Article

Open Access

AN EXPERIMENTAL INVESTIGATION INTO ENHANCED OIL RECOVERY (EOR) BY POLYMER FLOODING IN SANDSTONE RESERVOIRS UNDER HIGH TEMPERATURE AND HIGH SALINITY CON-DITIONS USING A COMBINATION OF TWO SYNTHETIC POLYMERS

Ali Mohsenatabar¹, Abbas Khaksar Manshad¹*, Ghasem Zargar¹, Amir H Mohammadi²*

¹ Department of Petroleum Engineering, Abadan Faculty of Petroleum Engineering, Petroleum University of Technology (PUT), Abadan, Iran

² Discipline of Chemical Engineering, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa

Received September 14, 2018; Accepted December 19, 2018

Abstract

Polymer flooding at high temperature and high salinity is a new challenge in the petroleum industry. Commonly used polymers are not effective at high temperatures and high salinity, and under harsh conditions, they are degraded and reduced viscosity. In this study, a combination of two synthetic polymers namely SAV37 and AN125VHM was used for polymer flooding tests. Initially, the stability of polymer solution in different weight percentages of the two polymers was investigated against increasing temperature and salinity. Then, 50% of each polymer was added to the flood in the 2000 ppm polymer concentration under the reservoir temperature of 85°C and the salinity of 150,000 ppm in the presence of divalent ions (Ca²⁺, Mg²⁺). The results show that the combination of 50% of the two polymers increases the time of arrival of the injected flood to production, so the recovery factor has increased compared to water flooding. Also, the relative permeability curve was obtained after a history matching using one of the commercial numerical simulators, which indicates the control of the injected fluid mobility at high temperature and high salinity conditions.

Keywords: Polymer flooding; High Temperature; High Salinity; Synthetic Polymer; Enhanced Oil Recovery (EOR).

1. Introduction

Polymer flooding is a chemical enhanced oil recovery (EOR) method. In this method, by adding water-soluble polymers, the viscosity of the injected fluid is increased and prevents the fingering phenomenon ^[1]. This property brings the sweeping fluid into a porous medium piston-like in the direction of the production well, and the remaining oil content in the porous medium is minimized ^[2]. The polymers used in this method are divided into two general synthetic and natural polymer groups ^[3]. The base of the synthetic polymer is acrylamide group, the most famous of which is the hydrolyzed polyacrylamide polymers ^[4]. Xanthan is one of the most famous polymers in the category of natural polymers ^[5]. Most of the world's reservoirs are in deep areas with high temperatures and high salinity. Commonly used polymers, such as those mentioned earlier, cannot be used in such environments ^[6]. In fact, in a harsh environment with high temperatures and high salinity, these polymers are degraded, and the viscosity of the injected fluid is reduced ^[7]. Acrylamide-based polymers are hydrolyzed in the high-temperature environment and have a negative charge ^[8]. Due to the presence of single and divalent ions in the porous medium, molecules with a negative charge due to hydrolysis at high temperatures are trapped by dual-value ions ^[9]. This process causes both the viscosity of the polymer solution to be reduced, and the polymer injection cannot be carried out in real, and by polymer adsorption on the surface of the rock, the permeability of the reservoir is

reduced and causes problems when injected. Figure 1 shows the trapping of acrylamide molecules by divalent ions ^[10].



Figure 1. Trapping the acrylamide molecule by divalent ion [11]

Natural polymers are also degraded under high temperatures and high salinity. In general, Xanthan gums are more stable than acrylamide at high salinity but are not stable at high temperatures ^[3]. As shown in Figure 2, these properties cause polymer molecules to be separated from the water phase and reduce the viscosity of the polymer solution, and in addition, by adsorption of polymer molecules on the surface of the rock, the permeability of the porous space decrease severely ^[12].



