Carboniferous deposit of the Usinsk oilfield, fresh water or a model of reservoir water (synthetic brine) with mineralization 62.1-74.7 g/l of the Usinsk oilfield and degassed oil from the Usinsk oilfield (thermally stabilized oil with the addition of 30% kerosene). The permeability of the models ranged from 0.893 to 2.300 μm²; the permeability of parallel columns differed by 1.2-1.9 times. The thermostating time of a heterogeneous reservoir model after treatment with an acid composition was 24 hours and the back pressure was 2 MPa. The effectiveness of the oil-displacing system was studied during the primary displacement of oil and in the course of displacing residual oil with water and steam from two parallel columns with different permeability, as well as under conditions simulating the cyclic steam treatment of producing wells.

The effect of the acid system on the process of oil displacement was studied as follows. First, oil was displaced with water until the products were completely water-flooded from both columns at a given temperature. Every 5-15 minutes, the temperature and the pressure at the inlet and outlet of the columns and the volumes of the displaced oil and water from each column were measured. Based on the data obtained, the gradient of pressure grad P, atm/m, filtration rate V, m/day, fluid mobility k/μ, μm²/(mPa·s), and the coefficient of oil displacement by water C_o, % were calculated. After displacing the oil with water, the bank of the oil-displacing composition was simultaneously injected into both columns, pushed by water for a predetermined distance, and thermostated for a certain time. Then injection of water was continued. In addition, we determined the pH of the fluid at the outlet of the columns and the concentration of urea, which was a part of the composition. Based on the data obtained, the pressure gradient, filtration rate, fluid mobility, and the absolute factor of oil displacement by composition and water were calculated.

3. Results and discussion

As a result of systematic investigations of the effect of pH and the ionic strength of aqueous electrolyte solutions on the interfacial tension of oils and their fractions, an electrocapillary model of the interfacial layer was developed by researchers of IPC SB RAS. The interfacial layer in this model has the properties of an ion-exchange membrane, which is an amphoteric adsorbed layer of the natural oil surfactants [1]. The model explains the extremal dependence of the interfacial tension of oils on the pH of aqueous phase by the existence of an double electrical layer (DEL), resulting from the ionization of the ionogenic groups of natural oil surfactants, which are heteroatomic compounds present in resins and asphaltenes. The model allows correlating the oil component composition with the physicochemical parameters of the interfacial layer. These parameters determine the mechanism of oil displacement by aqueous solutions: interfacial tension, adsorption of natural oil surfactants, composition and concentration of electrolytes of the aqueous phase. The electrocapillary model of the interfacial layer is thermodynamic, i.e. it is free from restrictions on the formation water salinity, in contrast to electrokinetic models of the double layer, e.g. the Gouy-Chapman model and more complex ones. Within this model, the dependence of the interfacial tension of oil σ on the pH of aqueous phase is expressed by the equation [1]:

\[
\sigma = \sigma_i - b \cdot 9^{2 \cdot [- \lg (a_{bhs} + K-I)]} - pH_i^2 + c \cdot 9^{4 \cdot [- \lg (a_{bhs} + K-I) - pHI - 2.303 \cdot X_0 \cdot R \cdot T \cdot \lg (1 + K_o I)}, (2)
\]

where pH is the ision point of the interfacial layer (pH of the maximum of the curve σ – pH); σ_i is the interfacial tension at the ision point; b is the integral capacitance of DEL; c is the parameter characterizing the dependence of the integral capacity of DEL on its potential; a_{bhs} is the activity of hydrogen ions of the aqueous phase; K is the constant ion exchange equilibrium for the interfacial membrane; I is the ionic strength of the aqueous phase; K_o is the adsorption constant for electrolyte ions in the interfacial layer; X_0 is the limiting adsorption of electrolyte ions in the interfacial layer; R is the universal gas constant; T is the temperature; \(\vartheta=2.303\cdot R\cdot T/F\); and F is the Faraday number.
Figure 2 shows the calculated (line) and experimental (points) dependencies of interfacial tension on pH for the high-viscosity oil of Permian-Carboniferous deposit of the Usinsk oilfield at the boundary with an aqueous solution of 1-1 electrolyte with constant ionic strength. The calculations were performed for the following values of the equation parameters: $\sigma_i = 37$ mN/m; $X_0 = 1.1 \cdot 10^{-6}$ mol/m$^2$; $K_a = 70$ kg/mol; $I = 0.1$ mol/kg; $K = 1 \cdot 10^{-12}$ kg/mol; $b = 0.15$ F/m$^2$; $c = 0.7$ F/(m$^2$·B$^2$). Various values of pH of the aqueous phase were set by solutions of acid and alkali, mixed in certain proportions.

