РАЗРАБОТКА НОВОЙ КОМПОЗИЦИИ С ЭФФЕКТИВНЫМИ БИОЦИДНЫМИ И НЕФТЕВЫТЕСНЯЮЩИМИ СВОЙСТВАМИ

Изучена эффективность нефтеотделяющих и биоцидных свойств разработанных композиционных смесей водорастворимого полимера – полиакриламида (ПАА) и некоторых поверхностно-активных веществ (ПАВ). На модельных установках, имитирующих образцы керна – коллектора, определены коэффициенты извлечения нефти (КИН) применительно к конкретному нефтяному месторождению с учетом химической сов-
местимости агентов вытеснения нефти с пластовыми флюидами. Выявлена антимикробная эффективность синтезированного соединения - 1-бутокси-3-оксазолидинметоксибутан (Biocide B) в составе смазочного масла M-8 и эмульсионной композиции Az-5. Изучены составленные композиции: Grotan-ОX + Biocide B в соотношении 1:1 и 1:3 (масс) и их антимикробные свойства в аналогичных условиях. Наблюдается некоторый синергизм действия при объединении этих компонентов, что приходит к улучшению биоцидных свойств. Показано, что наличие в композиции реагента Grotan-ОX в индивидуальной форме или в комбинации с биоцидом в низких концентрациях (0,5% масс) значительно повышает ее нефтевытесняющие способности (87%) и одновременно придает эффективные биоцидные свойства.

**Ключевые слова:** водорастворимые полимеры, ПАВ, нефтевытесняющие свойства, сульфат-восстанавливающие бактерии, биоцидность

**UDC:** 620.193.8:622.276.72


Vagif M. Farzaliyev, Elbay R. Babaev (✉)
Laboratory of Protective Additives, acad. A. Guliyev Institute of Chemistry of Additives of NAS of Azerbaijan, 2062, Boyukshor Highway, Baku, Az 1029, Azerbaijan Republic
E-mail: vagiffarzaliyev@rambler.ru, elbeibabaev@yahoo.de (✉)

Michael Streek
Special Additives International, Head of Product Management Fuel & Oil, Schülke & Mayr GmbH, Robert-Koch-Straße 2, 22851, Norderstedt, Germany
E-mail: michael.streek@schuelke.com

Eldar M. Movsumzade
Ufa State Oil Technical University, Kosmonavtov st., 1, Ufa, Republic of Bashkortostan, 450062, Russia
E-mail: eldarmm@yahoo.com

Pervin Sh. Mammadova
Laboratory of Additives to Cutting Fluids, acad. A. Guliyev Institute of Chemistry of Additives of NAS of Azerbaijan, 2062, Boyukshor Highway, Baku, Az 1029, Azerbaijan Republic
E-mail: pervin_mammadova@mail.ru

Irada M. Eyvazova
Laboratory of Additives to Fuels, acad.A. Guliyev Institute of Chemistry of Additives of NAS of Azerbaijan, 2062, Boyukshor Highway, Baku, Az 1029, Azerbaijan Republic
E-mail: irada.eyvazova@gmail.com

**DEVELOPMENT OF NEW COMPOSITION WITH EFFECTIVE BIOCIDAL AND OIL-DISPLACING PROPERTIES**

The efficiency of oil-displacing and biocidal properties of the developed composite mixes of water-soluble polymer – polyacrylamide and some surface-active agents was studied. On the model setups, simulating core - collector samples, the oil extracting coefficients were determined for a particular oil field taking into account the chemical compatibility of oil-displacing agents with the horizon fluids. Antimicrobial effectiveness of the synthesized compound - 1-butoxy-3-oxazolidine methoxybutane in the composition of M-8 lubricating oil and Az-5 emulsion was revealed. The following developed compositions - Grotan-ОX + Biocide B in the ratio of 1:1 and 1:3 (wt.). Their
antimicrobial properties in the similar conditions were studied. Some synergistic action is observed at combination of these components, which leads to improved biocidal properties. It was shown that the presence in the composition of Grotan-OX reagent both individually or in combination with biocide at low concentrations (0.5 wt.%) significantly improves its oil-displacing abilities (87%) and at the same time gives effective biocidal properties.

