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Study on Increasing Oil and Gas Recovery in Oilfield by Using Partially Hydrolyzed Polyacrylamide

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Polyacrylamide (PAM) is a linear water-soluble polymer, which is one of the most widely used varieties. Partially hydrolyzed polyacrylamide (HPAM) is currently widely used in domestic oilfield tertiary oil recovery. Practice has proved that the use of HPAM as a polymer flooding to improve oil recovery (EOR) effect is obvious, and has become the oil and gas production in the middle of a crucial part. Theoretically, polyacrylamide can play a role in mediating the rheological properties of water injection, increasing the viscosity of the driving fluid, improving the efficiency of water flooding and so on. However, in practical applications, it is necessary to select polyacrylamide with different molecular morphology or molecular weight according to the difference of geological environment conditions such as dielectric porosity and various ionic components and contents in groundwater. Therefore, it is of great theoretical and practical significance to correctly evaluate the molecular chain morphology of polyacrylamide in different geological environments and to make more effective use of existing resources for rationally explaining the mechanism of polymer flooding. In this study, through the detailed study on the properties of partially hydrolyzed polyacrylamide, it can be applied to oil and gas exploitation in oil field, which can provide reference for oil and gas recovery.

1. Introduction

Acrylamide polymer refers to the homopolymer of acrylamide and other monomers formed by the copolymer collectively. Industrial, where more than 50% of the acrylamide monomer polymer, are generally referred to as polyacrylamide (Chen et al., 2014). These polymers are generally linear water-soluble polymers, oil field is the most widely used one of the water-soluble polymer varieties. One of the most representative products is polyacrylamide and its hydrolyzate (which can be regarded as acrylamide and acrylic acid copolymer) (Kedir et al., 2014). With the development of oilfield in the later stage, the improvement of oil recovery technology has become one of the important measures for the sustainable development of oilfield. Polyacrylamide production, performance and application research has been paid more and more people's attention (Olajire, 2014). Polyacrylamide and its derivatives have been widely used in the tertiary oil recovery in the oil industry in recent years, which is an important means to improve the oil recovery. China needs a lot of oil dispensers every year to improve oil recovery.
At present, many domestic water-driven oil fields have entered the late (Samanta et al., 2013). During the period, due to the heterogeneity of the reservoir and the unfavorable flow ratio, there is still a large amount of residual oil in the formation after the waterflooding (Wei et al., 2016). It is generally shown that the oil well is high, the yield is low and the economic benefit of mining is poor. The international and domestic market demand for oil has increased year by year. In order to ensure the stability of oil field, increase production and solve the contradiction between oil production and market demand, chemical flooding recovery method in China's oil field research and application has been studied more and more widely and deeply (Zou et al., 2014). With the development of three mining technologies such as polymer flooding and the successful implementation of polymer flooding in Daqing in particular, a practical solution has been found for Daqing Oilfield to continue its high output and stable production. Daqing Oilfield has now completed the construction of polyacrylamide (PAM) plant, each year for Shantou to provide 50,000 tons of molecular child from 5 million

to 10 million polyacrylamide products, polymer injection technology for the oil field oil recovery technology Provided a reliable guarantee, but due to the continuous development of three mining technology in recent years, innovation, molecular weight of 5 million to 15 mill**ion polyacrylamide products can**not fully meet the performance of the three mining needs.

