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Advances in Polymer Flooding

Bing Wei

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Abstract

Polymer flooding, which has been successfully used in numerous enhanced oil recovery (EOR) projects in the world, was able to promote oil recovery by 12 to 15% of original oil in place (OOIP). When a reservoir is flooded with viscous polymer solution, the mobility ratio between water and oil becomes more favorable relative to conventional waterflooding, which leads to a significant increase in the volumetric sweep efficiency. Furthermore, recent research based on laboratory studies and pilot field testing has proved that the displacement efficiency (at pore scale) can also be improved due to the elasticity of polymer solution. Therefore, this chapter first introduces the recovery mechanisms that have been proposed to explain oil displacement by polymer flooding within oil reservoirs. The development of EOR polymers from chemical structure to physical property is also reviewed. The experience and learning of polymer flooding accumulated in the last 20 years in the Daqing Oilfield, China, which is the most successful oilfield in the world implementing polymer flooding technique, are summarized and discussed. The aim of this chapter is to provide a synopsis of polymer flooding as an emerging and advantageous EOR process and also provide a guideline for pilot design.

Keywords: enhanced oil recovery, polymer flooding, mechanism, polymer type, field application, experience

1. Introduction

As early as the 1960s, polymer flooding had been suggested as an oil recovery process to further increase oil recovery after waterflooding; the main purpose of adding polymer was to increase the viscosity of the displacing fluid, which is commonly water [1]. This work was followed by wide research attention to recognize the benefits of polymer flooding in oil recovery applications [2–4].

For most oil reservoirs, especially heterogeneous formations, at least half of the reserved oil still leaves behind after extensive waterflooding due to the unfavorable mobility ratio between water and oil. Once a preferential flow path is formed between injector and producer, the subsequently injected water would flow straight to the production well bypassing the oil bearing zones, which ultimately causes a low sweep efficiency and oil recovery. In order to cover the bypassed oil zones, polymer is usually used to thicken the injection water and makes the mobility of water and oil comparable. Through polymer flooding, the poor mobility ratio encountered in conventional waterflooding is corrected, and consequently the volumetric sweep efficiency of the water-flooded reservoirs can be significantly improved. Among all the EOR methods, polymer flooding is considered as one of the most promising technologies because of its technical and commercial feasibility. The worldwide interests in polymer flooding applications were further stimulated recently by the exciting field reports from the scaled use in Daqing oilfield in China, with incremental oil productions of up to 300,000 barrels per day [5].

The overall oil recovery efficiency in oil production processes is generally governed by two sub efficiencies, *i.e.*, macroscopic and microscopic recovery efficiency. The macroscopic recovery efficiency refers to the volume that the flooding agents are able to sweep; while microscopic recovery efficiency is a measure of the effectiveness of the displacing fluid(s) in mobilizing the oil trapped at pore scale by capillary forces. In other words, any mechanism that can improve either macroscale or microscale oil recovery efficiency is beneficial for increasing oil production [6].

The mechanisms of polymer flooding have been pursued since it incepted [7]. The well-established relationship between capillary number and oil recovery indicates that a substantial increase in oil recovery at the pore level (microscale) can be obtained only when the capillary number is increased by several thousand times. However, for polymer flooding, the capillary number is normally increased less than 100 times [8, 9]. Therefore, it was previously suggested that polymer flooding can only improve the volumetric sweep efficiency without any effect on the microscopic displacement efficiency [10]. However, in Daqing oilfield, China, the oil recovery factor using polymer flooding was increased by up to 13% OOIP, and this value seemed unachieved only relying on sweep efficiency improvement. This fact made researchers to revisit the oil recovery mechanisms occurred in polymer flooding. After almost 15 years' efforts, it was demonstrated that the incremental oil recovery by polymer flooding could also be explained by the simultaneous increased microscopic displacement efficiency due to the distinctive flow characteristic of polymer solutions.

Regarding EOR polymers, hydrolyzed polyacrylamides (HPAMs) are still the most widely used polymer to date in oilfields because of their availability in large quantity with customized properties (molecular weight, hydrolysis degree, etc.) and low manufacturing cost [11, 12]. However, it is known that polyacrylamides are very susceptible to chemical, mechanical, thermal, and microbial degradation, and this issue might affect its acceptance in type II and type III reservoirs having high temperature and salinity. As alternatives to HPAM, many novel polymers with tough properties have been proposed in the past several years, such as hydrophobically modified polymers and biopolymers [13].

Therefore, this chapter first summarizes all the oil recovery mechanisms involved in polymer flooding related to the sweep efficiency and displacement efficiency in order to assist people rapidly understand this popular and emerging EOR technique. Further, EOR polymers from chemical structure to physical properties are discussed. In the end, field experience and learning of polymer flooding in China are presented.

2. Oil recovery mechanisms of polymer flooding

2.1. Macroscopic sweep efficiency improvement

2.1.1. Mobility control

The primary objective of polymer flooding is to control the mobility of the aqueous phase. Mobility is defined as the ratio of the relative permeability to the displacing phase divided by the viscosity of the displacing phase. The dissolution of polymer to water reduces its mobility by thickening the aqueous phase and significantly diminishes the formation of viscous fingerings and/or channels [10, 14, 15]. Therefore, polymer flooding is very effective in improving the volumetric sweep efficiency.