Key words: water-soluble polymers, surface-active agents (surfactant), oil-displacing properties, sulfate-reducing bacteria (SRB), biocides

INTRODUCTION

A characteristic feature of the modern oil production is increasing the share of hardly extracted reserves and a considerable amount of residual oil.

At present there are a lot of developed and introduced chemical agents and compositions based on them for enhanced oil recovery (EOR). Chemical methods of EOR are used for additional extraction of oil from heavily drawn-out, flooded oil-bearing reservoirs with scattered, irregular oil-saturation. Efficiency of extraction of oil from oil bearing formations depends on many factors, one of which is the viscosity of the reactant injected into a well. To increase the viscosity, polymers can be used. For example, polyacrylamide (PAA) can significantly increase the viscosity of water even at low concentrations, reduce its mobility and thus raise coverage of bed by water-flooding [1]. Polymer solutions having a high viscosity better displace not only oil, and also associated formation water from the oil medium.

Another way for EOR is the use of surfactant species. It’s necessary to develop composition of surfactants for the specific characteristics of the reservoir bed: properties of oil and rock, salinity, temperature, pressure, permeability and porosity of the collector [2].

It should be noted that the reactants – the components of the compositions may be incompatible with other reagents in a single technological process.

In the technologies of EOR and preventing water flooding of oil-bearing beds there are used the appropriate reagents, often modified with components which give them various useful properties, including antimicrobial properties [2].

Among the microorganisms contained in oil-field waters, the most corrosion – dangerous ones are SRB. To extend the service life of the basic solutions and to decontaminate oil itself, in particular, to fight SRB there are widely used reagents with biocidal properties [3].

The research goal is developing PAA and surfactants based new effective compositions used in the oil fields as complex action reagents to displace the heavily extracted reserves of oil and providing highly effective protection of oil-field equipment from biological corrosion in the oil industry.

DESCRIPTION OF EXPERIMENTAL METHODS

As a research object oil (15 ml) of Balakhani field of Absheron Peninsula was used.

Antimicrobial properties of the synthesized additives and studied reagents were investigated in M-8 oil and Az-5 emulsion composition at a concentration of 0.06-0.5wt.% relative to the major physiological groups of microorganisms (aerobic and anaerobic bacteria and fungi), affecting oil. We used the hole method on the agar medium using suspensions of different cultures of microorganisms according to ГОСТ 9.052-88 and ГОСТ 9.082-77. For the tests there were used pure cultures which were widely spread in oil products and non-aggressive destroyers of the following species of aerobic bacteria and moulds: bacteria (Mycobacterium lacticolum, Pseudomonas aeruginosa), fungi (Aspergillus niger, Cladosporium-resionae, Penicillium chrosegenum, Penicillium cyclopium, Torula convolut, Trichoderma viride).

As a culture medium there were used meat-peptone agar (MPA) for bacteria and wort agar (WA) for fungi. The antimicrobial effectiveness was evaluated by diameter of microbial growth inhibition zones around the wells with and without additive; the more it is, the more the antimicrobial effectiveness is (Table 1).

Tests for bactericidal activity of the reagents also were carried out in the laboratory conditions on cumulative cultures with SRB (Disulfovibrio and Desulfotomaculum) in accordance with ГОСТ 9.085-78. The culture of bacteria was isolated from produced water of the well at Balakhani field and grown in standard Postgate’s medium of the following composition (g/l): NH₄Cl – 1.0; KH₂PO₄ – 0.5; MgSO₄·7H₂O – 2.0; Na₂SO₄ – 0.5; CaCl₂ – 0.1; Calcium lactate – 3.5. The medium was sterilized for 45 min at a temperature of 121±1 °C, cooled to 35 °C.

The pure culture of SRB was prepared according to the known method [4, 5].

70
The nature of the effects of the bactericides was determined by the presence or absence of black colonies of SRB [6].

The obtained results showed that Grotan-OX and (Grotan-OX + Biocide B) reagents in the ratio of 1:3 at concentration of 0.125-0.5% had a bactericidal effect on bacterial cells. The color of the indicator agar didn’t change. There was no growth of SRB.

To determine oil-driving ability of the developed compositions equipment, consisting of the glass columns with 30 cm diameter and 70 cm long and simulating reservoir model was used. Glass tubes were filled with the appropriate deposit sand. The model was impregnated with formation water and the excess water was collected and measured in a measuring beaker (Vₜ). Then the saturation of the model with oil was realized. A certain amount of the crude oil was passed through the reservoir model (the system worked under the vacuum). Oil partially displaced water from the pores, then the pore part was filled with oil. As a result, the reservoir model had a certain oil and water saturation. The volume of oil displaced in the beaker was measured and the oil recovery coefficient (ORC) was determined by the ratio of displaced oil to initial oil.

When developing the compositions for efficient recovery of residual oils studies were focused on the use of not expensive reagents, for example, large-tonnage industrial waste. In particular, there were tested kerosene-alkali waste (KAW) obtained in processing kerosene for neutralizing oil acids contained in the composition of kerosene with an aqueous alkaline solution. KAW contained 1.0-2.5% of NaOH.

To carry out the experimental work KAW based alkaline composition of additives conventionally called Az-5 was prepared. It was alkaline composition of additives based on the waste of oil-producing (KAW) and fat-producing (Soapstock) industries. Its working fluid was 2-5% aqueous solution with surface-active properties and protective effect on hydrogen sulfide and bacterial corrosion. Grotan-OX (Germany) reagent was also tested as an effective preservative for technical products.

As a water-soluble polymer PAA was used.

\[
\text{CH}_2\text{H}-\text{CH}-\text{C}-\text{O}\n\text{C}_\text{O}\n\text{NH}_2
\]

RESULTS AND DISCUSSIONS

Microbiological tests showed high antimicrobial activity of the test reagents microflora against hitting oil (aerobic and anaerobic bacteria and fungi), and SRB.

The results showed that the well-known and widely used preservative for technical products Grotan-OX in the composition obtained from local oil products of Az-5 emulsion had effective bactericidal properties against aerobic and anaerobic bacteria, including SRB. Biocide B synthesized by us on bactericidal properties in Az-5 emulsion composition was slightly worse than Grotan-OX. However, the compound was better than it, particularly on fungicidal properties in composition with M-8 oil. Further the following compositions -Grotan-OX + Biocide B in the ratio 1:1 and 1:3 (wt.) were studied. The combination of these substances led to improved biocidal properties, which allowed the use of smaller quantities of materials to achieve effective biocidal properties, thereby reducing the material consumption.

It’s known that for EOR there are used methods of maintaining reservoir pressure and it’s possible by injecting water or gas. In this situation there is created artificial hard water-pressure or gas-pressure mode, water is often injected into the reservoir through specific injection wells (water flooding reser-
However, in these processes in the reservoir there is a large amount of oil – capillary-retained, streamline. For efficient extraction of oil various reagents that improve oil washing properties or increase its viscosity, are added to the injection water.

Components of compositions were studied as oil-driving agent, individually or in the form of compositions with different ratio of components. The compositions are shown below (Table 3).

Oil-driving properties of the investigated reagents and compositions were measured on the established in vitro reservoir model.

In accordance with the research goal new oil-driving compositions based on aqueous solutions of various surfactants (KAW, Az-5, sulfanol, Grotan-OX) and a water-soluble polymer PAA were developed.

As it follows from the analysis of the experimental data recovery coefficient of crude oil from Balakhan field produced at water displacing oil in conditions of the model plant isn’t high (32%). When using individual reagents (KAW and Az-5 emulsion liquid), ORC is characterized by almost same low values (12-15%). Low oil-driving properties of these solutions are probably explained by chemical incompatibility of oil driving agents with bed liquids. When passing KAW through the sand saturated with formation water there is formed precipitate complicating its water loss.

The main factor, complicating oil production by water flooding in many fields, is the high salinity of formation water. Therefore, one of the main tasks in determining the most effective driving agent is studying its compatibility with the formation water. Qualitative analysis of the formation water samples indicates that it contains calcium, magnesium, sodium, potassium cations and hydrogen carbonates, sulfate, carboxylate, chloride anions (Table 4).