Chemical flooding is a very effective method to improve oil recovery, including polymer flooding, alkali / polymer flooding, and alkali / surfactant / polymer flooding. Partially hydrolyzed polyacrylamide flooding is a tertiary oil recovery technology developed in the early 1960s, which was characterized by the addition of high molecular weight polymers to the water to increase its viscosity and improve the flow of the displacement phase and the displaced phase ratio, and to expand the volume, therefore increasing the oil recovery (Bai et al., 2014). The partially hydrolyzed polyacrylamide flooding has the advantages of less oil displacement mechanism, relatively simple technology and low cost (Bai et al., 2015). It is more suitable for the actual situation of most oil fields in China. Therefore, the study of polyacrylamide flooding which is partially hydrolyzed is of great significance to improve the oilfield development effect, keep the crude oil stable and improve the final recovery rate of crude oil. The purpose of this study is to utilize the existing production equipment, equipment, production technology and production conditions to produce ultra-high molecular weight polyacrylamide products through the development of ultra-high molecular weight polymerization formulation to meet the needs of the third mining of the oil field and ensure the continued high output of Daqing **Oilfield**, Stable production, and enable enterprises to obtain the best value for money.

2. Properties of partially hydrolyzed polyacrylamide solutions in porous media

2.1 Rheological Properties of Partially Hydrolyzed Polyacrylamide Solution in Porous Media

Polymer molecules with a certain degree of flexibility in the polymer solution through the flow of porous media than in the rheometer flow is much more complex, and the polymer solution through the porous media rheological directly affect its oil displacement effect. Therefore, it is very important to analyze and study the rheological properties of the polymer solution through porous media and its influencing factors. Polymer flooding is a more successful method to enhance oil recovery. However, early polymer flooding theory suggested that polymer flooding could only increase the viscosity of injected water, improve the oil-water ratio, and enlarge the injected water in the oil layer Due to the relationship between capillary number and flooding efficiency, it is considered that polymer flooding cannot improve oil displacement efficiency and reduce residual oil saturation. Therefore, some people refer to polymer flooding as a modified water flooding, That is, secondary oil recovery. The theory is: (1) polymer flooding and water displacement for the same speed: (2) the viscosity of the polymer solution is generally about 30 times the viscosity of water; (3) polymers cannot reduce the interfacial tension between oil and water, so , When the polymer flooding the number of tubes cannot be increased to 10-3 above, that cannot significantly improve the displacement efficiency.

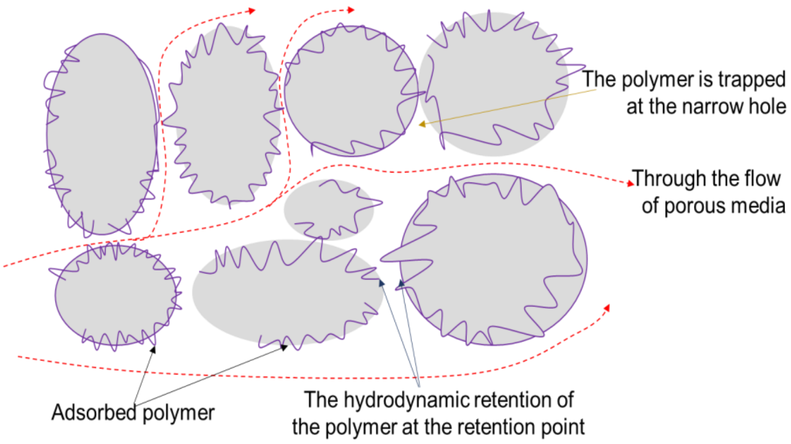

Figure 1: Retention mechanism of HPAM solution in porous media

When the polymer solution passes through the porous medium, there is interaction between the polymer molecules and the pore medium, which causes the polymer to remain in the porous medium, and reduces the permeability of the porous medium without considering the decrease in permeability. Calculating the apparent viscosity of the polymer solution through the porous media increases the apparent viscosity of the solution, affecting the clarity and reliability of the calculated results. In general, it is considered that there are three mechanisms of retention of the polymer solution through the porous medium (Figure 1). They are: (1) adsorption of polymers; (2) mechanical trapping; (3) hydrodynamic retention. As mentioned earlier, the rheology of polymer solutions is related to their molecular structure. The partially hydrolyzed polyacrylamide chains have the flexibility to exhibit viscoelastic fluids even at low concentrations. Xanthan gum molecules have a rod-like structure, the solution appears as a non-viscoelastic fluid. In addition, the pore structure itself and the geometry of the pores in the porous media also have a significant effect on the rheology of the polymer solution. The flow of the polymer solution in the porous medium is obviously much more complicated than the flow in the rheometer. Therefore, it is very important to further understand the viscoelastic effect of the polymerization solution through the porous medium.

