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## Applying of the associative polymer solutions to enhance oil recovery

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Abstract. Purpose of this report to inform the petroleum readership of recent advances in areas of the associative polymer flooding. Polymer flooding is the industrial enhanced oil recovery method, which successfully has applied in various types of reservoirs. The polymer flooding for high-temperature and high-salinity reservoir faces enormous challenges. Hydrolyzed polymer has been used as the main polymer type for the polymer flooding. Now researchers have turned their attention to associative polymer solutions. This report presents an overview of the associative polymer flooding. Some recent projects have shown an expanding technology. This report reviews published results of the use of associative polymers to enhance oil recovery in recent years. The associative polymer flooding is one enhanced oil recovery (EOR) method being developed recently to increase the oil supply. Polymer flooding application in high-temperature and high-salinity reservoirs is currently limited by polymers chemically and thermally degradation at high temperature and salinity. The associative polymer solutions improve the over-all reservoir conformance by providing mobility control. Water is injected after the polymer solution. Based on the number of new laboratory and pilot tests, field activity is continuing at a moderate level.

#### **1. Introduction**

In this report, the evaluation of several associative polymers is presented. In associative polymer flooding, a water-soluble associative polymer is added to the flood water. The applicability of the associative polymer flooding is carefully controlled by lab and pilot experiments. The associative polymer flooding can make the oil production process more efficient due to decreasing the water/oil mobility ratio. The processes associative polymer flooding have been described theoretically [1-3] and examined experimentally [4, 5]. There are multiple field applications of associative polymer flooding in China, Saudi Arabia and other countries [6].

The novelty of this report is that for the first time a review of laboratory work, pilot tests and industrial implementation of an innovative method of injection of associated polymers into oil reservoirs has been prepared. Injection of chemical reagents causes a range of physical and chemical mechanisms of oil displacement. Injection of aqueous solutions of polymers leads to a change in the properties of the reservoir water, a decrease in the relative mobility parameter and an improvement in the oil-washing properties of water. The decrease in the relative mobility of water and oil increases the coverage of the reservoir effect and the coefficient of oil displacement [7].

The method of injection of an aqueous polymer solution is the injection of a low-concentrated solution of a high-molecular polymer. Polymers are substances with a high molecular weight of about

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containing reservoirs with a relatively high viscosity of oil (up to 100 MPa\*s) and the ratio of the coefficients of mobility of water and oil and moderate heterogeneity. The method of polymer flooding is not used for the development of oil fields with gas caps, fractured reservoir, high permeability and active pressure of the bottom water. The increase in oil recovery in polymer flooding averages 3 - 10%. The size of the polymer slug varies from 0.1 to 0.4 porous volumes. When using the polymer, the ratio of mobility coefficients decreases and, accordingly, the coefficient of the sweep efficiency by area and net pay increases.

Basic mechanisms of enhanced oil recovery during the injection of aqueous solutions of polymers are water thickening, which leads to a decrease in the ratio of the mobilities of oil and water and reduce the possibility of water breakthrough to production wells, and the blockage of high permeability channels due to the adsorption of polymers on the surface of the rock [10]. It should be noted that the apparent viscosity of aqueous solutions of polymers  $\mu^*$  increases with increasing filtration rate and with decreasing size of pore channels. The apparent viscosity can be 10 - 20 times higher than measured. The apparent viscosity of the polymer solution is defined as

$$\mu^* = \tau / \gamma \tag{1}$$

where  $\tau$  shear stress,  $\gamma$  shear gradient.

At high shear gradients there is a mechanical destruction of polymer chains. This leads to a decrease in the viscosity and the resistance factor, and the resistance factor decreases faster than the viscosity of the polymer [11-15].

The adsorption of polymers by the surface of the porous medium increases with increasing the salinity of the reservoir water and reducing the permeability and can range from 0.007 to 0.75 kg/m<sup>3</sup>. The amount of adsorbed polymer depends on the structure of the porous medium, lithology of rocks and component composition, specific weight, filtration rate in a porous medium, temperature and pH of the medium [13]. Adsorption on the rock surface depends on the type of polymer.

Associative polymers, or multiply adherent polymers are a variety of polymers that have a higher thickening ability than traditional water-soluble polymers, such as polyacrylamide. Associative polymers are copolymers of a hydrophilic acrylamide monomer with a small amount of a hydrophobic monomer (0.3 - 4 mol%), such as a partially hydrolyzed acrylamide [16]. Copolymers have a block structure with two or more different structural blocks of a hydrophobic monomer located at a considerable distance from each other on a hydrophilic polymer chain. Copolymers are divided into regular and irregular copolymers. In the aqueous solution that has chemical polarity, the hydrophobic areas of polymer chains interact with each other and form associative links. Copolymers used as mobility control agents in EOR/IOR methods [2].

