Review on polymer flooding technology

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Abstract. In this paper, the research status of polymer flooding in China and abroad in recent years is reviewed, as well as the mechanism and application of polymer flooding are described. The research progress of several commonly used polymer flooding agents are introduced, including biopolymer, temperature and salt resistant monomer polymer, hydrophobic associating polymer, cross-linked polymer, comb polymer and star polymer. Based on the analysis of the properties, advantages and disadvantages of these flooding polymers, some suggestions are given for the problems existing in the current application of the polymer flooding technology. Also, suggestions of research direction of polymer flooding agent in the future are shared.

1. Introduction
Coal, oil and natural gas are important nonrenewable energy and chemical raw materials. Among them, oil is one of the most important energy resources which is called "the industrial blood". With the progress of human society and economic development, the consumption of oil in modern society is increasing, and thus oil resources have become increasingly scarce. China's oil fields belong to continental sedimentation, with the characteristics of serious anisotropism and viscous crude oil. Because of long-term uninterrupted exploitation, almost all domestic oil fields have been in high and ultra-high water cut stage. In order to improve oil recovery, the application of EOR(Enhanced Oil Recovery)technology has become the main trend, and polymer flooding is the main means of EOR in China [1]. The direction of polymer flooding development is to synthesis water-soluble, temperature and salt resistant polymers. In recent years, researchers in China and abroad have made considerable achievements in this field.

2. The definition of polymer flooding
Polymer flooding can improve the efficiency of oil recovery. At present, it is mostly used in the process of enhance oil recovery technology(EOR). Polymer has high viscoelasticity because of its long chain structure of high molecular weight, and it stretches oil droplets and oil film in the process of flow, so as to increase its carrying capacity [2]. Polymer flooding is an EOR technology that injects high viscosity polymer solution into the formation to greatly reduce the fluidity ratio, expand the swept volume and improve the oil recovery. Polymer flooding is beneficial to the later stage of development of oil and gas fields [3].

3. Polymer flooding mechanism
Polymer flooding refers to mixing polymer solution into injection water, and this increases the flow resistance and displacement pressure by increasing the viscosity of injection water. This will also force
the solution to flow to low-permeability layer, reduce the permeability of water phase, improve the mobility ratio of water and oil and increase the swept coefficient, therefore enhances the oil recovery [4]. Three main effects are produced after polymer is injected into oil layer: 1. To increase the viscosity of the injected water; 2. To decrease the permeability of oil reservoir due to the retention effect; and 3. To “sweep out” the residual oil in rock pores due to the “sponge effect” of polymer solution [5]. In order to achieve larger swept area and better EOR effect, higher viscosity of the prepared polymer solution is preferred. Based on the mechanism of polymer flooding, improving the viscosity of injected water and reducing the permeability of injected water are the core technologies of polymer flooding.

4. Water-soluble polymer agents for polymer flooding

4.1. Biopolymer

Xanthan gum, also known as xanthan polysaccharide, is a kind of monospore polysaccharide produced by pseudoxanthomonas, which is an important biopolymer. Nasr et al. [6] studied the viscosity of xanthan gum when changing the temperature, pH and salt content. It was found that temperature and salt content did not affect the xanthan gum’s property, and the xanthan gum solution maintained at least 80% of the original viscosity. In addition, it was found that xanthan gum was the most suitable solution for EOR when temperature increased to 120 ℃. Xanthan gum has excellent suspension ability, thicken ability, emulsification ability, water solubility and acid-base stability. Xanthan gum is widely used in polymer flooding technology. However, it still has great limitations, such as relatively poor wear-resistance and shear-resistance [7]. The molecular chain of Xanthan gum is more rigid than polyacrylamide, which can effectively resist mechanical damage. Nevertheless, it is sensitive to bacteria and is easy to be degraded by bacteria, which is able to block the reservoir profile. So it is necessary to use bactericide and deoxidizer for proper cleaning.