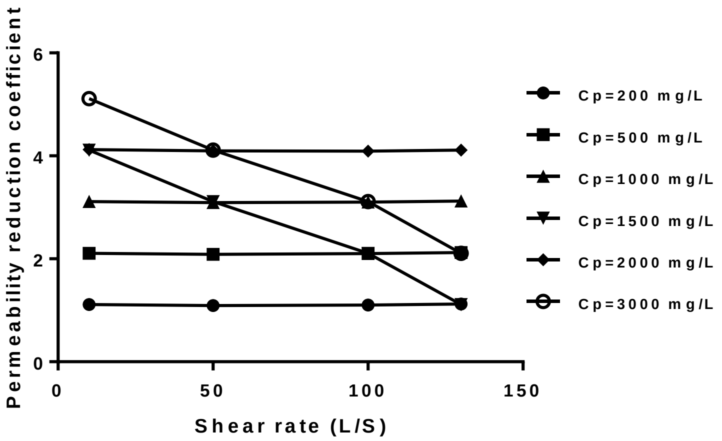

Figure 2: The relationship between the shear rate and the decrease coefficient of permeability

Figure 2 shows the change in the permeability reduction coefficient of the partially hydrolyzed polyacrylamide solution through the porous medium with different shear rates. It can be seen from the figure that with the increase of the shear rate (flow rate), the decrease rate of the permeability of the partially hydrolyzed polyacrylamide solution of the same concentration through the porous medium is slightly decreased due to the shear rate (flow rate) increment, the number of partially hydrolyzed polyacrylamide adsorbed on the surface of the rock decreases and the hydrodynamic capture is reduced. Corresponding to the same shear rate, the higher the concentration of the partially hydrolyzed polyacrylamide solution increases through the permeability of the porous medium, which is due to the higher concentration, and the amount of partially hydrolyzed polyacrylamide molecules adsorbed on the rock surface the greater the cause.

2.2 The viscoelastic effect of partially hydrolyzed polyacrylamide solution through porous media

Polyacrylamide, especially partially hydrolyzed polyacrylamide (HPAM) molecules, are flexible chain structures that are known in the polymer chemistry as random coils. Unlike cylindrical rigid particles, and highly flexible polymers, as far as possible, contain various formulations of the solution. To a large extent, this formulation is determined by the type of flow, and the type of molecule and solvent. This section will discuss the theoretical study of the stretching and orientation of partially hydrolyzed polyacrylamide solutions in simple steady-state tensile flows, and further studies and analysis. When passing through a porous medium, the polyacrylamide solution exhibits a dilatant characteristic at a higher flow rate due to the viscoelasticity of the polymer. In the shear flow field, the polymer molecules in the solution are shear-deformed by the shear force, which increases the degree of orientation and enlarges the Shaw (weakens the intermolecular internal friction and thus shows the shear viscosity of the solution as The shear rate increases and decreases.When the degree of molecular orientation reaches the maximum, the viscosity tends to be stable, but in the stretching flow field, the molecules are affected by the tensile stress and produce the extensional viscosity, which increases the apparent loss of the polymer solution.

The partially hydrolyzed polyacrylamide solutions flow through the viscoelastic effect of porous media. When the molecular conformation changes little, the elastic force is proportional to the deformation, similar to the elastic law of Hooke, so the entropy elasticity can be abstracted as a tiger spring. And macromolecules in the solvent movement by the viscous force can be seen as a rigid ball in the same way in the viscous medium. The result of this combination of elasticity and viscosity concept constitutes a mechanical model of two balls connected by a spring, as shown in Figure 3.

