Modeling of Surfactant Adsorption in the Carbonate Reservoir

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Abstract. The problem of surfactant absorption in carbonate reservoir during surfactant injection as enhanced oil recovery method becomes more on the front burner. Moreover, since reservoir simulation progress improves invariably it forces to apply special programs to reach enlargement of the amount of recoverable oil. Therefore, in this article surfactant adsorption in carbonate reservoir was simulated. As a result, it has been got that recovery was improved with surfactant application.

1. Introduction

Nowadays, most of oil and gas fields introduce tertiary development methods, including chemical oil recovery enhancement methods (EOR). Waterflooding of the developed formation by surfactants makes a huge contribution to increase in oil production in carbonate reservoirs, since they promote the interfacial tension on the water-oil surface, as well as a change in the contact angle of the wettability and the wettability of the rock subsequently (Wang et al., 2015, Barati et al., 2016). When oil is extracted from carbonate reservoir, the developers are faced with the problem of its hydrophobicity, as well as with high salinity of formation water, which together lead to the adsorption of surfactants injected into the formation (Sheng, J. J. 2013). Therefore, while designing and simulating the injection of surfactants, this problem has a priority.

To evaluate the effectiveness of various types of surfactants and analyze the problems of their adsorption, a hydrodynamic core model for one of the fields of the Republic of Tatarstan was constructed using tNavigator software package (Rock Flow Dynamics). The examined object is characterized by carbonate hydrophobic reservoir, therefore, it was assumed that surfactant flooding, considering this case, should significantly affect the volume of displaced oil. Based on laboratory research data, the simulation model was launched for few times with surfactant flooding process and without one.

The examined reservoir is located in southeast part of Tatarstan Republic, Russia, it is a fractured carbonate reservoir, and its oil-producing stratum is about 150 m thick with the depth of 1185 m. The analysis of rock physical property indicates that the porosity of reservoir is on the average 15%, and the permeability is about 150*10⁻³ μm². Stratigraphically the object belongs to the Bashkirian stage of the middle Carboniferous according to Russian stratigraphic table.

Oil properties were determined by chemical research. The main parameters of oil in the tier vary within the following limits: bubble pressure differs from 0.3 to 3.04 MPa (the average value - 1.96 MPa); gas oil ratio – from 0.59 to 5.8 m³/t (the average – 3.0 m³/t); dynamic viscosity of reservoir oil –
from 101.9 to 418.5 MPa\textperiodcentered s (243.2 MPa\textperiodcentered s); formation volume factor for single degassing – from 1.002 to 1.038 (1.001); compressibility – from 5.1 to 5.9 \times 10^{-5} 1/MPa, average value – 5.5 \times 10^{-5} 1/MPa.

Density of reservoir oil varies from 0.895 to 0.937 g/cm\textsuperscript{3} (0.921 g/cm\textsuperscript{3}), density of oil in surface conditions – from 0.921 to 0.950 g/cm\textsuperscript{3} (0.935 g/cm\textsuperscript{3}).

Bashkirian stage oils belong to the group of heavy, high-sulfur, paraffin, high-resin and with non-newtonian properties. The content of sulfur in samples ranges from 2.6 to 5.4\% by weight; the average content of asphaltenes – 9.41\% by weight; paraffins – 2.6\% by weight; resins – 36.9\% by weight.

2. The problem of surfactant adsorption
Surfactant flooding has played an essential role in enhanced oil recovery, lowering oil/water interfacial tension (IFT), emulsifying crude oil and altering the wettability of oil layer toward water-wet (Johannessen et al., 2013, Adams et al., 1987, Puerto et al., 2013, Wu et al., 2013). During surfactant flooding, the solution flows through the porous reservoir with huge surface areas, as a result, the inevitably loss of surfactant due to adsorption limits its extensive application in oil fields (Somasundaran et al., 1985).

Basically, adsorption is determined by a several forces such as: electrostatic attraction, covalent bonding, hydrogen bonding or non-polar interactions between the adsorbed particles, lateral associative interaction, solvation or desolvation (Somasundaran et al., 1975). The total adsorption is the cumulative result of some or all of the above forces (Fuerstenau, 1971). Mechanisms of surfactant adsorption are reviewed by Rui Zhang (2006) in terms of various forces involved and factors controlling them.

Surfactants are usually organic compounds that are amphiphilic, which means that they contain a hydrocarbon chain (hydrophobic “tail”) and a polar hydrophilic “head”. That is the reason why they are soluble in both organic solvents and water. They are able to concentrate at interfaces to alter the surface properties substantially. (Sheng, 2013)

According to the ionic nature of the head group surfactants are classified as anionic, cationic, nonionic, and zwitterionic. Anionics are the most common among chemical EOR projects with their low adsorption on sandstone rocks. Nonionic surfactants are more tolerant of high salinity, however, their IFT reduction function is not as good as anionic surfactants. (Sheng, 2011). In our paper nonionic surfactant was used – Neonol 9-12.