Vinylpyrrolidone (VP) is one of the important hydrophobic monomers used for copolymerization with acrylamide as working agents for the polymer flooding. Polyvinylpyrrolidone is a water-soluble polymer composed of monomeric units of N-vinylpyrrolidone (NVP). Polyvinylpyrrolidone was first synthesized by Walter Reppe. The patent for polyvinylpyrrolidone was registered in 1939. Polyvinylpyrrolidone is soluble in water and other polar solvents. In its dry form, polyvinylpyrrolidone has the appearance of a white or light-yellow puff of hygroscopic powder, which easily absorbs up to 40% of its weight in atmospheric water (figure 1). The molecular formula of polyvinylpyrrolidone is  $C_6H_9NO$ , the molar mass is 2.500 - 2.500.000 g / mol, the density is  $1.2 \text{ g / cm}^3$ , the melting point is 150-180 °C. Polyvinylpyrrolidone is readily soluble in water, forming water-soluble complexes, and is used to thicken water during polymer flooding. The polymer flooding is one of the key methods of EOR.

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**Figure 1.** Ball-and-stick model (a) and appearance in powder form of the N-vinylpyrrolidone molecule (b), a compound used in organic synthesis. Colour code: Carbon, C: black; Hydrogen, H: white; Oxygen, O: dark grey; Nitrogen, N: light grey. Source: *Discovery Studio Visualizer*.

Homogeneous polymer vinylpyrrolidone has good thermal stability in aqueous and saline solutions. Vinylpyrrolidone polymer is not a good agent for increasing the viscosity of an aqueous polymer solution. To achieve a viscosity equivalent to a viscosity similar to the viscosity of hydrolyzed polyacrylamide, working compound vinylpyrrolidone requires almost as 10 times concentration as hydrolyzed polyacrylamide [1, 3 and 6].

Synthetic polymers such as partially HPAM are not thermally stable. Thermal stability of hydrolyzed polyacrylamide can be improved by incorporating monomer such as NVP. The development of terpolymers with the incorporation of NVP brought stability of compound up to 120°C. The use of NVP increased the cost of the polymer and limited its molecular weight [15].

The cost of the polymer vinylpyrrolidone is three times higher than that of the polymer PAM101. The adsorption of the vinylpyrrolidone polymer is very high on the surface of the rocks. These two factors - cost and adsorption make the polymer vinylpyrrolidone economically unreasonable for application as a working agent for polymer flooding.

A copolymer of acrylamide (AM) / N-Vinylpyrrolidone was synthesized in an aqueous solution. As shown in [14], the addition of VP to AM can reduce the thermal hydrolysis of AM in the presence of divalent cations. The decrease in hydrolysis is directly proportional to the content of VP in the copolymer. A copolymer of acrylamide/ N-Vinylpyrrolidone with an equal weight ratio of monomers was stable at 120 °C in the presence of seawater for several months. The copolymerization provides a hydrogen bond between AM and VP [14].

The adsorption AM/ VP in the core, represented by sandstone, was lower compared to hydrolyzed polyacrylamide. Poly 1-vinyl-2-pyrrolidone (partially hydrolyzed acrylamide) copolymer that was obtained later had a higher decomposition temperature up to 23 °C than the homopolymer of acrylamide. The inclusion of VP in the AM chain increases shear resistance compared to the AM due to the large size of VP [11, 17 and 18]. VP helps better protect acrylamide from degradation, but a polymer with high molecular weight is difficult to obtain due to low polymerization activity [9, 10, and 19].

Currently, laboratory studies of associative polymers and HPAM are being actively conducted with the aim of preserving properties at high temperatures and salinity over a long period of time; corefloodings for different field conditions and mathematical modeling of the process of oil COTech IOP Publishing IOP Conf. Series: Materials Science and Engineering **700** (2019) 012062 doi:10.1088/1757-899X/700/1/012062

displacement with copolymer aqueous solutions are carried out. During corefloodings, the influence of various factors on the apparent viscosity, such as polymer concentration, copolymer composition, electrolyte concentration, temperature, shear rate, and surfactant concentration, was investigated.

## 2. Coreflooding by the associative polymer solutions

Below is a brief overview of polymer flooding in high-saline and high-temperature reservoirs. During polymer flooding in the pilot section of Guan-109 (7 injection and 12 producing wells) from December 2016 to December 2017, 0.102 PV of an aqueous polymer solution was injected. The viscosity of the associative polymer AP-P7 changed from 31.7 to 88.5 mPa \* s at a concentration of 1500-2500 mg / l. The formation water mineralization reached 26983 mg / l, and the formation temperature was 78 ° C. Oil production increased from 27.7 to 51.7 m<sup>3</sup> / day, and the water cut decreased from 92.3 to 90.1%. The binary system made it possible to improve the oil recovery coefficient by 26.3% after water flooding [5]. Table 1 presents studies of the thermal stability of various polymers and copolymers.