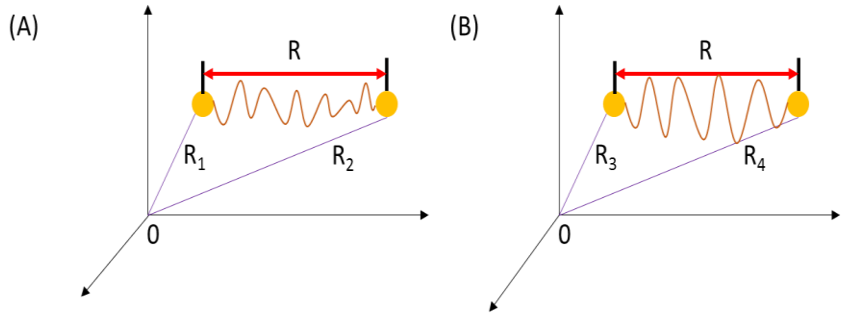

Figure 3: Diagrams of elastic dumbbell

As already mentioned, the rheological properties of the polymer solution are related to its molecular structure, and the partially hydrolyzed polyacrylamide molecular chain has a softness, and exhibits a viscoelastic fluid even at low concentrations. The xanthan gum molecule has a rod-like structure and its solution is a non-viscoelastic fluid. In addition, in the porous medium, the microstructures and geometries of the pores themselves have an important effect on the rheology of the polymer solution. The flow of the polymer solution in the porous medium is clearly much more complex than the flow in the rheometer. Therefore, it is important to further understand the viscoelastic effect of the polymerization solution through the porous medium.

Figure 4 shows the relationship between the elastic effect coefficient R_{ve} and the shear rate γ&, when the polyacrylamide solution passes through the porous medium. It can be seen from the figure that at the beginning R_{ve} decreases with increasing shear rate, indicating that the shear effect is greater than the elastic effect. When the shear rate reaches a certain value, R_{ve} increases with the shear rate. This is because at a relatively low flow rate, the flow velocity of the fluid in the core is very small, so it can be considered at this time the fluid molecules in the natural curled state, but there is no viscoelastic phenomenon or elasticity is small, mainly for the shear effect. With the increase of flow rate, the flow is mainly composed of shear flow, which is the elastic transition. The R_{ve} value corresponding to each velocity is measured by the gradual increase method. When the R_{ve} decreases with the increase of the shear rate, it means that the fluid molecules are subjected to the shear action more than the tensile action, and the fluid flow in the core is a smaller elastic phenomenon; when R_{ve} increases with the shear rate increases, indicating that the fluid molecules have been tensile deformation, the core of the fluid flow showed elastic behavior. When the R_{ve} begins to increase, the corresponding shear rate is the critical elastic shear rate.

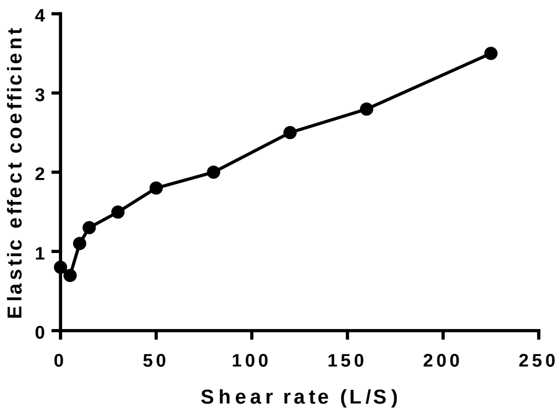

Figure 4: The relation between coefficient of elastic effect and shear rate.