An important mechanism of surfactants in carbonate reservoirs is changing wettability from oil-wet to more water-wet or wettability alteration. It has been explained with surfactant adsorption, moreover, relative permeabilities and capillary pressure curves are based on the degree of wettability alteration (Sheng, 2013).

One of the most significant factors during the successful surfactant flooding is reducing surfactant adsorption in the reservoir (Ahmadall et al., 1993). Some works have been conducted using various additives for adsorption reduction (Zhou et al., 2005, Shamsi Jazeyi et al. 2013, Le et al., 2011, Ahmadi et al., 2012). Alkali was studied as additives under conditions of low salinity (Al-hashim et al., 1996, Gupta et al., 2007), where mechanism of changing the charge density on the rock surfaces was considered. Wang et al. for reducing surfactant adsorption in carbonate reservoirs have studied polymer and it was found that a polymer layer formed on the rock surface leads to a decrease of points of active adsorption (Wang et al., 2013). However, other works, on the contrary, have proven that due to the dissolution and instability in high-temperature and high-salinity reservoirs such additives as alkali and polymers are inefficient (Dai et al., 2010, Lorenz et al., 1989). Therefore, process of reducing surfactant adsorption is a big challenge for a cost-effective surfactant flooding project (Wu et al., 2013).

There were carried out a lot of researches by math calculation of IFT reduction. Sheng et al. (2020) presented four models: UTCHEM model, Adibhatla et al. (2005) model, a proposed simple model and a CMG model.
Adsorption of nonionic surfactants is normally reversible with little hysteresis. Most nonionic surfactants are composed of polar groups forming hydrogen bonds with the hydroxyl groups on the solid surface. As far as the hydrogen bonding is weaker than the electrostatic interaction, the adsorption of the nonionic surfactant is less than one of ionic surfactants. In the article Rui Zhang (2006) examined the adsorption isotherm and differed it in three types: Langmuir type (L-type) which was considered as simple one represented by Langmuir equation (Langmuir, 1918) S-type and “double plateau” type (L–S type) which are more complex. According to these types of adsorption isotherm different types of adsorption models were created and researched.

Due to surfactants added for the EOR purpose, water-oil interfacial tension reduction increases the capillary number, therefore, residual oil saturation is reduced. According to Sheng, J. J. (2020), a strongly water-wet system should be preferred for oil recovery. However, early researchers found that the highest waterflooding oil recovery occurs at intermediate wetting conditions (von Engelhardt and Lubben, 1957).

In our case, we have oil-wet reservoir and it was purposed to alter this wettability simultaneously with reducing interfacial tension. There were used dependences of surfactant adsorption and interfacial tensions on the surfactant concentration shown on the figure 1.

![Figure 1. IFT and surfactant adsorption dependences on its concentrations.](image)

3. Modeling process

For the modeling of surfactant flooding process tNavigator software by (Rock Flow Dynamics company) was used which is one of the most popular and practical computer products in Russia applied for geological and hydrodynamic modeling, PVT analysis and history matching.

Firstly, chemical research of surfactant properties such as interfacial tension and surfactant adsorption dependences on concentrations was carried out, which results were used in further modeling using key words SURFADS, SURFST.

For the simulation the determined site was cut where three wells (2136, 2342, 2402) were applied for 9-year surfactant flooding process which was started in 2021. Before that only water was being injected into the reservoir by wells 2136, 2342, 2402, 2403.

In the simulation model from 2021 wells 2136, 2342, 2402 started pumping the surfactant. During the forecast period, wells 2342 and 2136 worked most actively, as can be seen from fluid path lines on the figure 2a. The figure 2b shows how oil was displaced by injectors up to oil saturation values of cells 0.1 from the area of injection wells impact in the area of production wells.
By the 2030 forecast year, production with the use of surfactant injection in the model reached 78 thousand tons for the trial site, compared with 50 thousand tons in the model, where only water was injected in the same period (figure 3).

4. Results
In the result of reservoir simulation of surfactant flooding we received that application of this method allows to get higher oil recovery. It is also necessary to take into account the features of the reservoir, such as, for example, the possible adsorption of reservoir, which was done in this work. As a result of the forecast, production increased by one and a half times, which proves the effectiveness of surfactant flooding. It is also proposed to continue using this type of EOR in this field and to increase the oil recovery factor.

5. Conclusion
Surfactant injection is believed to change wettability from oil-wet or more water-wet and to reduce interfacial tension. It is assumed that the wettability alteration is caused by surfactant adsorption on carbonate rock surfaces. Adsorption of surfactants and their mixtures at solid/solution interface is a complex process. The driving force for adsorption is a combination of the electrostatic interaction, the chemical interaction, the lateral chain–chain associative interaction, the hydrogen bonding and desolvation of the adsorbate species. It has to be considered during the modeling process due to its significance.
Surfactant flooding can improve oil recovery, so its modeling assists at the field development. For this reason, the work of simulation of two cases was carried: base case with water flooding and another one with surfactant injection. Hence, it was proved that in the second model the recovery is almost two times higher.

6. References

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