The electrocapillary model of the interface predicts the possibility of reducing the interfacial tension in both the alkaline and acidic pH ranges. Hence, in addition to use of alkaline buffer systems, the development and use of acidic buffer systems, such as solutions of complex acids and Lewis acids in coordinating solvents suggest themselves promising. Due to their high buffer capacity, these acid systems will have a prolonged effect and improved surface-active properties, which will allow them to be used as an effective acid agent in carbonate reservoirs of increased permeability of high-viscosity oil deposits.

The foregoing theoretical models were used for the development of an acid system based on surfactants, an inorganic acid adduct, and a polyhydric alcohol. This system is applicable in a wide range of temperatures, from 10 to 220 °C, in oil fields with terrigenous and carbonate reservoirs, under various geological and physical conditions. The technology of enhanced oil recovery using the composition is aimed at intensifying oil production by increasing the flow rates from producing wells and the injectivity of injection wells by pumping into injection and / or producing wells.

Figure 3 shows the results of the study of the rheological characteristics of oil thermostatted with an acid system. With an increase in the thermostating temperature of oil with solutions of systems based on an inorganic acid adduct and a polyol the pour point of oil decreases from -14 °C to -22 °C at 70 °C of thermostating and from -17 °C to -27 °C at 120 °C.

The dissolution rate of carbonate rock in the acid oil-displacing system decreases with an increase in the amount of urea included in the acid system from 22.1 to 19.2 g/m$^2$·h at 23 °C and from 27.1 to 6.3 g/m$^2$·h at 90 °C. Lower dissolution rate of carbonate rock in the acid oil-displacing system compared to the dissolution rate of carbonate rock, for example, in hydrochloric acid, allows a long-term impact on the formation rock without destruction of its structure and without the formation of cavities and sediments.

In Table 1 the results of filtration tests of the acid oil-displacing system are presented.
Figure 3. Temperature dependences of viscosity of the oil from the Usinsk oilfield before (initial oil) and after thermostating with the system at various temperatures in the presence of carbonate rock.

Table 1. Filtration characteristics and coefficient of oil displacement under simulated reservoir conditions: natural development conditions (model 1), at low temperatures; natural development conditions followed by cyclic thermal-steam treatment with the acid system (model 2).

| Model No | Gas permeability of columns (μm²) | Mobility ratio Before injection of the system | Mobility ratio After injection of the system | Coefficient of oil-displacement for columns (%) Before injection of the system | Coefficient of oil-displacement for columns (%) After injection of the system for experiment in general | Increment of the oil-displacement coefficient due to the application of the system (%) Before injection of the system | Increment of the oil-displacement coefficient due to the application of the system (%) After injection of the system for experiment in general |
|----------|-----------------------------------|---------------------------------------------|---------------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| 1        | 2.300                             | 1.200                                       | 25.5:1                                      | 2.6:1                                                                          | 29.6                                                                  | 2.9                                                                  | 45.9                                                                  | 38.1                                                                  | 16.3                                                               | 35.2                                                               |
|          | 1.100                             | 0.892                                       | 18.5:1                                      | 1:1.8                                                                          | 57.6                                                                  | 15.1                                                                  | 69.4                                                                  | 38.1                                                                  | 11.8                                                               | 23.0                                                               |
|          | average                           | average                                     |                                              |                                                                                | 25.8                                                                  | 17.4                                                                  |                                                                        |                                                                        | average 25.8                                                       | average 17.4                                                       |