3. Study on physical experiment of partially hydrolyzed polyacrylamide oil recovery by trailing displacement

Polymer flooding is a technique in which a high molecular weight water-soluble polymer is added to the injected water to increase the oil recovery by increasing the viscosity of the injected fluid and thereby improving the fluidity ratio of the reservoir fluid. The mechanism of oil flooding of polymer solution increases the viscosity ratio of oil-water two-phase flow by increasing the viscosity of the injected fluid phase, and then suppresses the water phase in the plane direction and the tongue-in phenomenon in the vertical direction, and increases the wavelength, and ultimately improve the oil recovery. In the ultra-high water-cut stage, the oil recovery rate is low, the water consumption is large, the remaining oil is dispersed, the well conditions deteriorate, and the development benefit is low. However, from the use of reserves and annual production, the ultra-high water-cut oilfield is still the main body of development. Volume and remaining recoverable reserves occupy a very important position in the country. Therefore, the recovery rate of ultra-high water-cut oil fields is an important economic factor restricting the sustainable development of the country.

3.1 Experimental flow of polymer flooding method

(1) To the two-dimensional flat panel visualization model filled with quartz wonderful, while filling the side of the water, this process on the one hand Jian Shi quartz sand, on the other hand emptying the volume of the air volume of the sand body until the end of the filling, measuring the weight of sand W1;
(2) To configure the different viscosity of the simulated crude oil, and oil-soluble Sudan red staining, and then into the 1000 mL of the intermediate container;
(3) Connect the test pipeline, check the interface to ensure that the pump open when the interface seal;
(4) Open the advection pump According to the experimental scheme design speed of 2.0 mL / min and crude oil viscosity of 5mPa · s and 25 mPa · s experiments, the intermediate container of simulated crude oil into the plate model, until no simulated water out, meter displacement water volume V2 build model primitive oil saturation Soi;
(5) The first stage of the diagonal injection of two wells in the production of oil production, configuration 1500 mg / mL of polymer solution and methyl blue staining. When the model develops to 35% of the pump, there is volume V3;
(6) The second phase of the closure of a diagonal production wells and injection wells: open the five-point model of the central production wells, with ordinary dyeing water drive. When the wellhead output water content reached 98%, stop the end of the experiment, and drive out the oil phase volume V4;
(7) Calculate the recovery rate η under different design experiments.
The measured cavity volume is about V_b
Fill the sand body volume: v1 = W1/p1
Model pore volume: $V_b = V_b – V_1$
Original oil saturation: Soi = V_2/V_p
Recovery rate: η = V3 +V_4/V_2

3.2 Experimental data

According to the design of the film displacement polymer precipitation method obtained in the experimental data shown in Table 1:
It can be seen from Table 1 that the recovery rate of the polymer flooding method decreases slightly with the increase of crude oil viscosity when the model is driven at the same speed, sand body density and sand filling weight. Because of the large viscosity of the aqueous polymer solution, the greater the difference in viscosity between the polymer solution and the crude oil in the first stage, the higher the recovery rate when the predominant flow ratio is higher. In the experiment, the final oil recovery of the experiment is about 4% higher than that of the oil displacement method. If the crude oil viscosity is 2.0 L / min or 5 mPa · s, the law improves the final recovery of the model. When the concentration of polymer is constant, as the concentration of crosslinker increases, the rate of gel formation increases and the gel strength increases. However, when the concentration of the cross-linking agent is increased to a certain extent, the gelation speed is too fast and the stability of the formed gel is poor. The reason is that the crosslinking agent concentration is too large, between the polymer and crosslinking agent, excessive cross-linking, causing gel dehydration shrinkage

Table 1: The statistics from episodic polymer displacement oil recovery with different viscosity of crude oil

No.	Sand body density (g/cm3)	Crude oil viscosity (mPa.s)	Sand mass	Displacement speed (mL/min)	Saturated oil (mL)	The degree of recovery (%)	The amount of oil (mL)	Recovery rate (%)
1	3.51	5	2050	2	557.6	40	265.2	57.14
2	3.26	25	3010	2	566.6	40	305.1	55.26
3	3.65	50	4050	2	657.5	40	320.1	65.23