Mobility ratio (M) is the key parameter to quantify the mobility contrast between aqueous phase and oil phase. The mobility ratio for waterflooding is given by the following expression (Eq. 1) [14]:

$$M = \frac{\lambda_w}{\lambda_o} = \frac{k_{rw}/\mu_w}{k_{ro}/\mu_o} = \frac{k_{rw}\mu_o}{k_{ro}\mu_w} \quad (1)$$

where λ is the fluid mobility, k_r is the relative permeability, and μ is the fluid viscosity; the subscripts w and o denote water phase and oil phase, respectively.

The conventional concept of mobility ratio (M) distinguishes “favorable” mobility conditions when $M \leq 1$ and “unfavorable” mobility conditions when $M > 1$ [16, 17]. From this point, it can be easily understood that polymer flooding enables the correct mobility ratio (M) to a favorable level by increasing the viscosity of water (μ_w).

2.1.2. Disproportionate permeability reduction (DPR)

In addition to viscosity increase, another mechanism, DPR, can also facilitate polymer flooding to improve the macroscopic sweep efficiency. Disproportionate permeability reduction means polymer considerably reduces the water relative permeability (k_{rw}) while producing minimum reduction in the oil relative permeability [18–20].

The reasons causing DPR in polymer flooding include: 1) Segregation of flow pathways (water and oil); 2) Shrinking/swelling of polymer; 3) Layer formation on pore wall by adsorbed polymer; and 4) Wettability alteration [21–25]. However, it was believed that polymer

adsorption and segregation of flow pathways were the dominant mechanisms compared to other two mechanisms [26–29].

2.1.3. Flow resistance induced by polymer elasticity

Flow resistance is the third mechanism that can improve volumetric or macroscopic sweep efficiency during polymer flooding. The effect of viscoelastic fluid on the formation of an “internal cake” (frictional pressure drop) was reported by Dehghanpour and Kuru [30]. They observed that polymer solution with higher elasticity yielded significantly higher pressure drop during flow through porous media. A similar trend was obtained by Urbissinova et al. [31], who evaluated the contribution of polymer’s elasticity in EOR. Likewise, they observed that the polymer solution having higher elasticity corresponds to higher flow resistance to flow through porous media than the polymer with lower elasticity, even though their shear viscosities were identical, which in turn improved the macroscopic sweep efficiency and oil recovery (**Figure 1**) [32, 33]. This mechanism may also improve the microscopic displacement efficiency by displacing residual oil immobilized by capillary forces and rock configuration [8]. Furthermore, the elasticity can also maintain the stability of the propagating front and minimize fingers as shown in **Figure 2** [34].

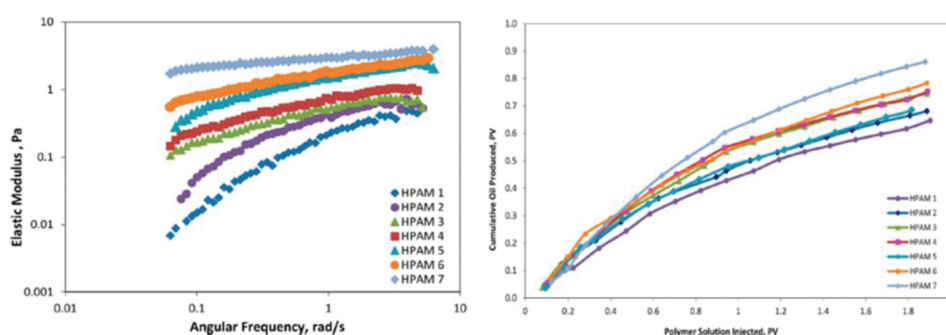


Figure 1. The effect of polymer elasticity on oil recovery (similar viscosity). (Source: [33])

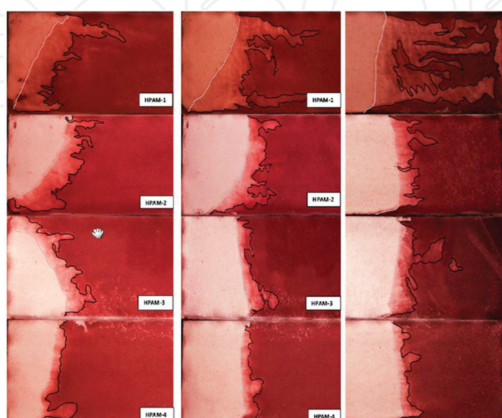


Figure 2. Propagating front of polymer solution. (Source: [34]) (Elasticity: HPAM-4>HPAM-3>HPAM-2>HPAM-1)

2.2. Microscopic displacement efficiency improvement

In the last decade, it has been confirmed that polymer flooding can increase the microscopic displacement efficiency by mobilizing and displacing residual oil saturation (trapped by capillary forces). This phenomenon was attributed to the elasticity of the polymer solutions.