Table 1	. The thermal	stability	of various	polymers	and co	polymers	[9].
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Polymers and copolymers	Salinity (ppm)	T ( <sup>0</sup> C)	Time (days)	Comments	References
HPAM	30 000	85	100	-	[7]
HPAM	20 000	90	619	-	[20]
AMPS-AM	30 000	100	200	Higher cost	[7]
AMPS-AM	33 560	93	100	Higher cost	[14]
NaAMPS	33 560	121	100	Higher cost	[14]
VP-AM	33 756	121	100	Lower molecular weight, lower viscosity	[21]

Interesting results in core flooding were obtained by testing the polymer Zetag 8187G, which is a copolymer of acrylamide and a quaternized cationic monomer [12]. In laboratory studies on polymer flooding of the core of low-permeable sandstone at high temperatures (85 °C) and in high-saline brine (150 000 ppm,  $Ca^{2+}$ ,  $Mg^{2+}$ ), an oil displacement coefficient of 60.95% was achieved when pumping an aqueous polymer solution of 33.68% of the total pore volume.

A ter-polymer containing N-vinylpyrrolidone, which is intended for polymer flooding in high-salt and high-temperature collectors, was investigated during core flooding (table 2).

Test	Core ID	1 <sup>st</sup> flood	Recovery (% OOIP)	Polymer flood	Oil displacement ratio (% OOIP)	Crude type
Test 3	A3	Fresh Water	16.7	Superpusher, 20 cc	5.8	А

Table 2. Experimental layout of core displacement study at 82 °C.

Crude oil type A had viscosity ranged from 1 to 1.68 mPa\*s (1.6 mPa\*s at 60  $^{0}$ C) and density of oil was 0.78 g/cm<sup>3</sup>. During the experiments, it was found that at a concentration of 400 ppm of N-vinylpyrrolidone ter-polymer at a concentration of 92,000 ppm and a temperature of 82 °C modeled in the sample, the maximum displacement coefficient reaches 22.5% of the total oil volume (table 3). In previous studies of a polymer such as VP, with a polymer concentration of 2000 ppm and a temperature of 85 °C in a core sample of sandstone, the displacement coefficient was 13.5% [22].

Laboratory studies of the terpolymer N-vinylpyrrolidone showed that oil recovery may increase up to 22.5% (Figure 2).

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Table 3. Core polymer flooding in high-saline and high-temperature core samples.

Polymer	Polymer concentration (ppm)	Temperature (°C)	Core type	Oil displacement ratio (%)	References
AP-P7	1500-2500	78	Sandstone	26.4	[5]
Copolymer of acrylamide and quaternized cationic monomer	2000	85	Sandstone	60.9	[12]
Terpolymer containing N- vinylpyrrolidone	400	82	Sandpack	22.5	[23]



Figure 2. Oil recovery in case of flooding with a terpolymer vinylpyrrolidone.

#### **3.** Conclusions

Injection of aqueous solutions of traditional polyacrylamide polymers under conditions of increased salinity of formation water and the content of calcium and magnesium salts becomes unstable, disruption of the structure of polymers occurs and the effect of water layer thickening disappears. In contrast to traditional polymer flooding, in such conditions, polymer flooding with associative polymers, that is, polymers that are polymerized with several monomers, can find effective application. The viscoelastic system of associative polymers is created by the interaction of hydrophobic parts of the chain, and not due to the introduction of an additional crosslinker. Polymer flooding by associative polymers is applicable in a wider range of reservoir temperatures and salinity compared to traditional polymer flooding. In this regard, in recent years, interest in the use of polymer flooding associative polymers has been growing. In this article, we considered an associative polymer and previous experiments with polymers in reservoir conditions with high salinity and high temperature. Polymers with polymerization of vinylpyrrolidone contribute to an additional increase in oil recovery when the core is flooded at a temperature of 86 °C and a salinity of 92,000 ppm. Polymer flooding by associative polymers of a new type has not been tested at the proper level in oil fields. Laboratory studies and comparing them with the latest research in this area are very necessary. With proper planning, logistics and in conditions of low crude oil prices, the injection of aqueous solutions of associative polymers can be cost-effective.

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- EOR Enchanced Oil Recovery
- IOR Improved Oil recovery
- VP Vinylpyrrolidone
- NVP N-vinylpyrrolidone
- HPAM Hydrolyzed Poly-Acrylamide
- AM Acrylamide
- OOIP Original Oil in Place

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