Figure 2. The absorption of polymer molecules on the surface of the porous medium

Therefore, the use of new polymers in environments with high temperatures and high salinity is a new challenge in the polymer industry. Various polymers have been introduced for such environments. In the group of synthetic polymers, sulfate polymers and Co-polymer and Ter-polymers were designed for use at high temperature and high salinity conditions. Sulfate polymers are relatively expensive ^[13]. Some studies have been conducted on the development of acrylamide polymers. Hourdet et al. synthesized a high temperature resistant polymer that has poly (N-isopropyl acrylamide) (PNIPAM) and polyethylene (PEO) structures so that polymer is a series of blocks at low temperature in water that can be solubilized, but with increasing temperature the solubility of these blocks decrease, and polymer make the adhesion, and the viscosity decrease does not occur ^[14]. The main problem with this polymer is low molecular weight, and a high viscosity solution requires a high concentration of polymer, which has two major problems; one is the high cost of supplying polymer and other problems during the injection and low injection capacity ^[13]. In addition, the sulfating of polyacrylamide can make the polymer resistant to high temperatures. Therefore, polymers called AMPS were introduced. Although these polymers can withstand temperatures up to 120°C, they are very expensive, and the use of these polymers alone is not economical ^[15]. Also, new studies have shown that the use of nano silicates with polyacrylamide can create conditions that are stable at high temperatures and high levels of salinity ^[16]. In the group of the natural polymer, some studies have also been conducted that can be used at high temperature and high salinity conditions. The most recent of these polymers is the polymer of Schizophyllan. This polymer is obtained from the fungus of the body of dead trees ^[17]. This polymer is stable at high salinity (200,000 ppm) and high temperature (120°C) ^[18]. But economically it is not profitable and has a high cost than oil prices. In general, the use of synthetic polymers is better than natural polymer, since they are easy to produce and low cost, they are not subjected to bacterial degradation in the reservoir, and fewer problems with injection. Therefore, the production of acrylamide-based

synthetic polymers that can withstand high temperatures and salinity can have economic benefit. SNF has produced acrylamide-based polymers that can be used under high temperature and high salinity. As Figure 3 shows, polymer family of SAV is in the Super-pusher group, which can be used at high temperatures and high salinity.



Figure 3. Different group of polymers with temperature and salinity tolerance ^[19]

In this study, two samples of the company's polymers (SNF) were selected. By studying the rheological properties under the influence of temperature and salinity, a solution was used for flooding at high temperature and high salinity condition. To prepare a 6000 ppm polymer solution, two polymer samples, SAV37, and AN125VHM were combined in various weight percentages, each in brine and formation water with a salinity of 10,000 ppm and 150,000 ppm at 25 to 85°C. After studying the rheological properties of the solutions, the best weight percent composition of the polymer was chosen for injection. After determining the best polymer solution, its stability was studied over time. Then, by considering the oil viscosity, the 2000 ppm concentration of polymer was used for polymer flooding. The polymer flooding was applied on the sandstone core sample under constant pressure at 85°C, the salinity of the formation water of 150000 ppm and confining pressure of 2000 psi around the core.

2. Experimental

2.1. Materials

2.1.1. Core sample

Two sandstone samples were selected from Aghajari formation in one of the Iranian oil fields. After coring and cores preparation, their petrophysical properties including porosity and permeability were measured in different ways. Table 1 shows the characteristics of each sample.

Table 1.	Information of core samples.
----------	------------------------------

Core ID	S-1	S-2
Length (cm)	7.602	7.602
Diameter (cm)	3.686	3.687
Pore Volume (cm ³) @14.7psi	15.833	11.221
Porosity-Gas (%)	19.040	13.685
Porosity-Water (%)	19.519	12.145
Permeability (brine water-mD)	17.956	17.450

2.1.2. Crude oil

The sample of crude oil used in this study was selected from the Gachsaran oil field of Iran. This oil sample is light crude oil. The characteristics of the oil sample at two different temperatures are summarized in Table 2.

Table 2. Crude oil properties at two different temperatures

Temperature, °C/°F	Density, g/cm ³	Viscosity, cP
25/77	0.8421	34.847
85/185	0.8515	5.0247

2.1.3. Electrolyte

Two samples of brine were used for injection, and one was considered as synthetic formation water. The brine used for water flooding and the polymer solution was concentrated in 10000 ppm of NaCl in deionized water. Brine was prepared by adding specific electrolytes with different percentages with a total concentration of 150000 ppm. The used electrolytes and the values of used weights are summarized in Table 3.