Wang et al. [8] first studied this subject by evaluating the effectiveness of polymer flooding in displacing “residual oil” after waterflooding under different conditions as follows. (1) Residual oil in “dead ends”; (2) Residual oil films on rock; (3) Residual oil in pore throats trapped by capillary forces; (4) Residual oil un-swept in microscale heterogeneous portions of the porous media (**Figure 3**). In all cases, it was observed that residual oil was further reduced after polymer flooding. The proposed mechanisms improving the microscopic displacement efficiency during polymer flooding include pulling effect, stripping effect, oil thread, and shear thickening effect, which are discussed in the subsequent paragraphs.

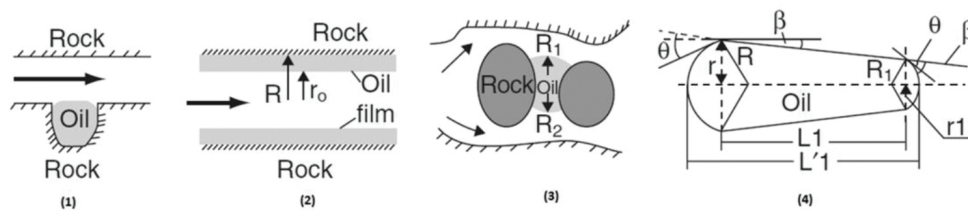


Figure 3. Simplified models of residual oil distribution after waterflooding. (Source: [35])

2.2.1. Pulling effect

It was found that if an elastic fluid flows over dead ends, normal stresses between oil and polymer solution are generated in addition to the shear stresses resulting from the long molecular chains [36, 37]. Therefore, polymer molecules impose a larger force on oil droplets and thus pull them out of dead ends. The amount of residual oil pulled out from dead ends seems proportional to the elasticity of the driving fluid (**Figure 4**). The viscoelastic polymer pushes the fluid ahead and pulls the fluids beside and behind, while the nonelastic fluids (water and glycerin) as shown in **Figure 4** are also capable of pushing the fluids ahead but cannot “pull” out oil from the dead end.

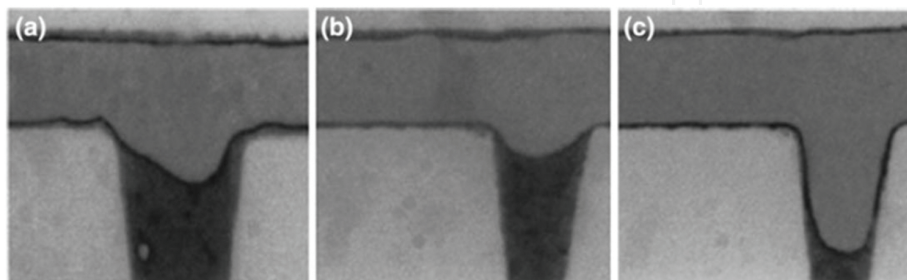


Figure 4. Residual oil in the dead ends after a: water; b: glycerin (without elasticity); c: HPAM flooding (source: [5])

This effect has been further investigated through numerical simulation of polymer flooding over dead ends [38, 39]. A simplified physical model with dead end geometry was used (**Figure 5**). A modified upper-convected Maxwell (MUCM) model which considered viscosity, elasticity, and also non-Newtonian power law behaviors of polymer solution was established. Using this model, the contours of velocity and stream function can be drawn and the microscopic efficiency quantified (**Figure 6**).

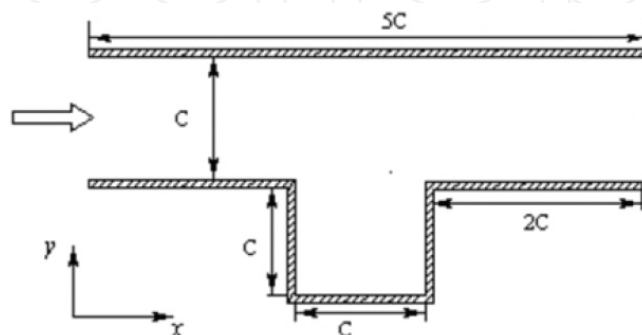


Figure 5. Micropore with dead end model. (Source: [38])

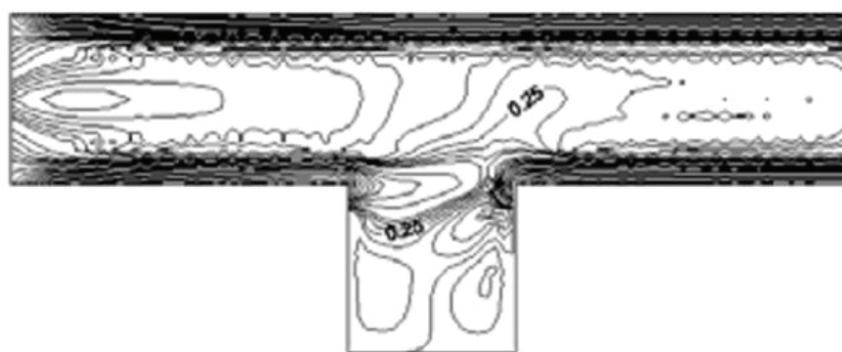


Figure 6. An example of the stress contour determined by the MUCM model. (Source: [38])

2.2.2. Stripping effect

For oil-wet porous media, residual oil is attached on the rock surface in the form of a continuous oil film (**Figure 3(2)**). Wang et al. [8, 36] compared the velocity profile of a Newtonian and a non-Newtonian fluid in a capillary and observed that the velocity gradient near the capillary wall for the elastic fluid is noticeably higher than that for the Newtonian fluid (**Figure 7**). Therefore, a stronger force is produced during flow of polymer solutions compared to water, which thus facilitates stripping the oil films off rock surface and eventually promotes the microscopic displacement efficiency [39–42]. The alteration in wettability from oil-wet to more water-wet due to the stripping effect would also increase oil recovery.