4.2. Synthetic water-soluble polymers

4.2.1 Temperature and salt resistant monomer polymer. Temperature and salt resistant monomer polymer is to introduce the large side group which is not easy to hydrolyze but also can inhibit hydrolysis of amide group into HPAM molecular chain to synthesize different copolymers, so as to improve the temperature and salt resistance of polymer flooding agent. HPAM has strong hydrophilicity and is easy to dissolve in water to form hydrogen bond, so it has strong tackify effect. At the same time, the electrical repulsion effect exists among the molecular chains, which makes the molecular chains can be fully expanded to obtain high hydrodynamic volume [8]. The flexible chain in polymer aqueous solution has the conformation of random coil under high temperature and high salinity condition, and the crimp phenomenon of molecular chain enhances the viscosity of polymer solution. However, the flexible chain is easy to be degraded due to mechanical loss, which limits its application. This polymer is suitable for the special formation environment of high temperature and high salt conditions [9].

Liu Kun et al. [10] produced the highly viscoelastic flow gel formed by temperature and salt resistant cross linker and polymer, which can effectively block the large pore channels and reduce the permeability of the sweeping phase, as well as increase the injection pressure of the low-pressure wells and achieve the combination of deep profile control and displacement. It can not only improve the viscosity of the reservoir displacing medium and further reduce the fingering and tonguing phenomenon in polymer flooding, but also enlarge swept volume and improve polymer flooding effect.

4.2.2 Hydrophobic associating polymer. Hydrophobic associating water-soluble polymer is to introduce hydrophobic groups on the hydrophilic macromolecular chain of polymer. The introduction of hydrophobic groups results in hydrophobic associating within and between molecules, forming a huge three-dimensional network structure, so the polymer has good shear resistance and salt resistance.
Due to its special network structure and physical crosslinking of macromolecular chains, hydrophobic associating polymers can recover certain viscosity when the shear force is reduced. Hydrophobic associating polymer has good temperature and salt resistance, as well as thicken performance, which can meet the operation demand of EOR technology in oil field [11].

Feng et al. [12] synthesized a hydrophobic associating polymer flooding agent P(AM/AA/BEM) with high temperature resistance, salt resistance and good solubility in weak alkaline environment. It showed excellent thicken property, heat resistance (90°C), salt tolerance (20 g/L) and shear thinning ability. There was strong synergistic effect between P(AM/AA/BEM) and SDBS. When 400 mg/L SDBS was added in 1g/L P (AM/AA/BEM), the viscosity of hybrid system increased 3.3 times. P (AM/AA/BEM) showed better thicken property, heat and shearing resistance and salt tolerance than partially hydrolyzed polyacrylamide (HPAM).

Hydrophobic associating polymer has good shear recovery property, viscoelasticity property and tackify property. Now some researchers have produced hydrophobic associating polymer with many advantages, such as temperature resistance, salt resistance, shear resistance, and so on [13]. Since the mechanism research of this polymer has been relatively mature, researchers should strengthen the study on mechanical properties, solubility, wear resistance and creep resistance of hydrophobic associating polymer in the future.

4.3. Cross-linked polymer
Crosslinking refers to the process of chemical reaction between polymer macromolecular chains, which forms chemical bond, so cross-linked polymer has three-dimensional network structure. Cross-linked polymer has very good compatibility, and its wear resistance, solvent resistance, creep resistance, thermal stability and mechanical property can be highly improved due to the crosslinking effect. If the cross-linking reaction takes place between different polymers, especially between two incompatible polymers, the compatibility of the two polymers can be greatly improved, and even the incompatible components can be changed into compatible components [14].

Wang et al. [15] studied the oil recovery by adding the combination of cross-linked polymer and expanded particles into the water injection reservoir. The experimental results show that the shear resistance of this cross-linked polymer is strong, and this polymer greatly enhanced the oil recovery properly.

Cross-linked polymer flooding technology is a kind of high efficiency flooding technology developed on the basis of profile control and water shutoff technology, which has excellent performance, low cost and obvious effect of EOR. The cross-linked polymer solution system has good fluidity and low viscosity, which makes the cross-linked polymer solution play a good role in improving reservoir property and fluid property. However, the cross-linked polymer is not stable enough in acid and alkali solution, so the study in this field should be strengthened in the future [16].

4.4. Comb polymer
The characteristic of this polymer is that the side chain of the polymer has both lipophilic and hydrophilic groups. Due to the mutual repulsion of lipophilic and hydrophilic groups, the curl and entanglement within and between the molecules are reduced, and thus the polymer chain is arranged in the shape of comb in the aqueous solution. Compared with linear polymer, comb polymer has better solution performance because of its special side chain structure. Liu Yuwen [17] evaluated the properties of KYPAM salt resistant polymer. The results showed that the tackify ability of KYPAM salt resistant polymer was 68%-74% higher than that of Japan MO-4000, and the amount of polymer used could be reduced by 20%-27% under the condition of Shengli Oilfield. KYPAM salt resistant polymer will replace polyacrylamide as a new generation of high efficiency oil flooding agent for EOR technology.