Table 3. Electrolytic Information for synthetic formation water

Electrolyte	Weight, g	Molecular weight, g/mol
NaCl	110	58.44
KCI	2	75.56
CaCl ₂	5	110.98
MgCl ₂	33	95.22

2.1.4. Polymer

The SAV37, AN125VHM polymers from SNF Company were used to make polymer solutions. The AN125VHM polymer is a copolymer, 25% of which is made up of AMPS polymer. The SAV family of polymers is a polymer that has the N-vinyl-pyrollidone group in its structure. These specimens are known as high temperature and salinity resistant polymers worldwide. The characteristics of these two polymers are summarized in Table 4.

Table 4. Properties of polymers*

Polymer	Company	Form	Molecular weight
SAV37	SNF SAS	White powder	2-5 MMD
AN125VHM	SNF SAS		6-8 MMD

* More information is available upon request to the authors

As shown in Table 5, 5 polymer solutions at a salinity of 10000 ppm and 6000 ppm polymer concentration were studied from 25 to 85°C. Then the salts in the water were added to the solutions to achieve a salinity of 150000 ppm. The viscosity of the solutions was then measured at 25°C and 85°C. Then, a percentage of a mixture of two polymers was considered for flooding. A magnetic and thermal stirrer was used to make a polymer solution. Brookfield rheometer was also used to measure the viscosity of solutions.

Table 5. The combined percentages of the two used polymers

Solution	SAV37	AN125VHM
1	2 gr (100%)	0
2	1.4 gr (70%)	0.6 gr (30%)
3	1 gr (50%)	1 gr (50%)
4	0.6 gr (30%)	1.4 gr (70%)
5	0	2 gr (100%)

Total polymer concentration 6000 ppm

2.1.5. Core flooding

At first, the samples were saturated with water, then a sample of oil was injected into the core sample with varying oil rate to allow samples to reach the connate water saturation. Then, at different pressures, the oil rate was measured to determine the relative permeability of the oil in the connate water saturation. Then one of the samples was considered for water flooding. The 10000 ppm brine flooding was done under the constant pressure of 10 psi between two ends of the cores. When the flood was reached to residual oil saturation, the relative permeability of the water was measured. Regarding tests on different weight percentages of polymers, a polymer with 50% by weight of each of the polymers was considered. Therefore, another core sample was flooded with the polymer. Since the viscosity of oil at 85 °C was 5.247 cp, 2000 ppm concentration of polymer was considered for polymer flooding. Polymer flooding was performed under constant pressure of 14 psi at two ends of cores. When the injection reached to residual oil saturation, the relative permeability of the polymer solution was measured. Figure 4 shows the schematic of the flooding device.



Figure 4. A schematic of the flooding device

3. Results and discussion

3.1. Rheological properties of the polymer

In this study, the combination of two SAV37 and AN125VHM polymers with different weight percentages in the 6000 ppm of polymer concentration were studied. First, the stability of polymer solutions in salinity of 10000 ppm of salt was studied with increasing temperature so that the viscosity of the solutions decreases with increasing temperature according to Figure 5. Of course, with increasing concentration of polymer AN125VHM, the viscosity of the polymer solution increases and at high temperatures, the solution with a concentration of 100 % of the AN125VHM polymer has the highest viscosity.

The stability of polymer solution viscosity was investigated by increasing salt in solution in the presence of divalent ions (Ca^{2+}, Mg^{2+}) and rising temperature from 25 to 85°C. As the following figures show, the viscosity of solutions decreases with increasing the salinity of the polymer solution from 10000 ppm to 150000 ppm (presence of divalent ions). According to the graphs shown in Figure 6, the variation in viscosity of the solution decreases when the percentage of concentration of AN125VHM is increased. Therefore, the graphs show that the concentration of this polymer is susceptible to divalent salts and reduces viscosity. But in lower percentages of this trend, viscosity reduction is less. Therefore, three different concentrations of the polymer were selected to increase the temperature.

As shown in Figure 7, the use of SAV37 in solution alone lowers viscosity in high salinity and temperatures. However, the viscosity of the solution increases with the addition of polymer AN125VHM. As the figure shows, the weight ratio of 50% per polymer shows a higher

viscosity in a saline solution of 150000 ppm with increasing temperature. Therefore, 50 weight percent of each polymer was selected for flooding.