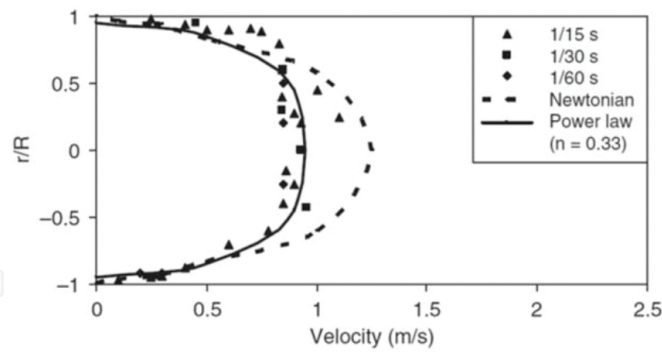


Figure 7. Velocity profiles of water and an HPAM solution in a capillary. (Source: [36])

2.2.3. Oil thread

The third possible mechanism related to the elastic property of polymers is oil thread. Oil is pulled out by polymers into oil columns and then forms oil threads as they aggregate with the residual oil downstream [5, 43]. However, due to the high interfacial tension between oil and polymer solution, the long oil column would be destabilized and broken into oil droplets, the oil droplets will be probably re-entrapped by capillary forces [44]. Elastic polymer solutions are able to stabilize oil threads as a result of the normal stress. It is believed that the normal force bearing on the convex surface of oil thread is larger than the normal force bearing on the concave surface. The essential consequence of this effect is to stabilize oil threads and prevent them from deforming, which therefore improves the displacement efficiency [41]. Furthermore, this force increases with the Deborah number (N_{Deh}), which is a dimensionless number commonly employed to describe the elasticity of polymer solutions in porous media (**Figure 8**).

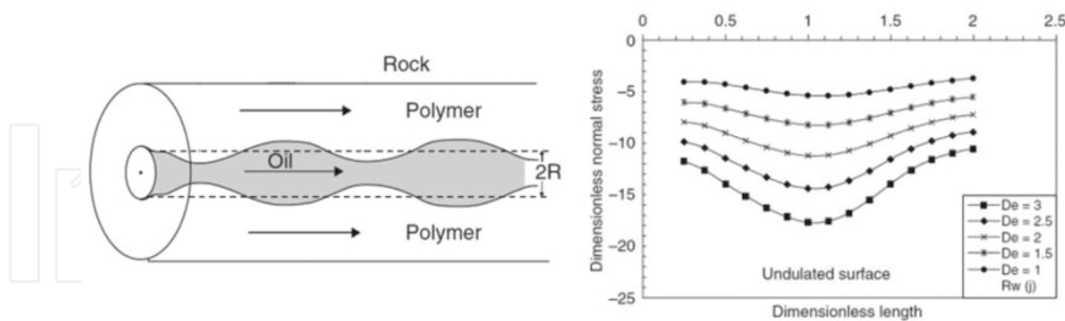


Figure 8. Illustration of the oil thread mechanism. (Source: [43])

2.3.4. Shear thickening

The flow behavior of polymers as a function of shear rate (flow velocity gradient) in porous media can be generally divided into three regions: Newtonian, shear thinning, and shear thickening as shown in **Figure 9**. When polymer molecules flow through a series of pore bodies and pore throats, the flow field experiences elongation and contraction. Shear thickening

phenomenon would occur when the flow velocity is so high that the polymer molecules do not have sufficient relaxation time to re-coil to adapt the flow geometry. The stretched polymer chains result in a high apparent viscosity (shear thickening). This effect can help the driving fluid to rapidly displace the mobile but hard-to-displace oil or to displace the bypassed oil in small-scale heterogeneities more effectively [45]. Therefore, the shear thickening effect is considered as one of the possible mechanisms for microscopic displacement efficiency improvement in polymer flooding [46]. Moreover, the high apparent viscosity is also beneficial for promoting the macroscopic sweep efficiency [47].

