NOVO POLIMERO AQUOSO PARA RESERVATORIOS DE ALTA TEMPERATURA

NEW AQUEOUS POLYMER FOR HIGH-TEMPERATURE RESERVOIRS

НОВЫЙ ВОДОРАСТВОРИМЫЙ ПОЛИМЕР ДЛЯ УВЕЛИЧЕНИЯ НЕФТЕОТДАЧИ

SAVINYKH Yu. V.^{1*}; LANG L. D.²

¹Tomsk Polytechnic University, Institute of Petroleum Chemistry SB RAS, 30 Lenin Avenue, Tomsk, Russia.
(phone: +7-913-861-65-65)

²JV Vietsovpetro, 105A Le Loi st., Vungtau, Vietnam
(e-mail: langld.rd@vietsov.com.vn)

* *Corresponding author: Savinykh Yu. V.*
e-mail: yu-sav2007@yandex.ru

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RESUMO

A injeção de polímeros é um método tecnologicamente simples e altamente eficaz de recuperação aprimorada de petróleo. O método baseia-se na adição de uma pequena quantidade de polímero em injeções convencionais de água de reservatórios de petróleo. O aumento da viscosidade e a redução da mobilidade da água injetada são para igualar a frente de deslocamento retardando o movimento da água nas zonas altamente permeáveis e restringindo a formação do dedo da água. Esses fatores ajudam a aumentar a eficiência da varredura e a eficiência do deslocamento de óleo-água durante a inundação. A injeção de polímeros tem sido usada com sucesso em reservatórios de clastos e carbonatos, bem como em reservatórios de baixa permeabilidade, como por exemplo, em uma fundação fraturada. No entanto, a maior parte do gel polimérico atual usado para controlar os fluxos de água é deteriorado por um alto teor de íons Ca^{2+} e Mg^{2+} na água de formação ou na água injetada. Da mesma forma, os géis de polímero perdem sua estabilidade na alta temperatura do reservatório (acima de 70 °C). O desenvolvimento de polímero solúvel em água, que não altera suas propriedades reológicas sob alta salinidade e alta temperatura (acima de 100 °C), é muito importante na produção *offshore*, onde a água do mar é comumente usada para a injeção (alta salinidade de 30-40 g/l).

Palavras-chave: *composição de polímeros, polímero irradiado, recuperação de óleo.*

ABSTRACT

Polymer flooding is technologically simple and highly effective method of enhanced oil recovery. The method is based on adding a small amount of polymer in conventional water flooding of oil reservoirs. The increase in viscosity and the reduction of the mobility of injected water are to equalize the displacement front by slowing the moving of water in the highly permeable zones and restricting the formation of water finger. These factors help to increase the sweep efficiency and oil-water displacement efficiency during flooding. Polymer flooding has been used successfully in clastic and carbonate reservoirs, as well as in low-permeability reservoirs such as a fractured basement. However, most of the current polymer gel used for control water flows are decayed by a high content of ions Ca^{2+} and Mg^{2+} in formation water or in injected water. Similarly, polymer gels lose their stability at high reservoir temperature (above 70°C). Developing water-soluble polymer, which does not change their rheological properties under high salinity and high temperature (over 100°C), is very important when producing offshore, where sea water is commonly used for flooding (high salinity of 30-40 g/l).

Keywords: *polymer composition, irradiated polymer, oil recovery.*

АННОТАЦИЯ

Полимерное заводнение - это технологически простой и высокоэффективный метод повышения нефтеотдачи пластов, основанный на добавке к воде небольшого количества водорастворимых полимеров при заводнении нефтяных пластов. Увеличение вязкости и снижение подвижности воды способствуют выравниванию фронта вытеснения, замедляют ее продвижение в высокопроницаемых зонах, уменьшают вязкостное языкообразование. Эти факторы приводят к повышению коэффициентов охвата и вытеснения при заводнении. Полимерное заводнение успешно применяется в терригенных и карбонатных коллекторах, как низкопроницаемых, так и трещиноватых. Однако, большинство полимерных гелей, применяемых в настоящее время для ограничения водопритокков, разрушаются при повышенном содержании ионов Ca^{2+} и Mg^{2+} в пластовой или закачиваемой воде. Также полимерные гели теряют стабильность при температуре пласта выше 70°C . Получение водорастворимых полимеров, не меняющих свои реологические свойства при высоких концентрациях солей и температуре более 100°C , актуально при разработке месторождений в шельфовой зоне, где для заводнения используется морская вода с содержанием солей 30-40 г/л. В работе такой полимер был получен радиационной сополимеризацией поливинилпирролидона и акриламида. Раствор этого полимера устойчив в морской воде при температуре до 120°C . Среднее значение приращения коэффициента нефтеотдачи при заводнении с применением оторочки полимера на моделях слоистого неоднородного пласта составило 12 %.