Figure 5. Viscosity changes of polymer solution at 6,000 ppm concentration with increasing temperature in various weight percentages of two SAV37 and AN125VHM polymer.



Figure 6. Viscosity changes of polymer solutions at 25 $^{\circ}$ C with increasing salinity from 10000 ppm to 150000 ppm in the presence of dual value ions

In the reservoir under field conditions, due to the large dimensions of the reservoir, the viscosity of the polymer must be stable within the time course of polymer flooding. In this study, with regard to the fact that the injection of polymer in the concentration of polymer 2000 ppm was considered, the polymer viscosity was measured at 185°F for 30 days. According to the normalized viscosity curve (Figure 8), the solution was highly stable during this period.



Figure 7. Viscosity changes of polymer solutions in salinity of 150,000 ppm solution with increasing temperature in three different amounts of weight percentages of polymers



Figure 8. Under temperature viscosity stability for 30 days

3.2. Core flooding

Flooding results show that the combination of two polymers is 50% of each polymer which is effective under high temperature and high salinity, and the recovery of the oil is higher than the water flooding ratio. Also, the time of injected fluid arrival for production (break-through time) has increased, which in fact represents the control of the sweeping fluid mobility. Figure 9 shows the recovery of oil.

According to Figure 10, the amount of residual oil saturation in the polymer flooding is lower compared to water flooding, which in fact represents the mobility control in the porous medium due to the addition of the polymer.

As shown in Figure 11, water production was started during water flooding after 0.16 volume of pore volume injected, while in the polymer flooding the water was produced after injection of 0.28 volume of pore volume injected. Also, the amount of fluid injected has always been less than water flooding for polymer flooding.

Relative permeability curve for water and polymer flooding conditions were obtained using one of the commercial simulators after the history matching of production history using the

Corey relative permeability equation. As shown in Figure 12, the relative permeability diagram of the oil moves to the right, indicating that the oil is swept better during polymer flooding compared to water flood. Also, the relative permeability curve of the water shows a lower gradient and moves downwards indicating the mobility control by increasing the polymer and the efficiency of the polymer at high temperatures and high salinity.



Figure 9. Oil recovery curve in two modes of water and polymer flooding at high temperatures and salinity



Figure 11. Cumulative water production graph during water and polymer flooding



Figure 10. Curve of oil saturation during water and polymer flooding



Figure 12. The relative permeability curve of water and oil in the conditions of polymer and water flooding

4. Conclusion

By adding AN125VHM polymer, the viscosity of the water is higher in comparison with the condition when SAV37 polymer is added to the solution. But according to the obtained graphs, the AN125VHM polymer has a viscosity reduction at high temperatures and high salinity compared to SAV37. Among the combined percentages of these two polymers together, 50% for each, shows better stability and the high viscosity at high temperatures and high salinity. Therefore, in this combination, a percentage of each of the 2000 ppm polymer solution was selected for polymer flooding. As the results show, polymer flooding was effective at 85°C and salinity of 150000 ppm (in the presence of a large number of divalent ions), and a 23% increase in EOR was obtained in comparison with water flooding. Also, relative permeability diagrams indicate the mobility control of displacing fluid in polymer flooding compared to water flooding. Some experimental studies must be conducted in future on adsorption of polymer on the rock surface and its impact on residual oil saturation. Effect of ions (Na⁺, Ca^{2+,} and Mg²⁺) on the rheology of the polymer solutions should be studied exclusively.

References

- [1] Shah DO. Improved oil recovery by surfactant and polymer flooding: Elsevier, 2012.
- [2] Taylor K, and Nasr-El-Din H. Water-soluble hydrophobically associating polymers for improved oil recovery: a literature review. in SPE International Symposium on Oilfield Chemistry, 1995.

