Research Article

The Use of Polymeric Reactants for EOR and Waterproofing

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Abstract Solving the problem of unsustainable production of oil, the main natural resource over the world is sufficiently important and urgent task. Excessive watering of crude oil is one of the main problems that has been faced the oil industry. The most wide world methods used for increasing oil recovery were physical and chemical methods. The use of polymeric reactants can successfully reduce water cut and increase the oil recovery factor. Developing reactants based on nano-particles is an important direction of improving polymeric materials to increase oil recovery.

1. Introduction

Solving the problem of unsustainable production of oil, the main natural resource over the world is sufficiently important and urgent task. Excessive watering of crude oil is one of the main problems that has been faced the oil industry. The most wide world methods used for increasing oil recovery were physical and chemical methods. The use of polymeric reactants can successfully reduce water cut and increase the oil recovery factor.

Developing reactants based on nano-particles is an important direction of improving polymeric materials to increase oil recovery.

One of the main problems in the development of oil and gas reservoirs is the irrational use of mineral resources. In order to achieve the goals for the development of this sector of oil industry, we need to develop and introduce modern methods of EOR.

It should be noted that this problem is actual , not only for one or two of the oil-producing countries, but also for the major of these countries, where the average enhanced oil recovery projects that are using in oil industry is about 30% [2].

The actual problem is the high water cut, which increases the cost of oil production and leads to corrosion problems of pipelines and equipments.

Thus, for example, in US water cut in oil reaches 90% [3], whereas in certain oil fields of the world this figure rises to 98%. Average water content in the Russian Federation is about 86% [4].

To date, the effectiveness of oil recovery using the existing developed methods is considered unsatisfactory in all oil-producing countries.

The main method of oil extraction is the displacement of oil by water (water flooding). As a result of the using of water flooding in the oil reservoir, two types of residual oil are formed. The first type of the residual oil is formed in the washed with water areas of the oil reservoir that contains more heavy components (resins, asphalt) than the initial oil [5].

The situation of fluids in the pore spaces is defined by rock wettability [6, 7]. In the hydrophilic rock, water wets the surface of the reservoir, while the residual oil is displaced into the interior part of the pores as separate droplets which have been locked in the pores of the formation.

The wetting liquid in the hydrophobic rock is oil, and residual oil is contained as a film on the surface.

The reasons for formation of residual oil of the first type are the high interfacial tension at the water-oil contact and the huge total surface oil contact with the rock [8]. Capillary-resist and oil film represent about 30% of the total residual oil.

The second type of residual oil differs little from the initial oil deposits, since it is formed as a result of not full displacement of the oil from heterogeneous reservoirs. The reasons for the formation of the residual oil of the second type is the heterogeneous structure of the reservoir rock (the presence of zones of different permeability), and various filtration rates of the displaced and the displacing fluids [6, 9].

The residual oil of the second type includes [8,10]: oil remaining in the low-permeability formations and the areas not covered by the water (27%); oil in the stagnant (no water moving) zones of homogeneous reservoirs (19%); Oil remaining in the lenses and screens impermeable not penetrated by wells (24%). Thus, the residual oil of the second type is the main reserve with increasing sweep efficiency by water flooding.

Currently a sufficiently large number of different EOR methods is applied. Among which we can distinguish the following EOR methods [2, 11, 12]:

- Thermal methods, which provide heat input or generate it directly into productive reservoirs. These include technologies of steam injection (cyclic or continuous), injection of hot water, in-situ combustion;
- Gas methods, which refer to the category of injection into the reservoir Carbon dioxide CO₂, Nitrogen N, Hydrocarbon and flue gases;
- Physic-chemical methods that involve injection into the reservoir reactants, lowering the interfacial tension to reduce the degree of blocking oil in hydrophilic rocks. This also includes the using of polymers solutions and other chemicals, which are often intended to change the filtration flows and injectivity profile alignment.

According to the report of the International Agency of Energy, IAE, the main criteria for selecting the method of enhanced oil recovery are: density and viscosity of oil, the recovery rate on the current time, the type of rock, formations depths, permeability and temperature [11].

It is known around that the world the share of using thermal EOR represents 42% of all the projects used in oil industry, the share of physical and chemical methods - 31%, and gas methods - 27% [2, 13].

In the US, it was found that the primary use of EOR was Gas methods of EOR (130 out of 194 acting Projects in 2010), whereas the projects using thermal and physic-chemical methods of EOR were respectively 61 and 3 [2]. Adherence of gas EOR and their intensive developments is explained primarily by the existence of large sources of carbon dioxide and a developed system of pipelines, which are able to deliver the required amount of gas to the basins of the largest fields in the United States.