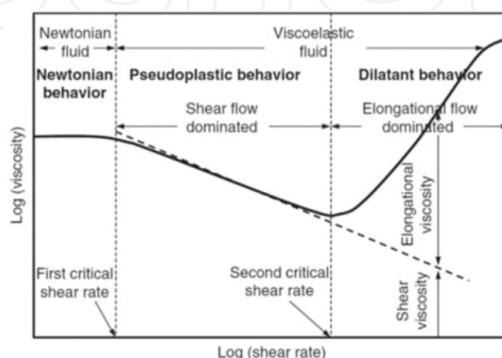


Figure 9. Flow behavior of viscoelastic fluid. (Source: [48])

3. EOR polymers

3.1. Synthetic Polymers

HPAM, partially hydrolyzed polyacrylamide, is by far the most used polymer in EOR application, which is a copolymer of PAM and PAA obtained by partial hydrolysis of PAM or copolymerization of sodium acrylate and acrylamide [49]. The chemical structure of HPAM is shown in **Figure 10**. For most cases, the degree of hydrolysis of the acrylamide monomers ranges from 25 to 35%. The fact that the monomeric units have to be hydrolyzed is probably related to the formation of the corresponding salt. The negative charges loaded onto polymer backbone due to the hydrolysis are responsible for prominent stretching (electric repulsion) of polymer chains, which results in viscosity increase. On the other hand, the degree of hydrolysis cannot be too high, otherwise, HPAM becomes too sensitive to salinity and hardness of brine (shielding effect) [50].

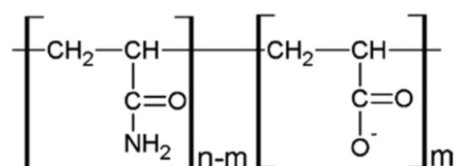


Figure 10. Chemical structure of HPAM.

However, given the harsh conditions present in most of oil reservoirs, problems and limitation arise with the use of conventional HPAM because of the significant chemical and mechanical degradation. Therefore, other tolerant polymers such as hydrophobically associating polymers and biopolymers have been proposed in the market [51].

The design of hydrophobically associating polymers is based on the concept of association between hydrophobic groups that are incorporated in the backbone of the polymers. These hydrophobic groups could be randomly or block-like distributed, and coupled at one or both ends. When the polymer is dissolved in water, the hydrophobic groups associate forming micro-domains, which leads to increase in the hydrodynamic volume and accordingly yields an improved thickening capacity [52]. **Figure 11** shows the structure of a typical hydrophobically associating polymer.

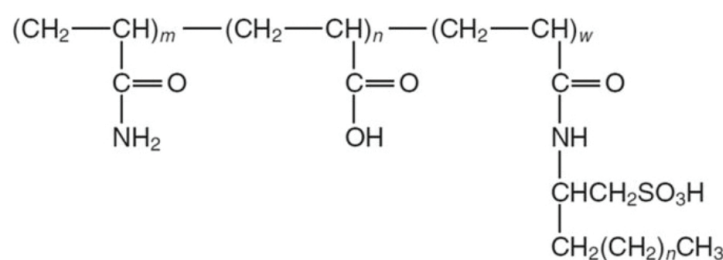


Figure 11. Structure of a hydrophobically associating polymer. (Source: [48])

Recently, Zaitoun et al. reported a new class of novel EOR polymers, which contain nVP (n-Vinyl-Pyrrolidone) and ATBS (Acrylamido tert-Butyl Sulfonate). The presence of nVP can enhance the thermal stability of polymers, while the function of ATBS is to improve both thermal stability and salinity tolerance. **Figure 12** shows the chemical structure of nVP and ATBS as well as the commercial names of the polymers.

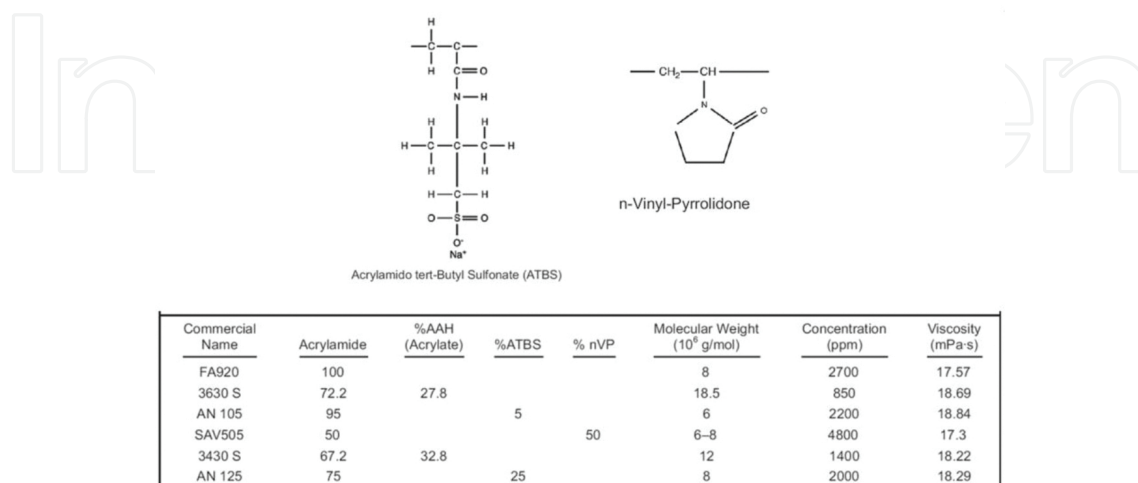


Figure 12. Chemical composition of the polymers. (Source: [53])

KYPAM is a commercial EOR polymer, which is produced by Beijing Hengju, China and is being widely used in many oilfields such as Daqing and Shengli, etc. It is a typical salinity-tolerant EOR polymer, which is functioned by different types of groups. The basic structure of KYPAM is shown in **Figure 13**.