Ключевые слова: радиационная полимеризация, полимерное заводнение, нефтеотдача

INTRODUCTION

Polymer flooding is a very mature method with more than 40 years of applications. It has been shown to be effective in recovering unswept oil by improving the mobility ratio. Many examples of technically successful polymer field projects are reported in some literature [1, 2]. Field practice has shown that polymer flooding can increase recovery of 5-30% of OOIP. The total cost of polymer flooding is actually less than for water flooding due to decreased water production and increased oil production. The efficiency of the process is in the range of 0.7 to 1.75 lb of polymer per bbl of incremental oil production [3].

The newly developed polymer was obtained by copolymerization of polyvinylpyrrolidone (PVP) and acrylamide (AM). Polyvinylpyrrolidone is soluble in seawater, but its solution has a low viscosity of 30-40 MPa.s at a very high polymer concentration such as 5% by weight. Polyacrylamide is perfectly soluble in fresh water and its solution has a high viscosity, though, it is easily hydrolyzed and precipitated in seawater due to the reaction with divalent metal ions such as Ca^{2+} and Mg^{2+} , which reduce the solution viscosity. Under the influence of high temperature, the polymer is fully precipitated and subsequently, the polymer solution viscosity will be completely lost. New polymer product (so call A-806) was synthesized by the chemical interaction of acrylamide with polyvinylpyrrolidone. This polymer has highly

water-soluble and does not decay in high salinity water and a high temperature of 120°C .

METHODS

Preparation of copolymer A-806 was performed in two stages. At the first stage, the polyvinylpyrrolidone was irradiated inside a chamber with source of γ -radiation. During irradiating polyvinylpyrrolidone, the reaction between the active radicals in polymer matrix forms peroxides due to the irradiation and the oxygen in the air. Peroxides are thermostable at room temperature and begin to decompose to forms free radicals at temperatures over 50°C . Next, the reaction was conducted by irradiated polyvinylpyrrolidone with acrylamide in the aquatic environment at temperature $T = 70^\circ\text{C}$.

Small-angle x-rays scattering (SAXS) and photoelectron spectroscopy methods (PESM) were used for the analysis of polymers [4,5]. SAXS is a small-angle scattering technique by which nanoscale density differences in a sample can be quantified. This means that it can determine nanoparticle size distributions, resolve the size and shape of (monodisperse) macromolecules, determine pore sizes, characteristic distances of partially ordered materials, and much more. SAXS has been used for the determination of the microscale or nanoscale structure of particle systems in terms of such parameters as averaged particle sizes, shapes, distribution, and surface-to-volume ratio. PESM of polymers were obtained by use of on AEI (Kratos) ES200B X-ray photoelectron

spectrometer, operated in the FRR mode, using unmonochromatized Mg K X-radiation. The data were collected with a computer, the latter being used for most of the data analysis.

RESULTS

Studies of thermal stability of copolymer A-806 solution and original polymer PVP solution with concentration of 2500 ppm in seawater at temperature of 120°C have shown that the viscosity of copolymer A-806 solution was increased from 5.78 to 7.3 MPa·s for the first 5 days, and then it was decreased from 7.3 to 6.52 MPa·s for the next 5 days. However, it was still higher than the initial value (up to temperature exposure). Subsequently, for a period of 10 - 30 days, the viscosity was slowly decreased and equaled to 4.7 MPa·s after 30 days of temperature exposure (changing rate of 81%). During this time, the viscosity of the original polymer PVP solution was drastically decreased, from 1.81 to 0.68 MPa·s (or 3 times) for the first 5 days, and then it was just slightly reduced (Fig. 1).