In Russia (and as in former USSR), the most developed are the physical and chemical EOR. The share of oil produced due the use of physic-chemical EOR exceeds 80% of the total oil production by the use of EOR methods [14].

The main physical and chemical EOR technologies are based on injection of surfactant solutions, alkalis, gel and sediment-reactants, polymer solutions and polymer-disperse systems, [8, 15].

In Russia, polymer technology impacts find wide enough application.

In the polymer flooding is widely used set of polymeric reactants, such as biopolymers "Xanthan" and "Product BP-92", hydrolyzed polyacrylonitrile (PAN), polyethylene oxides, methacrylic acid polymers [5]. However, the technology based on Polyacrylamide (PAM) is the most widely used.

There are several main ways to use polymers in the technology of EOR [16]:

- As agents that are reducing the ratio of mobility of water and Oil (polymer flooding).
- As cross linked polymeric systems that can be cross linked in deep formation and during processing of bottom zones to block zones of high permeability.

Almost in all of the original projects of the polymer flooding was partially used hydrolyzed polyacrylamide [5]. Due to the high molecular weight of hydrolyzed polyacrylamide, the viscosity of solution can significantly be increased. In addition to that, anionic repulsion between the molecules of the polymer and segments of one molecule leads to stretching and coupling the molecules, thereby also reduces the mobility of the solution [16].

One of the unique features of polyacrylamide is the ability to reduce the mobility in the porous medium to a greater extent than would be expected in the measurement of viscosity under standard conditions [17]. This is due to the appearance of elastic turbulence flow of the polymer solution in porous media and leads to a multiple increase in filtration resistance. Herewith, the transition of the polymer solution from the pore channel into the pore accompanied by ripple rate of filtration and leads to a more complete extraction of oil [18].

When polymeric edge is moving, an adsorption of the acrylamide kind occurs, whose magnitude, in static conditions, is 0.1-0.2 mg / g for quartz sand, 0.45-0.55 mg / g for sandstone and limestone [17]. On the one hand, the polymer solution first comes into the high permeability channels and narrows them on account of adsorption, which leads to lower water permeability and leveling the dynamic inhomogeneities of the liquid flow [19]. However, the minimum adsorbed polymer kind is one of the basic requirements, as this can lead to the loss of mobility regulation and the formation of oil shaft.

There are certain restrictions for the use of polymer flooding in EOR. These include temperature more than 90 C, at which degradation of polyacrylamide begins; high salinity of formation water, in which the destruction of the polymer solution structure occurs.

The injection of the polymer solution in reservoirs of low-permeability (permeability of less than 40md) may be technically impossible because of the high pressure [5].

Also polyacrylamide is exposed to mechanical degradation under the influence of high shear loads. This is especially true when passing the pumps, valves and measuring plates. There is evidence that in some mixing stations, mechanical destruction of polyacrylamide may be up to 25-35% [20].

Polymer flooding is recommended only in the early stage of field development. The higher the water content of recoverable oil, the less effective was the process of polymer flooding. These results based on both laboratory and field tests.

According to specialists [21], the use of polymeric compositions for the processing of bottom-hole zone with the aim of with the aim of alignment of the injectivity profile is more efficient technology than the creation of large rims that excite remote formation zones.

There is widespread use of cross-linked polymer systems. In the polymer solution a cross linking agent is introduced. This agent binds the molecules of the polymer between themselves and with the walls of the pores [8, 22]. As polymers, the polysaccharides and hydroxyethyl may used. But polyacrylamide is the most commonly used. As cross linking agents, the multivalent metal cations (chromium, aluminum, iron) may used.

In early development of this technology, it has been found that the resulting gel is not always possible to inject into the remote areas of the formation away from bottom-hole zone. The gelation time is a very important parameter. Today, there are several ways to solve this problem. Among which is the management of the gelation time by means of variations in concentrations of the polymer and cross linker, as well as the pH of the environment.

For example, in earlier works in this sector of the oil industry, the effect of the concentration of polyacrylamide and cross linker (based on chromium acetate) on the gel formation time has been studied in detail [23, 24]. It was noted that the gelation time increases inversely proportional to the polymer concentration and cross linker.