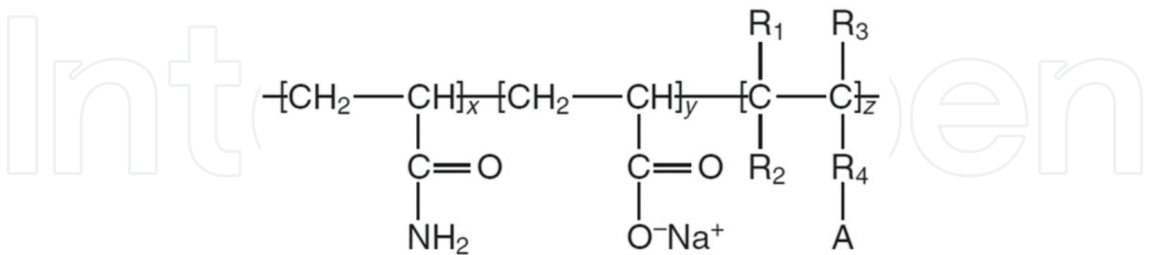


Figure 13. Structure of KYPAM. (Source: [54])

where R_1 , R_2 , and R_3 could be either H or alkyl. A represents an ionic functional group that is tolerant to Ca^{2+} and/or Mg^{2+} . The elasticity of KYPAM is controlled by R_1 , R_2 , and R_3 , and R_4 determines the salinity tolerance of KYPAM.

KYPAM has been successfully used in China; a good example is Lamadian Field, Daqing. In 2001, the northwestern block of Lamadian field carried out a field test using KYPAM. Polymer solution which was prepared with produced water was injected in May 2001. **Figure 14** illustrates the average water cut change during KYPAM test and HPAM test in a neighbor block. It should be emphasized that the HPAM solution was prepared with fresh water. It was observed that the average water cut was reduced by 15% by KYPAM compared to conventional HPAM [55].

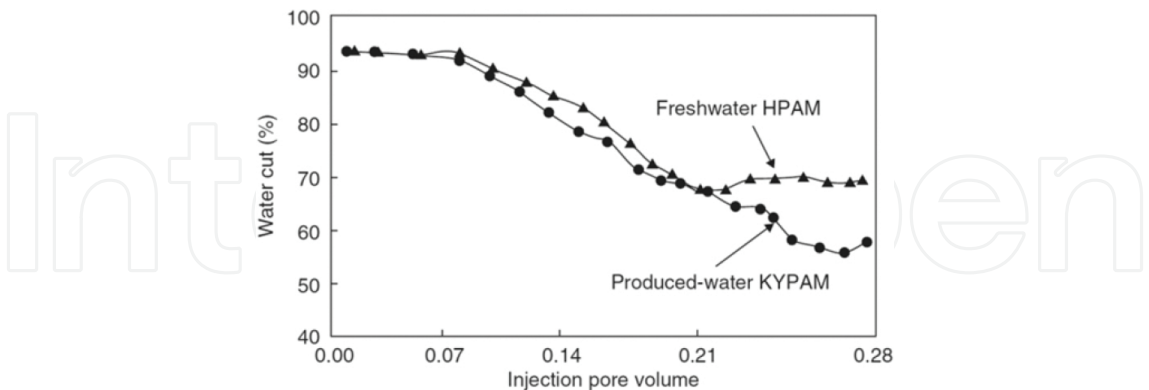


Figure 14. Effect of HPAM and KYPAM on water cut. (Source: [55])

3.2. Biopolymers

In addition to the synthetic polymers, another kind of polymer frequently used is biopolymer, such as xanthan gum. Xanthan gum is a polymersaccharide which is produced by fermentation

of glucose or fructose by different bacteria. The chemical structure of xanthan gum as shown in **Figure 15** illustrates the presence of two glucose units, two mannose units, and one glucuronic acid unit with a molar ratio of 2.8-2-2 [56]. X-ray diffraction studies proved that xanthan backbone has a helical structure where the side chains fold down along the helix. The average molecular weight of xanthan gum used in EOR processes is from 1–15 million.

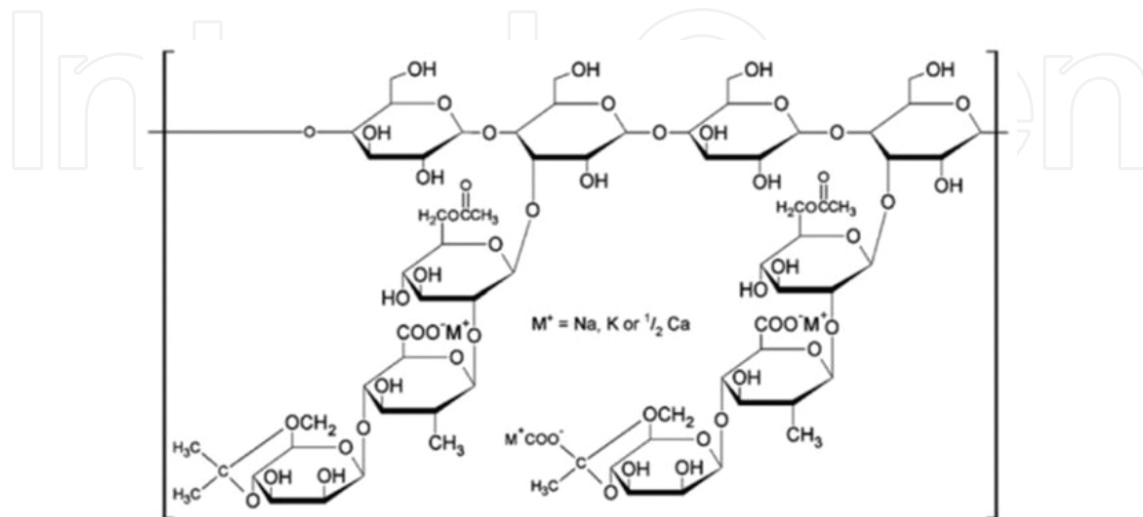


Figure 15. Chemical structure of xanthan gum. (Source: [57])

Due to its unique structure, xanthan gum is quite resistant to mechanical shear and salinity. The chemical and physical properties of xanthan gum related to EOR use have been systematically investigated in our previous reports [58–61]. It was demonstrated that xanthan gum experienced less viscosity loss when exposed to harsh reservoir conditions compared with HPAM and hydrophobic polymers. Therefore, a piston-like flow pattern was established during xanthan gum propagation in porous media.

A successful pilot test using xanthan gum was conducted in the 7th block in Shengli oilfield, China (65°C, 5500TDS). The injection of xanthan gum solution was launched after the waterflooding was exhausted. Totally, 0.356PV polymer solution with a concentration of 480PV·mg/L was injected into the target formation (Ng⁵⁵); the whole process took about 825days. The results indicated that a reduction in water cut from 97 to 92% was observed [13].

Hydroxyethylcellulose (HEC) is another biopolymer that has been implemented in oilfields. HEC was produced from insoluble cellulose by chemical modification. Unlike xanthan gum, HEC is a synthetically produced biopolymer and thus does not contain cellular debris, which has been implicated as a cause of formation plugging. As a result of the nonionic feature and rigid backbone, HEC is able to withstand high salt concentration, temperature, and mechanical shear.

HEC is particularly suitable for polymer flooding low temperature but high salinity formations resulting from its tolerance to high salinities, where HPAM and even hydrophobic polymers are discarded due to precipitation. In 1992, a joint field trial of Total and Tatneft was performed in the Romashkino field, Tatarstan. The temperature of this reservoir was 38°C with a salinity

of 250g/L. According to the report, the production of 1 million tons of incremental oil was produced due to the injection of 350 tons of HEC [62].

Other potential EOR biopolymers are scleroglucan, simusan, AGBP, welan gum, and so on. However, it seems that these biopolymers have not been implemented in oilfields so far.

4. Experience of polymer flooding and learning in china

Unquestionably, Daqing Oilfield is the most successful example in polymer flooding technology in China and even in the world. Laboratory research investigating the potential of polymer flooding was started in the 1960s. After a few pilot tests, the largest polymer flooding was implemented at Daqing from 2006, which has contributed 22.3% of the total oil production by 2007. At the end of 2007, oil production dedicated by polymer flooding was more than 10 million tons per year [12]. Based on these successful experiences, the use of polymer flooding in the Dagang, Shengli, Karamay oilfields, etc., is being considered or has already been proved.

According to the observations of the response, polymer flooding process can be divided into five stages as shown in **Figure 16** [63].

1. **Initial stage.** Polymer solution is injected into formations and injection pressure increases, but water cut does not start to decrease yet.
2. **Water cut decreasing stage.** Injection pressure keeps increasing and the water cut decrease can be seen.
3. **Stable stage.** Water cut and production are relatively stable.
4. **Water cut increasing stage.** After a stable period, the water cut starts to rapidly increase. The produced polymer concentration is quite high.
5. **Post-water drive stage.** A water drive is followed up.

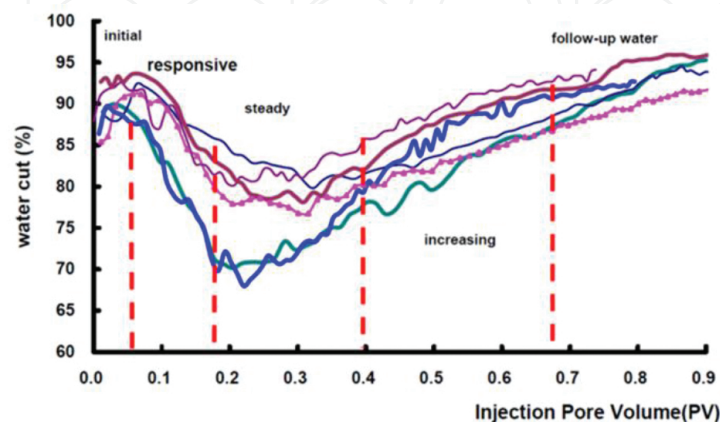


Figure 16. Water cut change during polymer flooding. (Source: [12])

Many key indices including water cut, fluid production capability, injection capability, and injection profile change at different stages of polymer flooding. The most definitive index is water cut, which is increased at the initial stage and also the last stage. Water cut starts to drop at the second stage, which is a response to polymer injection.