4. Conclusion

The interfacial viscosity between polyacrylamide solution and oil contact surface and the elastic modulus of polyacrylamide solution are affected by the concentration of polyacrylamide solution, the degree of mineralization of prepared water and the molecular weight of polyacrylamide. With the increase of solution concentration and the molecular weight of polyacrylamide increases, the interfacial viscosity and elastic modulus increase. With the increase of the salinity of the prepared water, the increase of interfacial viscosity and elastic modulus will decrease. On the basis of the oil displacement method, the polymer aqueous solution was injected in the first stage, the viscosity of the injected water was increased, the unfavorable flow ratio was changed, and the first stage waterflooding recovery rate was further improved. And the viscosity of the polymer advantage, in the oil and water front to form a fixed barrier for the second phase of the water transfer to improve the environment to lay the foundation. It can be concluded that the polymer solution provides a higher resistance coefficient and the ability to improve the ratio of oil and water with the increase of hydrophobic monomer content under the condition of good injection performance by seepage characteristics and homogenization model. The recovery of oil recovery is increased under the same permeability condition, but the recovery of oil recovery is obviously decreased when the content of hydrophobic monomer is higher than a certain value. When the hydrophobicity is partially degraded, the partial hydrolysis of polyacrylamide is the highest in oil recovery due to good implant. Under the condition of a certain permeability, the amount of hydrophobic monomer increases with the increase of the amount of hydrophobic monomer, and the polymer solution to drive the front edge of the parallel effect of the effect was significantly enhanced, affected by the volume increase.

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Reference

Bai Y., Xiong C., Shang X., Xin Y., 2014. Experimental study on ethanolamine/surfactant flooding for enhanced oil recovery, Energy & Fuels, 28(3), 1829-1837, DOI: 10.1021/ef402313n.

Bai Y., Xiong, C., Wei F., Li J., Shu Y., 2015. Gelation study on a hydrophobically associating polymer/polyethylenimine gel system for water shut-off treatment, Energy & Fuels, 29(2), 447-458, DOI: 10.1021/ef502505k.

Chen H.X., Tang H.M., Gong X.P., Wang J.J., Liu Y.G., 2014. Effect of partially hydrolyzed polyacrylamide on emulsification stability of wastewater produced from polymer flooding, Journal of Petroleum Science and Engineering, 133, 431-439, DOI: 10.1016/j.petrol.2015.06.031.

Kedir A.S., Seland J.G., Skauge A., Skauge T., 2014. Nanoparticles for Enhanced Oil Recovery: Influence of pH on Aluminum-Cross-linked Partially Hydrolyzed Polyacrylamide-Investigation by Rheology and NMR, Energy & Fuels, 28(4), 2343-2351, DOI: 10.1021/ef402376q.

Olajire A.A., 2014. Review of ASP EOR (alkaline surfactant polymer enhanced oil recovery) technology in the petroleum industry: Prospects and challenges, Energy, 77, 963-98, DOI: 10.1016/j.energy.2014.09.005.

Samanta A., Ojha K., Sarkar A., Mandal A., 2013, Mobility control and enhanced oil recovery using partially hydrolysed polyacrylamide (PHPA), International Journal of Oil, Gas and Coal Technology, 6(3), 245-258, DOI: 10.1504/Ijogct.2013.052236.

Wei B., Li Q., Jin F., Li H., Wang C., 2016, The potential of a novel nanofluid in enhancing oil recovery, Energy & Fuels, 30(4), 2882-2891, DOI: 10.1021/acs.energyfuels.6b00244.

Zou C., Gu T., Xiao P., Ge T., Wang M., 2014, Experimental study of cucurbit [7] uril derivatives modified acrylamide polymer for enhanced oil recovery, Industrial & Engineering Chemistry Research, 53(18), 7570-7578, DOI: 10.1021/ie4037824.