The increasing of system A-806 viscosity for the first 5 to 10 days with the temperature exposure at $T = 120\text{ }^{\circ}\text{C}$ is explained by the recombination of the residual active irradiated polymer in the centers, i.e. the process of cross-linking the polymer chains PVP with AM was continued after the irradiation.

It should be noted that the difference in obtained results from 3 parallel thermal tests (with exposure at $T = 120\text{ }^{\circ}\text{C}$), an increase of viscosity during the first 5 days and a decrease of viscosity for the next period were minor in the range of 3 to 5%.

The dependence of polymer solution viscosity on temperature and concentration are shown in Fig. 2. The results showed that viscosity of polymer solution was increased with the increase of its concentration and was reduced with the increase of temperature. The viscosity was strongly reduced with the increase of temperature at low polymer concentrations (3.6 and 2.5 times at the temperature of 30 °C to 90°C with the concentration of 2000 and 3000 ppm, respectively) (Fig. 2).

Small-angle x-rays scattering and photoelectron spectroscopy methods show that in an aqueous medium the polymer exists in the form of helium particles with a hydrodynamic radius of 102 nm.

DISCUSSION

The hydrodynamic radius (RH) of polymer A-806 is a specific parameter, which reflects the possibility of obtaining a copolymer solution with low concentration. The results show that the system of polymer A-806 is a mixture of different size helium particles. There are two basic intervals: one part of the gel with the radius RH has a value of 10 - 102 nm. The gel with such size and at low concentrations is well distributed and stable in aqueous solutions. Another part of the gel with large size (macro) is characterized by RH in the range 103 - 104 nm - a hydrogel. At low concentrations, the hydrogel is unstable and difficult dissolving in aqueous solutions.

The modeling of polymer flooding was conducted on sandstone core samples of Lower Miocene of White Tiger field (offshore Eastern Sea, Southern Vietnam). Core samples have an average porosity of 17,7% (changing range of 13 - 33,5%) and average permeability of 239 mD (changing range of 0.5 - 2650 mD). Reservoirs temperature is 80 - 110°C. The average viscosity of oil formation is 1.531 MPa·s *in situ* (changing range of 1.074 - 1.989 MPa·s).

To simulate cross-flow that occurred between two layers with different permeability in polymer solution slug injection, the dual-layered reservoir model was built from two layers of sandstone core with different permeability $K_1 \neq K_2$. Besides, there was a thin rubber mesh with holes diameters of 2 mm layering between them. This rubber mesh aim is to support a hydrodynamic connection between the two core layers and also to prevent the fluid from moving along the contact between these two core layers (Fig.3). The main characteristics of dual-layered reservoir models were shown in table 1. The permeability ratios between two layers (layers K1 and K2) of dual-layered reservoir models K1/K2 are changed from 54/763 to 208/52.

The conditions and procedures for laboratory tests:

a) Working fluids

- Viscosity of simulated formation oil (a mixture of 80% of crude oil from well BH-27 and 20% kerosene) at a temperature of 120°C: 1.586 MPa·s;

- Viscosity of seawater at a temperature of 120°C: 0.238 MPa·s;

- Viscosity of A-806 polymer solution (concentration of 2500 ppm) at a temperature of 120°C: 1.12 MPa·s.

b) Test conditions

- Injecting polymer slug after the reservoir

model was flooded out;

- Injection rate (the same for water and polymer): 2 m/day;
- The volume of polymer slug (for all tests): 0.20 V_{pore};
- Testing temperature: 120°C;
- Pore pressure: 100 atm;
- Effective overburden pressure: 100 atm.

For laboratory study, 7 tests of water and polymer injection were performed on different dual-layered reservoir models at reservoir conditions [6-10]. For all experiments, the injection of the polymer into reservoir models had started after the reservoir models was flooded out (after injecting about 6 pore volume of water through the reservoir model), and then the polymer slug volume of 0.2 pore volume was used. After all, the water injection was renewed following the polymer slug.

Oil recovery results of polymer injection experiments are shown in table 2. The increase of oil recovery, in comparison with water injection, was obtained for all polymer injection tests and it was varied from 4.7 to 16.6% (average 12.0%). The average permeability recovery coefficient is 19% and change from 2.7 to 32.3%.

CONCLUSION

The copolymerization of PVP and AM is enabled to obtain a water-soluble polymer, which is stable in seawater at temperature up to 120°C. The results of polymer injection test on dual-layered reservoir model with A-806 polymer showed that the average increment of oil recovery was 12% in comparison with water injection.