As a result of experimental studies, it was found that the treatment of a reservoir with the acid oil-displacing system under conditions of natural development and then under cyclic thermal-steam stimulation contributes to an increase in the oil-displacement ratio of heterogeneous reservoir models. The increment in oil displacement coefficients ranges from 11.8 to 35.2% for the columns. Upon the average, the increment in oil displacement coefficients for heterogeneous reservoir models ranged from 17.4 to 25.8%. The high oil-displacement capacity of the acid system is due to the low interfacial tension at the boundary with the oil, the high washing capacity of surfactants present in the composition, and optimal conditions resulted from the formation of a large-capacity inorganic buffer system. Adduct of an inorganic acid reacts with the polyol to form a stronger acid capable of interacting with the carbonate rock, increasing its injectivity, which also contributes to oil displacement.
Cyclic thermal-steam reservoir treatment, performed after pre-treatment with an acid system of prolonged action, can significantly increase the oil displacement coefficients by reducing the viscosity of oil due to the increase in temperature and the dissolution of carbon dioxide formed during the hydrolysis of carbamide, which is a component of the system. Field tests were successfully carried out in experimental sites of the Permian-Carboniferous pool of high-viscosity oil of the Usinsk oilfield, which were developed in the natural mode under steam stimulation. The injection of the acid composition into 10 low-productive production wells of the Usinsk oilfield allowed increasing the oil production rate by 5.5-14.8 tons/day without any steam stimulation. The liquid rate has increased by 15-25 m³/day, while incremental oil production was 28 thousand tons, i.e. more than 2000 tons/well [2].

In 2017-2018 the works on oil recovery improvement using thermal-steam stimulation were performed. The duration of the effect was 12 months, and the incremental oil production on the site was 27,000 tons or ~ 3.75 tons/day per each production well. Due to the injection of the system before the cyclic thermal-steam treatment, the additional increase in oil production rate was 20% compared with the previous cycle. Pilot works exhibited a high efficiency of technology. Significant effects were obtained on oil production enhancement. The technology is environmentally safe and technologically efficient. The industrial use of technology has considerable promise for high-viscosity oil deposits.

4. Conclusion
Thus, the acid composition of prolonged action based on surfactant, inorganic acid adduct, and polyol is an effective oil-displacing system having a low interfacial tension at the boundary with oil. The increment of oil displacement coefficients for models of a heterogeneous reservoir using an acid oil-displacing system was 17.4-25.8% on average per model. The dissolution rate of the carbonate rock in the acid oil-displacing system decreases with an increase in the amount of urea included in the composition of acid system from 22.1 to 19.2 g/m²-h at 23 °C and from 27.1 to 6.3g/m²-h at 90 °C. After thermostating with the system and carbonate reservoir at 70-120 °C, the oil viscosity decreases 1.2-2.7 times.

The acid system of prolonged action could be used as a composition increasing the efficiency of development due to the oil recovery improvement and increase in reservoir coverage and oil displacement. The acid oil-displacing composition could be pumped into injection, steam injection and steam cyclic wells. It is a low-viscosity, low-pour point, safety liquid, which makes it easy-to-use in the winter period. For the preparation and injection of the acid composition under field conditions, standard oilfield equipment is used. The acid system is applicable both at the early and late stages of development of fields with difficult-to-recover reserves, including deposits of high-viscosity oil.

Acknowledgments
The work was performed within the framework of the Project “V.46.2.3. Physical chemistry and rheology of oil and polydisperse oil-containing systems in the processes of enhanced oil recovery and oil transport (No. 0370-2019-0002)”

References
[1] Altunina L K. and Kuvshinov V A 2007 Rus. Chem. Rev. 76 10 1034-1052
[2] Altunina L K, Kuvshinov V A, Kuvshinov I V, Stasiieva L A, Chertenkov M V, Shkrabyuk L S and Andreev D V 2017 Oil industry 7 26-29
[3] Raffan P, Broekhuis A A and Picchioni F 2016 Journal of Petroleum Science and Engineering 145 723-733
[4] Abass A 2014 Olajire Energy 77 963-982
[5] Sorrell S, Speirs J, Bentley R, Brandt A and Miller R 2010 Energy Policy 38 5290–5295