- [3] Kamal MS, Sultan AS, Al-Mubaiyedh UA, Hussein IA. Review on Polymer Flooding: Rheology, Adsorption, Stability, and Field Applications of Various Polymer Systems. Journal Polymer Reviews, 2015; 55(3): 491-530.
- [4] Zhao X, Liu L, Wang Y, Dai H, Wang D, and Cai H. Influences of partially hydrolyzed polyacrylamide (HPAM) residue on the flocculation behavior of oily wastewater produced from polymer flooding. Separation and Purification Technology, 2008; 62: 199-204.
- [5] Ghoumrassi-Barr S, and Aliouche D. A Rheological Study of Xanthan Polymer for Enhanced Oil Recovery. Journal of Macromolecular Science, Part B, 2016; 55: 793-809.
- [6] Yanbiao ZFYGL, and Jiangbo L. Development of Chemical Oil Displacement Agent for High Temperature and High Salinity Reservoir. Advances in Fine Fetrochemicals, 2005; 5:
- [7] Wu Y, Mahmoudkhani A, Watson P, Fenderson TR, and Nair M. Development of new polymers with better performance under conditions of high temperature and high salinity. in SPE EOR Conference at Oil and Gas West Asia, 2012.
- [8] Rellegadla S, Prajapat G, and Agrawal A. Polymers for enhanced oil recovery: fundamentals and selection criteria, Applied Microbiology and Biotechnology, 2017; 101: 4387-4402.
- [9] Zhu D, Zhang J, Han Y, Wang H, and Feng Y. Laboratory study on the potential EOR use of HPAM/VES hybrid in high-temperature and high-salinity oil reservoirs. Journal of Chemistry, 2013; Article ID 927519.
- [10] Chen Q, Wang Y, Lu Z, and Feng Y. Thermoviscosifying polymer used for enhanced oil recovery: rheological behaviors and core flooding test. Polymer Bulletin, 2013; 70: 391-401.
- [11] Rashidi M. Physico-chemistry characterization of sulfonated polyacrylamide polymers for use in polymer flooding, 2010, PhD Thesis, The University of Bergen, Norway.
- [12] Kamal MS, Sultan AS, Al-Mubaiyedh UA, Hussein IA, and Feng Y. Rheological Properties of Thermoviscosifying Polymers in High-temperature and High-salinity Environments. The Canadian Journal of Chemical Engineering, vol. 93, pp. 1194-1200, 2015.
- [13] Wang Y, Lu ZY, Han YG, Feng YJ, and Tang CL. A novel thermoviscosifying water-soluble polymer for enhancing oil recovery from high-temperature and high-salinity oil reservoirs. in Advanced Materials Research, 2011, pp. 654-657.
- [14] Tamsilian Y, and Ramazani A. Smart polymer flooding process. ed: Google Patents, 2015.
- [15] Vermolen E, van Haasterecht MJ, Masalmeh SK, Faber MJ, Boersma DM, and Gruenenfelder MA.Pushing the envelope for polymer flooding towards high-temperature and high-salinity reservoirs with polyacrylamide based ter-polymers. in SPE Middle East Oil and Gas Show and Conference, 2011.
- [16] Zhu D, Wei L, Wang B, and Feng Y. Aqueous hybrids of silica nanoparticles and hydrophobically associating hydrolyzed polyacrylamide used for EOR in high-temperature and high-salinity reservoirs. Energies, 2014; 7: 3858-3871, 2014.
- [17] Wengel M, Kothe E, Schmidt CM, Heide K, and Gleixner G. Degradation of organic matter from black shales and charcoal by the wood-rotting fungus Schizophyllum commune and release of DOC and heavy metals in the aqueous phase. Science of the Total Environment, vol. 367, pp. 383-393, 2006.
- [18] Quadri SMR, Jiran L, Shoaib M, Hashmet MR, AlSumaiti AM, and Alhassan SM. Application of biopolymer to improve oil recovery in high temperature high salinity carbonate reservoirs. in Abu Dhabi International Petroleum Exhibition and Conference, 2015.
- [19] SNF. Available: http://www.snf-group.com/markets/oil-gas/

Dr. Abbas Khaksar Manshad, Department of Petroleum Engineering, Abadan Faculty of Petroleum Engineering, Petroleum University of Technology (PUT), Abadan, Iran

To whom correspondence should be addressed: Prof. Dr. Amir H Mohammadi, Discipline of Chemical Engineering, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa