Review Article

Analysis of the effects of partially hydrolyzed polyamide on oil reservoir rocks

ABSTRACT

The increase in the need for crude oil led to the use of polymer solutions to ensure the moistening (lubrication) of the pores moistened with water and crude oil and the provision of new channels for the transfer of petroleum fluids to the extraction well. That is precisely why this article analyzes the mode of action of partially hydrolyzed polyamide in contact with oil reservoir rocks and especially describes a new numerical simulation model, based on the flow equations determined as a result of washing some cores with polymer solutions. At the same time, we created a numerical model based on the flow of polyacrylamide through reservoir rocks, which was compared with the simulation data.

Comment [m1]: Include data values

Keywords: partially hydrolyzed polyacrylamide, tertiary recovery, crude oil, polymer

1. INTRODUCTION

When water is injected into a crude oil reservoir to maintain pressure and push crude oil to the surface, substantial amounts of crude oil will be left behind.

At the microscopic level, crude oil droplets or immobile crude oil films will be trapped by capillary barriers in the pores [1]. Regardless of whether the crude oil is captured as a film or droplets the saturation of the end point will depend on the wettability. For a water-wet system, the crude oil will be trapped as droplets in the pores, and the end point of crude oil saturation will be high and also reached as the early stage [8-11].

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For a crude oil-wet system, much larger amounts of water are required to reach final saturation, but the amount of crude oil captured capillaryly, as it is a thin film on the pore surface, will be less compared to a water-wet system .

The lowest residual saturation is achieved for a mixed-wet case. At the macroscopic level crude oil will be avoided due to gravity segregation, channeling of water into fractures or high permeability zones, or due to viscous channels (formation of water channels reaching the surface at a relatively early stage of injection, bypassing large reservoir volumes) [12,13] .

Additionally, crude oil may be trapped in compartments that are unrelated to the rest of the field.

A process to enhance additional crude oil recovery will increase crude oil recovery by improving microscopic or macroscopic displacement compared to what would be achieved by water injection (or other secondary recovery methods). This will speed up crude oil production so that more of the in-place crude oil can be extracted before the well is, for economic and technical reasons, abandoned [14,15].

Displacement at the microscopic level will be enhanced by reducing (e.g. surfactants or immiscible gases) or eliminating (e.g. miscible gases or solvent) the interfacial tension between the injected phase and the crude oil, or by favorably modifying the formation wettability (e.g. by surfactants or water chemistry optimization).

Displacement at the macroscopic level is generally referred to as compliance control and will usually have the additional effect of reducing water production [3].

It can be achieved by diverting water at depth by reducing the mobility ratio between the water phase and the crude oil phase. The latter can be done either by increasing the mobility of the crude oil phase or decreasing the mobility of the water phase [16-20].

Increasing the mobility of crude oil can be achieved by increasing its permeability or decreasing its viscosity. Crude oil viscosity reduction will be a thermal recovery mechanism where its viscosity is reduced by heating. Lowering the water mobility can be achieved by adding polymer to the water phase. The water-crude mobility ratio can be considerably improved by polymer injection and the increase in the viscosity of the aqueous phase leads to an improved macroscopic displacement [ ].

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2. Injection of polymer solutions to increase crude oil recovery

The crude oil remaining after displacement over the entire surface due to the heterogeneities in the deposit and the "viscous fingering" phenomenon is the target for polymer injection. Certain polymers (due to elastic properties) can exert normal forces, affecting the capillary captured crude oil. However, if these effects are significant enough to reduce residual crude oil saturation (enhance microscopic nickel displacement) and lead to additional crude oil production beyond that expected from a simple increase in viscosity, it is still a reason to debate in this thesis.

Adding polymer to the injected water will increase viscosity and reduce permeability; therefore, displacement is improved and water intrusion is delayed and crude oil production is accelerated.

The monitoring of fluid mobility in the deposit is a generic notion, by which the processes of advanced oil recovery are described with the aim of increasing the efficiency of volumetric washing by improving the ratio between the mobilities of displacing and displaced fluids. Part of the types of processes that make up this category also achieve an improvement in displacement efficiency. Mobility control, in a crude oil displacement process, is considered to be achieved if the ratio *M* of the mobilities is less than or equal to unity.

Reducing this ratio has the effect of increasing the efficiency of volumetric washing; In some situations, for example, in the case of deposits with large variations in directional permeability, it is advantageous to achieve an *M* value much lower than unity.

By indexing with a and, respectively, *b* the characteristics related to the displacing, respectively displaced fluid, the ratio of mobilities can be written in the form:

$$M = \frac{\frac{k_{ra}}{\mu_a}}{\frac{k_{rb}}{\mu_b}} (1)$$

Thus, the ways in which these parameters can be modified can be highlighted, namely: changing the permeability of the rock to the displacing and/or displaced fluid, as well as changing the viscosities of the fluids.

Since the costs are extremely high, the modification of the properties of the displaced fluid (crude oil) or the permeability relative to it, most of the mobility control processes that are of practical interest, consist of adding chemicals to the injected fluid to increase its apparent viscosity or to reduce the effective permeability of the rock to the injected fluid.

Chemical substances added to the injection fluid consist, most often, of polymers or surfactants.

Therefore, the displacement over the entire surface will depend on the mobility ratio, Ψ, which is the ratio between the mobility of the displacing and displaced fluid phases. In this work, in order to avoid the confusion of the molecular weight, denoted by the letter *M*, introduced later in the specialized literature, we approached the following notations *w, o* and *p* for water, crude oil and later the solution to polymer.

$$\psi = \frac{\lambda_w}{\lambda_o} = \frac{\eta_o}{\eta_w}\frac{k_w}{k_o} (2)$$

Lowering the mobility ratio will smooth the displacement front, regardless of whether the irregularity of the water front is caused by "viscous fingering" or heterogeneities (ie, water entering areas of high permeability).

"Viscous fingering" is caused by the self-reinforcing mechanism of random instabilities, as it is easier for water to move where it is already at higher saturation, where water permeability k_w is strongly dependent on water saturation, s_w, as illustrated in generic relative permeability figure 1.

The impact of changing the mobility ratio on crude oil recovery can be illustrated by calculating the fractional water flux versus saturation for different mobility ratios.

According to Darcy's law for one-dimensional linear flow (eg a cylindrical core), the fractional flow of water,f_w will be given by the relation:

$$f_w(s_w) = \frac{q_w}{q_o+q_w} = \frac{\frac{k_w(s_w)}{\eta_w}}{\frac{k_w(s_w)}{\eta_w}+\frac{k_o(s_w)}{\eta_o}} (3),$$

where k_w is the relative permeability of water.

Using the synthetic relative permeabilities from figure 1 and varying the water viscosity, the fractional flow of water as a function of crude oil saturation is illustrated in figure 2.

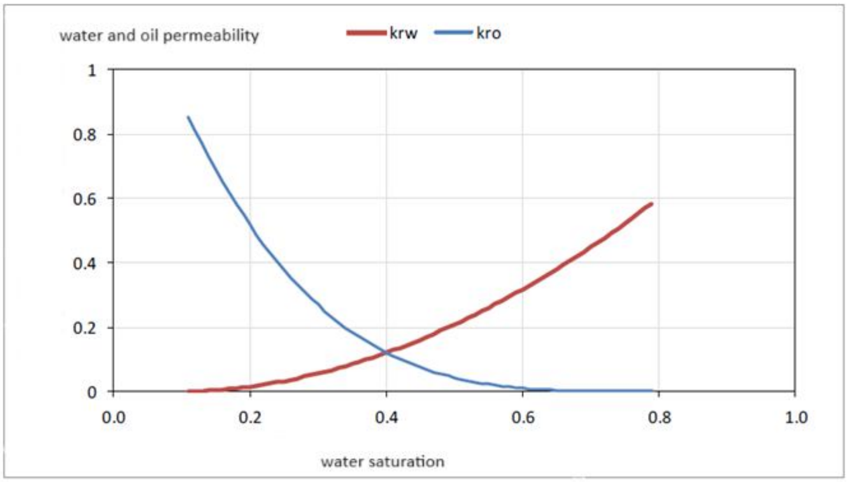

Fig. 1. Generic relative permeability curve.

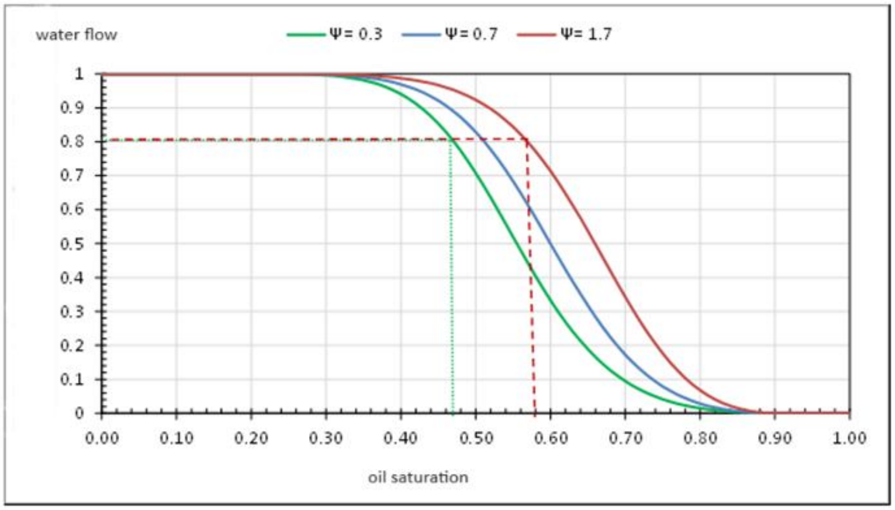

Fig.2. Fractional water flow rate as a function of crude oil saturation for different mobility ratios

This is plotted against crude oil saturation to illustrate that for the same fractional water flow, the crude oil saturation in the core decreases with decreasing mobility ratio, showing an increase in crude oil production for lower water mobility even in the simple case of a homogeneous linear core.

For example, at an impurity of f_w = 80%, at the lowest water viscosity, more precisely at the highest mobility ratio, the crude oil saturation in the core is 58%. If the viscosity of water increases then the mobility ratio is reduced to 0.7%, the saturation of crude oil at the same value of impurities will be 52% and will continue to decrease to a value of 47% only if the viscosity of water increases twice as much as viscosity of crude oil, showing that for the same impurities, the amount of crude oil will increase if the viscosity of water is increased.

Above, we paid attention only to the change in viscosity. The polymer, in the vast majority of cases, will change its permeability due to adsorption and trapping of polymer molecules, so that $kp<kw$. This will further improve the mobility ratio over what is expected to result from viscosity considerations alone. The permeability reduction effect will also be maintained during post-flooding with polymeric water, positively influencing displacement.

A water-soluble polymer will also affect water permeability more than crude oil permeability, an effect often disproportionately explored in permeability reduction operations.

1.3.SUPERABSORBENT POLYMER COMPOSITES FOR ENHANCED CRUDE RECOVERY

Composite polymer superabsorbent is a clay-reinforced three-dimensionally cross-linked hydrophilic polymer capable of swelling and potentially retaining huge volumes of water [5].

Experiments using it as a blocking agent have been carried out in some oil fields in China to meet the need for improved crude oil recovery [6].

After a long-term waterflooding operation, the water content of the crude oil increased, which effectively led to a decrease in production.

Higher water content in crude oil can cause many problems such as increased corrosion, sand production, emulsion formation and disposal, etc.

There is an urgent need to reduce the water content of crude oil. One of the methods to reduce water content is to adjust the flow of crude oil into the production well.

As explained earlier, the partially hydrolyzed polyacrylamide currently used as a polymer for increasing crude oil recovery has some disadvantages, especially from their sensitivity to salinity and high temperatures.

In his research, Syuhada [7] reported that bentonite-infiltrated super-absorbent polymer composites have higher mechanical and thermal resistance. In addition, bentonite infiltration makes these superabsorbent polymer composites less sensitive to other chemicals, especially surfactants and other minerals contained in the reservoir water.

The swelling mechanisms with a huge increase in volume and high absorption capacity in superabsorbent polymer composites can theoretically increase the thickness of the polymer layer attached to the inner pore wall of the reservoir rock so that it is less or even completely covered by a polymer which was inflated. This will clearly help improve crude oil recovery as the fraction of crude oil captured in the porous rocks becomes much smaller.

Based on the research results, it can be concluded that the super absorbent polymer composites show good mechanical, thermal and rheological properties compared to the existing polymer. However, further research is needed to test its suitability as a polymer for increasing crude oil recovery.

Many unprofitable projects were the result of inadequate description of deposits or problems with the polymer system used.

In recent years, polymer flooding technology has been extensively field tested and can be classified as a proven technology.

However, there are limitations to current polymer technology such as degradation (thermal, physical, bacterial and chemical) or polymer rheology.

Partially hydrolyzed polyacrylamide, as the polymer most commonly used today, also suffers from strict temperature and salinity limitations.

It is important to choose the right polymer for a particular field. Reservoir permeability, crude oil viscosity, are used to determine the optimum molecular weight polymer.

The composition of the rock and the adsorption level of the polymer is used to determine the best degree of hydrolysis.

Partially hydrolyzed polyacrylamide is one of the most common polymers used in crude oil recovery enhancement so far, although its properties suffer sharply due to crude oil salinity and high temperature (more than 70 °C).

Superabsorbent polymer composites offer a light in overcoming this problem, having the ability to swell and hold huge volumes of water and their stability to temperature and salinity can be improved by copolymerization.

Currently, polymer injection is the most common water-based method for enhanced crude oil recovery.

The first pilot was carried out in 1959 and indicated that the method would be profitable and the conduct and results conform to the theory of those times, which does not differ much from the current theory.

Literature reviews by Standnes and Skjevrak and Manrique, E., Ahmadi, M., & Samani, S. on polymer projects have shown that these projects are more effective the earlier they are implemented. While there may be good reasons for an earlier water injection (understanding the reservoir type, calibrating models, establishing a baseline, etc.), injecting polymer solutions secondary will generally be preferable in terms of crude oil production and reducing water production.

As mentioned, an additional advantage of polymer injection is the reduction/delay of water production, reducing the energy and effort required to lift, separate, displace and reinject large quantities of often radioactive water. On the other hand, there is also a significant disadvantage of potential polymer solution production, but if the project is successfully designed, this will happen to us.

2. METHODOLOGY

The numerical model created to model the flow of partially hydrolyzed polyacrylamide polymer in limestone consists of the equations:

$$\frac{\partial R}{\partial t} = 0{,}0265\frac{\partial \mu}{\partial t} + 0{,}1228$$

$$\frac{\partial R}{\partial t} = 2{,}0081 ln(\frac{\partial s}{\partial t}) - 2{,}3134$$

$$\frac{\partial R}{\partial t} = 2{,}0671\ (\frac{\partial k}{\partial t})^2 - 37{,}97\frac{\partial k}{\partial t} + 168{,}8$$

$$\frac{\partial R}{\partial t} = 0{,}028 ln\left(\frac{\partial \emptyset}{\partial t}\right) + 0{,}1273$$

$$\frac{\partial R}{\partial t} = 4{,}2962(\frac{\partial c}{\partial t})^2 - 77{,}493\frac{\partial c}{\partial t} + 319{,}23$$

The numerical model created for modeling the flow of partially hydrolyzed polyacrylamide polymer in sands consists of the equations:

$$\frac{\partial R}{\partial t} = 0{,}0057(\frac{\partial \mu}{\partial t})^6 + 0{,}3188\ (\frac{\partial \mu}{\partial t})^5 - 7{,}3169\ (\frac{\partial \mu}{\partial t})^4 + 88{,}181(\frac{\partial \mu}{\partial t})^3 - 589{,}032(\frac{\partial \mu}{\partial t})^2 + 2069{,}6\frac{\partial \mu}{\partial t} - 2990{,}5$$

$$\frac{\partial R}{\partial t} = -1{,}2518\ \left(\frac{\partial s}{\partial t}\right)^6 + 69{,}109\ \left(\frac{\partial s}{\partial t}\right)^5 - 1561{,}3\ \left(\frac{\partial s}{\partial t}\right)^4 + 18488\ \left(\frac{\partial s}{\partial t}\right)^3 - 121126\ (\frac{\partial s}{\partial t})^2 + 416742\frac{\partial s}{\partial t} - 588928$$

$$\frac{\partial R}{\partial t} = 10{,}313(\frac{\partial k}{\partial t})^5 - 480{,}04(\frac{\partial k}{\partial t})^4 + 8692{,}6(\frac{\partial k}{\partial t})^3 - 76537(\frac{\partial k}{\partial t})^2 + 328477x\frac{\partial k}{\partial t} - 551353$$

$$\frac{\partial R}{\partial t} = 0{,}2711 ln\frac{\partial \emptyset}{\partial t} - 0{,}3264$$

$$\frac{\partial R}{\partial t} = -0{,}2823(\frac{\partial c}{\partial t})^2 + 8{,}0204\frac{\partial c}{\partial t} - 26{,}167$$

where: *p, μ, S, k* and *Ø*are the pressure, viscosity, saturation, permeability and porosity of the porous medium.

Results obtained through simulation and later in the laboratory are as follows:

Table 1. Water saturation of productiv area

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Lenght, m	Water saturation at 10 days, Experimental	Water saturation at 10 days,model	Water saturation at 100 days,Experimental	Water saturation at 100 days, model
1	0,6	0,62	0,75	0,76
2	0,5	0,53	0,7	0,71
3	0,4	0,43	0,68	0,68
5	0,2	0,205	0,65	0,66

Table 2. Polimer concentration at 300 days

Lenght, m	Polimer concentration at 300 days models	Polimer concentration at 300 days experimental
25	0	0
30	0,5	0,51
35	0,7	0,71
40	0,8	0,81
45	0,9	0,91
50	1,0	1,1
55	0,5	0,51
60	0	0

Table 3. Polimer concentration at 800 days

Lenght, m	Polimer concentration at 800 days Models	Polimer concentration at 800 days Experimental
150	0	0
160	0,2	0,21
170	0,4	0,41
180	0,6	0,61
190	0,7	0,71
200	0,8	0,81
220	0,4	0,41
240	0	0

In conclusion, we can state that the numerical model is very close to the experimental simulation.

Conclusion and discutssion

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There is great hope that polymer can play an important role in increasing oil production, given the new recovery technologies that have evolved and shown some success in recovering more than 10% of global production.

The present work, as a whole, sums up four chapters in which an image of the specialized literature contained in the first three chapters is presented and the last chapter is dedicated to own studies on the behavior of polymers in crude oil deposits.

The work aimed to bring a new breath to the oil and gas extraction industry by presenting the main polymer additives currently used in crude oil extraction, numerical modeling of their behavior in reservoir rocks, establishing the effects of polymers on the quality of the extracted crude oils, but also analyzing the effects of polymers on collector rocks.

Thus, in the first part of this paper, we paid special attention to the change in polymer viscosity. The polymer, in the vast majority of cases, changes its permeability due to the adsorption and trapping of polymer molecules. This will further improve the mobility ratio over what is expected as results, just from viscosity considerations. The permeability reduction effect will also be maintained during post-flooding with polymer water, positively influencing the displacement.

Regarding superabsorbent polymer composites for increasing crude oil recovery, bentonite-infiltrated superabsorbent polymer composites have been noted to have higher mechanical and thermal strength. In addition, bentonite infiltration makes these superabsorbent polymer composites less sensitive to other chemicals, especially surfactants and other minerals contained in the water in the reservoir.

Based on the research results, it can be concluded that the super absorbent polymer composites show good mechanical, thermal and rheological properties compared to the existing polymer. However, further research is needed to test its suitability as a polymer for increasing crude oil recovery.

One of the biggest concerns, especially for acrylamide-based polymers, is the potential shear degradation of the material. Thus, in evaluating potential polymeric materials for increasing crude oil recovery, an important consideration is resistance to shear degradation. The purpose of this section within the first part was to summarize studies in which not only shear degradation considerations were described, but also to experimentally evaluate these aspects.

The result suggests that some types of polymers degrade more than others and that high shear rates permanently influence the viscosity (and subsequent performance) of all acrylamide-based copolymers.

Related to the thermal degradation aspect of polymers, there are a variety of techniques to demonstrate that polymeric materials withstand elevated reservoir temperatures. Short-term effects studies can assess the effect of increasing temperature on solution viscosity or the decomposition of polymeric materials at elevated temperatures using thermogravimetric analysis to measure the mass loss of a material as a function of temperature and time in a controlled atmosphere.

This type of analysis would primarily provide information on the degradation of the core structure, since hydrolysis would not cause significant changes in the mass of the sample (considering the molecular mass of acrylamide (71.08 g/mol) compared to acrylic acid (72, 06 g/mol).

Regardless of the conclusions drawn from the results of thermogravimetric analysis, it is important to recognize that the experimental technique is primarily an assessment of the effects of temperature on the basic structure of the polymer.

One of the main challenges in chemical degradation studies is evaluating the effect of oxygen on chemical degradation. The main long-term concern for polymeric materials (especially polyacrylamide and derivatives) is hydrolysis. Hydrolysis involves the conversion of amide groups to carboxylic acid groups, which influence the charge distribution of the polymeric material, leading to precipitation in the presence of divalent cations. Hydrolysis is a function of pH and can occur at moderate temperatures. In reality, any pH effect will coexist with thermal effects. The general procedure for evaluating hydrolysis should involve some form of aging (at high temperature and/or high salinity for long periods of time), which is followed by evaluation of relevant polymer properties (such as viscosity, degree of hydrolysis and/or degree of degradation).

Polymer flooding for enhanced crude oil recovery is determined by the injectivity of the polymer solution (defined as the ratio of volumetric injection rate to pressure drop), which should allow practical injection rates to be used in field applications. To overcome this problem, several models have been developed to understand the rheological behavior of polymer solutions flowing through porous media under different flow velocity conditions.

Polymer retention in porous media is caused by polymer adsorption on the rock surface, mechanical pinning (adhesion) of polymer molecules at pore throat constrictions small relative to the size of the polymer molecules, and hydrodynamic retention which "is caused by hydrodynamic traction forces that grip polymer molecules in regions of stagnant flow”. The mechanical grip (adhesion) of the polymer increases significantly as the permeability of the rock decreases.

The general approach is that polymer adsorption is the dominant mechanism for polymer retention, even though all polymer retention mechanisms may be involved during polymer flooding in crude oil field rocks due to the intrinsic heterogeneity of geological formations.

In other words, it states that polymer retention in porous media depends on polymer type, polymer molecular weight (MV), polymer concentration, flow rate, temperature, polymer mud volume size, salinity of reservoir water (i.e. adsorption increases with increasing reservoir water salinity), absolute rock permeability, crude oil saturation, rock wettability and mineralogy.

Currently, polymer flooding is a well-established crude oil recovery enhancement process for mobility control that has been successfully demonstrated to provide effective efficiency in field applications in recent years.

However, widespread worldwide application of this crude oil recovery enhancement technology will depend on the development of advanced polymer systems that are both cost-effective and environmentally friendly.

The adsorption on the surface of the rocks determined the reduction of the mobility of the polymer but also the modification of the gel structure by the modification (crossing) of the polymer (of the polymer chains) which led to clogging (blocking of the pores) and increasing the possibility of fluid flow. In the laboratory we determined the adsorption of silicon for a solution of polyacrylamide of 0.05% partially hydrolyzed concentration in water, it increases from the value of 0.01 mg/m^2 to 0.05 mg/m^2 when the concentration in NaCl increases from 0 .5% to 10% in are we showed that adsorption increases for pH values lower than 7.

Comment [m6]: The summary should be ADD in Abstract

As a first conclusion, it is stated that for a porous sand medium with a permeability of 140 mD, replacing saline water with 20 g/l NaCl, a presence of the polymer with a concentration of 400 ppm was observed in the effluent, and this value being approximately stabilized after 5 injected pore volumes.

Reference

Comment [m7]: Review to recommended standard

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