When studying KAW solutions compatibility with the formation water it has been established that viscosity of naphthenic acids sodium salts increases when mixing with the formation water. Interaction of KAW aqueous solutions with calcium and magnesium cations, as well as carboxylate anions contained in the formation water, leads to the complication of oil displacement process. Schematically, the chemism of this process can be shown by the following equations:
1. Dissociation of naphthenic acids:
\[ C_{2n}H_{2n+1}COONa \rightleftharpoons C_{2n}H_{2n+1}COO^- + nNa^+ \]
2. Interaction of carboxylate anions with calcium cations, contained in the formation water in quantities:
\[ 2(C_{2n}H_{2n+1}COO^-) + 2nCa^{2+} \rightleftharpoons (C_{2n}H_{2n+1}COO)_2Ca \]

Table 4
The chemical composition of water samples from Balakhani field

<table>
<thead>
<tr>
<th>Ions in the mix</th>
<th>mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ca^{2+}</td>
</tr>
<tr>
<td>2</td>
<td>Mg^{2+}</td>
</tr>
<tr>
<td>3</td>
<td>Na^+ + K^+</td>
</tr>
<tr>
<td>4</td>
<td>HCO_3^-</td>
</tr>
<tr>
<td>5</td>
<td>HSO_4^-</td>
</tr>
<tr>
<td>6</td>
<td>RCOO^-</td>
</tr>
<tr>
<td>7</td>
<td>Cl^-</td>
</tr>
</tbody>
</table>

Reducing the filtration characteristics of samples of core – collector occurs as a result of partial adsorption and mechanical trapping the polymer with porous medium.

The processes of driving non-polar liquids from porous systems are based on the viscous properties of relatively concentrated solutions of polymers.

With increasing concentration of PAA solutions there is observed a decrease of oil-driving speed. The high viscosity allows to implement a piston displacement mechanism for increasing ORC. During the filtration through model core samples of polymer solutions it can be seen that a part of the sample pores undergoes to blocking with polymer particles. This is caused by the adsorption of the polymer on the surface of the porous medium, which reduces the size and change the shape of the filtration channels.

The main reason for the formation of corrosive environment and accumulation of iron sulfide in the oil reservoir is the vital activity of SRB, entering into the reservoir with water at a perimeter flooding. The participation of microorganisms in the corrosion process is limited with the direct effects of their metabolic products (carbon dioxide, hydrogen sulfide, ammonia, organic and inorganic acids) on metallic structure, and also with the intensification of the electrochemical reactions on the surface of the corroding object.

Except bio corrosion, the microorganisms cause clogging of the oil reservoir with microbial bio-mass accumulation and metabolic products of bacteria that leads to significant reduction of oil recovery and decrease in ORC. Vital functions of the bacterial microflora is responsible for biodegradation of chemical oil-driving agents, as well as changes in the quality and composition of the oil.

There are various classes of compounds that inhibit the growth of SRB. However, the most effective means of protection from SRB are multifunctional action reagents, having both properties of bactericides and corrosion inhibitors, increasing the oil recovery and having a number of other important properties.

CONCLUSION

Addition of 0.5 g of surfactant (sulfanol) to compounds (II) and (IV) promotes raising recovery ratio values from 12 and 15% to 38 and 52% respectively.

Oil-driving compositions (VIII and IX) are characterized by high values of ORC (78 and 87%) respectively, that is probably connected with decreasing concentration of alkaline component (KAW).

By generalization of the experimental data we can conclude that in conditions of microbiological contamination of oilfield systems the developed new multifunctional compositions (VIII-IX) having efficient oil-driving properties at the same time can significantly reduce the corrosion activity of oilfield waters.

REFERENCES


6. Методика контроля микробиологической зараженности нефтепромысловых вод и оценка защитного и бактерицидного действия реагентов РД 39-3-973-83. Уфа: Изд-ние ВНИИСПТнефти.


6. Методика контроля микробиологической зараженности нефтепромысловых вод и оценка защитного и бактерицидного действия реагентов РД 39-3-973-83. Уфа: Изд-ние ВНИИСПТнефти.