The simulation of polymer slug injection using dual-layered reservoir model has shown that the viscosity ratios between polymer solution (low concentration of 2500 ppm) and injected water in range from 3 to 5 are the most appropriated in order to bring in the effectiveness for polymer injection in matured clastic reservoirs with high temperatures up to 120 °C and high salinity from 30 to 40 g/l.

REFERENCES

1. Abidin, A. Z., Puspasari, T., Nugroho, W. A. Polymers for Enhanced Oil Recovery Technology. *Procedia Chemistry*, **2012**, no. 4, p.11.

2. Asgharik, K. and Nakutnyy, P. Experimental results of polymer flooding of heavy oil Reservoirs. *Proceedings of Canadian International Petroleum Conference*, 17–19 June **2008**, Calgary.
3. Pope G.A., Overview of Chemical EOR, *Casper EOR Workshop*, October 26th **2007**. The University of Texas, Austin. (2007).
4. Proctor, A., Sherwood, P. Data analysis technique in x-ray photoelectron spectroscopy. *Anal. Chem.*, **1982**, Vol. 54(1) – p. 13.
5. Li, T., Senesi, A. J., Lee, B. Small angle X-ray scattering for nanoparticle research. *Chem. Rev.*, **2016**, Vol.116(18).- p.11128.
6. Kadyrov, R.R., Patlay, D.A., Hasanova, D.K., Bayburdov, T.A., Stupenkova, L.L. Water shutoff job in porous-fractured carbonate reservoirs using water-swellabl. *Oil industry*, **2014**, no.4, p.70.
7. Karmakar, G. P., Chakraborty, C., Improved oil recovery using polymeric gelants: A review., *Indian J. Chem. Technol.*, **2006**, Vol.13.- p.162.
8. Levitt, D. B., Pope, G. A., Selection and Screening of Polymers for Enhanced Oil Recovery. SPE 113845, SPE/DOE Symposium on Improved Oil Recovery, 20-23 April **2008**, Tulsa, Oklahoma.
9. Milovidov, L. N., Kolchanova, T. I. World application of EOR. *Neftegazpromyslovoe delo*, **2002**, no. 8, p.46.
10. Rogachev, M. K., Kondrashev, A. O., Kondrashev, F., *Water-shut-off polymeric composition for low-permeable reservoirs*. *Oil industry*, **2014**, no.4, p.63.

Figure 1. The change of viscosity of PVP and copolymer A-806 solutions with exposure time at $T=120^{\circ}\text{C}$ (concentration of 2500 ppm, in seawater). 1 – PVP, 2 – A-806-1, 3 – A-806-2, 4 – A-806-3

Figure 2. The dependence of polymer solution viscosity on temperature and concentration. The particle size of polymers in ppm: 1 – 3000, 2 – 2500, 3 – 2000

Figure3. Scheme assembly of dual-layered reservoir model for polymer injection

Table 1. Main characteristics of the dual-layered reservoir model for polymer injection.

No.	Model number	Core sampling depth, m	Gas permeability ratio K1/K, frac.	Porosity, %	Residual water saturation, %
1	I-2	3168.8	54/763	19.5	23.5
2	II-1	3178.1	131/378	18.6	23.8
3	II-2	3185.5	208/521	19.7	22.8
4	III-1	3163.1	86/290	20.5	21.5
5	III-2	3184.8	131/586	19.7	21.3
6	IV-1	3185.8	280/895	19.3	22.8
7	IV-2	3186.9	162/870	20.2	29.1

Table2. Results of polymer injection on dual-layered reservoir model.

No.	Model number	Oil recovery by water injection, %	Oil recovery by polymer injection,%	Increment of oil recovery, %	Permeability recovery coefficient, frac.
1	I-2	41.1	56.5	15.4	0.027
2	II-1	39.7	51.2	11.5	0.211
3	II-2	50.7	66.3	15.6	0.071
4	III-1	47.5	52.2	4.7	0.323
5	III-2	47.3	60.2	12.9	0.272
6	IV-1	53.6	61.1	7.5	0.145
7	IV-2	52.6	69.2	16.6	0.278
Average		47.5	59.5	12.0	0.190