Comb polymer has obvious advantages in solubility, but it has disadvantages in shear resistance and thermal stability. In the future, researchers should strengthen the experimental research and mechanism discussion in these two aspects [18].
4.5. Star polymer
Star polymer is a kind of water-soluble polymer formed by the connection of star cores and many polymer molecules. Since the main chain of the star polymer is star shaped, the rigidity of the polymer molecular chain is effectively enhanced, and the polymer has regular molecular structure. This makes the molecular chain of the polymer not easy to curl, which enlarged the hydraulic radius of the molecular chain rotation, and significantly enhanced the temperature resistance, salt resistance, as well as tackify ability of the polymer. Star polymer is widely used in oil field as oil flooding agent, mud assistant agent, plugging agent, and so on [19].

Star polymer has excellent temperature resistance ability, salt resistance ability and tackify ability. However, it has some shortcomings in acid-alkali stability, shear resistance ability and wear resistance ability. In the future, researchers should strengthen the experimental study on acid-alkali stability, shear resistance ability, wear resistance ability, and solubility of star polymer [20].

5. Requirements for polymer flooding agent
The shear stability, viscoelasticity, salt tolerance ability, thermal stability and biological stability of polymer are factors that affect polymer flooding [21]. Therefore, the selection of polymers to improve the oilfield EOR efficiency should meet the following requirements: the polymers should have good water solubility and injection performance; they should have certain thermal stability and shear degradation resistance ability; they should have good chemical and biological stability; they should not pollute the oil reservoir and the environment; they should be low cost and easy to transport [22]. Therefore, the research direction of major oil fields abroad and in China is mostly focused on the study of cheap and high-quality polymers, such as hydrophobic associating compounds, modified polyacrylamide, and so on.

6. Difficulties in polymer flooding technology and its solutions
Polymer flooding technology brings great economic benefits, at the same time, it also faces serious polymer flooding plugging problem. Polymer flooding may cause damage to the reservoir and well casing [23]. The main problems in polymer flooding technology are as follows: the adsorption and shear action of porous media will greatly reduce the viscosity of polymer solution; the properties of polymer solution will change under high temperature and high salinity conditions; the polymer solution may react with the metal ions in the original formation to generate compounds that are difficult to degrade, which causes formation plugging and reduces oil recovery [24]. For the old oilfields whose EOR has reached the middle and late stage, it is urgent to solve this contradiction, which directly affects the economic benefits of the oilfields.

The methods to solve the problems of polymer flooding technology include: 1. Develop shear resistant polymers, or polymers that can recovery a certain viscosity after shear reduction, such as hydrophobic associating polymer. 2. Develop polymers that are more resistant to high temperature and salinity. 3. Degradation of polymers to solve the reservoir plugging problem [25].

7. Conclusions
China applies high degree of EOR industrialization among the world, and the research and application of polymer flooding technology are at the forefront of the world. In recent years, the oil production of EOR technology has accounted for 6% of China's total oil production, and has increased year by year. EOR technology is a strategic requirement to slow down the aging speed of most oilfields in China, maintain stable crude oil production and reduce the dependence of China on foreign crude oil. In addition to China, the United States and Canada, polymer pilot test projects or large-scale polymer flooding projects are being carried out in Argentina (EI Tordillo oilfield), Germany (Bockstedt oilfield), Venezuela (Furrial oilfield), India (Jhalora oilfield) and other countries[26]. According to the exploitation of major oil fields around the world, polymer flooding technology is technically and economically successful. Although the number of polymer flooding projects accounts for a small proportion of current EOR projects under the influence of factors such as low oil price and high
operation cost, its application prospect is broad. According to the current reports of polymer flooding technology, the range of EOR of polymer flooding technology in the world is 5%-30% [27]. It is hoped that researchers can develop polymer flooding agents with good comprehensive properties such as low price, temperature resistance, salt resistance and shear resistance, so as to meet the growing demand of modern petroleum industry.

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