There are many different modifications of cross linked polymer reactants. For example, technology has been proposed to increase oil recovery using encapsulated polymeric systems [25, 26]. These systems represent a dispersion of Micro-gel particles that formed by mixing solutions of polyacrylamide and cross linker (aluminum sulfate or aluminum polyoxochloride). A distinctive feature of the proposed technology is the low concentration of the polymer and cross linker as well as the ability to control sizes produced during cross linking of the polymer particles by varying the concentration of the polymer and the cross linker. The technology is based on water-swallowable polymers and presents an injection of cross linked Polyacrylamide in the form of 0.5-1% pulverulent composition. The swelling and gelation of this cross linked Polyacrylamide occurs at 70° C, under prolonged contact with water [21].

SNF Company offers a large number of reactants based on cross linked polymeric systems. Brand FP-107 is a high molecular weight polymer having a degree of hydrolysis (DH) of 13-18% with improved thermo-stability. Reactant FP-207 is based on weakly anionic polymer and it has a long cross-linking time (due to low charging). Reactant FP-207B has a reduced molecular weight, so that there is the possibility of increasing the concentration of the polymer and form a more dense gel.

The technology of GelFlow Company Mirrico is based on the use of cross linked polymeric and/or thermotropic gel forming systems. This technology contributes in increasing of reservoir coverage using plug flow process (GelFlow-Max), as well as in aligning of injectivity profile (GelFlow, GelFlow-T -increased thermal resistance).

Ready-made reactants that represent radiation-cross-linked polyacrylamide were suggested for EOR. These include reactants like Ritin-10 [27], Temposkrin [28] and Polikar. The difference between the polymer-gelled system Ritin-10 and the chemically cross linked polymers is to provide in advance gelled structures under the radiation processing [27]. Such a cross linking method has several advantages as it does not require the use of expensive measuring devices in the industry and by the reducing of mechanical destruction during injection of the reactants. It should be noted that the radiation-cross-linked reactants represent gelled dispersion of fine particles of size from 0.2 to 4.0 mm [28], so that they have penetration ability only when exposed to large pores and cracks.

In Russia, from those reactants that based on hydrolyzed polyacrylonitriles are brands GIPAN and GEOPAN. The use of "GIPAN" becomes effective only when using highly mineralized water [5]. Reactant "GEOPAN" is a polymeric gelling system based on hydrolyzed polymethacrylate and polyacrylonitrile. It forms a cross-linked polymer system by reaction with polyvalent metal cations.

Reactants based on biopolymers possess higher resistance to mechanical and temperature influences than reactants based on the polyacrylamide. The most actively used in Russia is biopolymer BP-92. 2,000 injection and production wells were processed using reactants based on biopolymers, whereby additional 3 million tons of oil produced [18].

The main disadvantage of biopolymers based technologies is the high cost; however, the possibility of their application in the form of the fermentation liquid can significantly reduce the cost by eliminating the steps of isolation and drying.

The increasing in complexity of conditions of oil production imposes higher requirements to the application of the polymeric reactants and causes the need of developing new approaches to their creation. Due to the huge oil reserves in low-permeability reservoirs, the production of hydrocarbons from them represents particular interest in the oil industry. For example, the share of such oil reserves represents in the total balance of the Russian reserves is up to 40% [29]. Because of the factor of oil recovery from low-permeability reservoirs is significantly lower than the average factor of the high-permeability reservoirs; a great interest presents nano-structured reactants that have a unique penetrating power. Fast and successful growth of technology based on nano-particles barely affects the oil industry in Russia, whereas existing methods of the synthesis of nano-materials, with different basis, have competitive advantage over existing synthesis of reactants. The ability of nano-particles to penetrate the smallest pores of oil-saturated reservoir allows involving in the development of huge oil reserves, whereas oil production from them using the existing technologies is not possible. Experimental studies have shown that the choice of polymer systems based on nano-particles can improve oil recovery in low-permeability reservoirs in about 0.20 - 0.25 [30].

It was reported [31] that reactants based on pre-cross linked nano-particles polymer has been successfully tested on field experiments with the conditions of heterogeneous reservoir permeability of 0.1 md, high salinity of formation water (300 g / L) and high temperature up to 130° C.

Pre-cross linked polymer nano-reactants, that forming gel on a predetermined distance from the bottom hole of the formation zone is much less subjected to mechanical destruction as it passes through the ground equipment. The effect of using such technology can last for 1.5-2 years, whereas the effect of using of various viscoelastic formulations is observed in six months [21].

For the needs of the petroleum industry and for the development of more low permeability reservoirs that include great amount of oil and gas reserves, the development of reactants based on nano-structured polymers and the organization of their production are urgent and important tasks.

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