After more than 20 years of pilot testing and large-scale commercial applications in polymer flooding in China, a wealth of experience and learning has been accumulated as follows.

4.1. Well pattern design

When designing a polymer flooding project, a number of guidelines should be followed. Designs should accommodate the variations in geological properties for different parts of the field. To optimize the well pattern, the parameters of connectivity factor, permeability ratio, and well spacing should be counted [63].

Connectivity factor is defined as the pore volume accessed by polymer solution divided by the total PV of the oil zone. It was proved that the incremental oil recovery by polymer flooding markedly decreased when this factor is lower than 70%. Therefore, well pattern and polymer molecular weight must be well considered to make this value greater than 70%.

The effect of well pattern on the incremental oil recovery by polymer flooding was compared based on numerical simulations. The results indicated that the magnitudes of incremental oil recovery are very close for the well patterns of line-drive, staggered drive, 4-spot, 5-spot, and 9-spot. However, 5-spot pattern seems attractive for polymer flooding owing to the proper injection pressure and connectivity.

Regarding well spacing, at Daqing, for the oil zones having permeability higher than 400md, net pay thicker than 5m, and V_k greater than 0.65, the well spacing is designed from 200–250 m. However, for the oil zones having lower permeability (>200md), net pay ranging from 1–5m, and V_k less than 0.65, 150–175 m is an reasonable spacing. The prerequisite of any well spacing is to ensure connectivity higher than 70%.

4.2. Polymer injection design

Before a polymer flooding operation, three parameters that are closely related to economic and technical feasibility must be considered. These parameters include polymer molecular weight, polymer concentration, and polymer volume.

The efficiency and the economics of polymer flooding are somehow governed by polymer molecular weight. The selection of the molecular weight is strongly dependent on two factors. High-molecular-weight polymer is normally preferential to minimize the cost from the economic point of view. However, on the other hand, the molecular weight must be small enough to allow polymer to enter and propagate through the porous media. Therefore, for a given rock permeability and pore size, the maximum molecular weight is almost definitized. The ratio of pore throat radius to the root mean square radius of gyration of the polymer must

be greater than 5 to eliminate any plugging problem [64]. **Figure 17** plots the maximum molecular weight versus rock permeability.

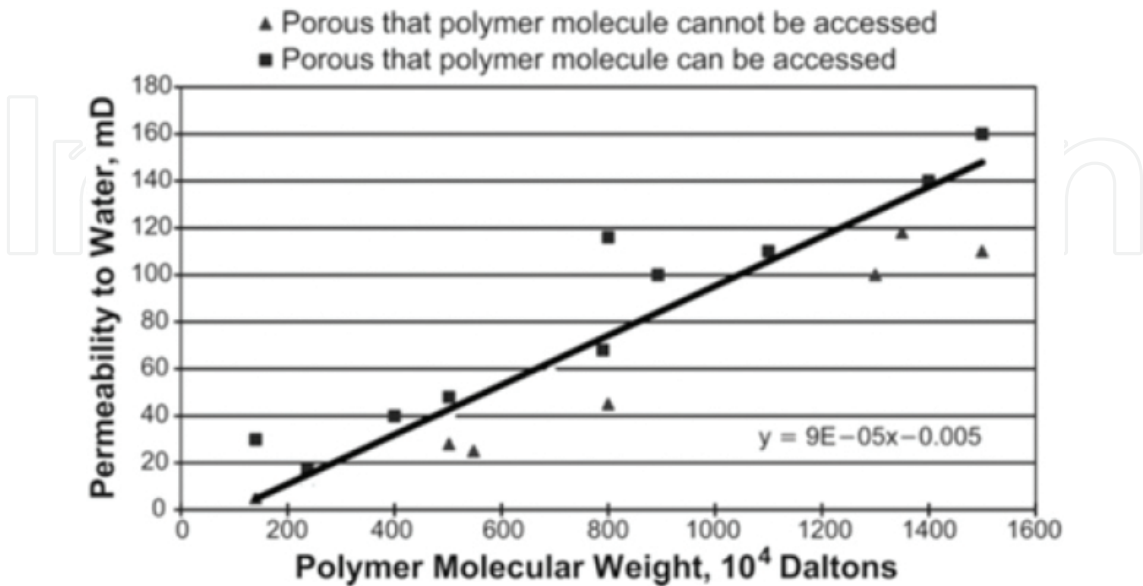


Figure 17. Allowed polymer molecular weight vs permeability. (Source: [65])

The effectiveness of polymer flooding with higher concentration has been technically verified at Daqing. By using higher concentration polymer slugs, the in-depth vertical sweep can be improved in the early stage of polymer flooding. Furthermore, the increased water cut at the third stage of polymer flooding can be significantly mitigated. They found that the water-intake profile became more uniform after injecting 2200 to 2500mg/L polymer solution [66]. This technological trend was also studied in our previous work for heavy oil recovery [59].

According to more than 200 reports of polymer flooding, the average amount of injected polymer solution was from 19 to 150 lb/acre-ft, which is equivalent to 23.3 to 184.2 mg/L·PV if the porosity is 30%. At Daqing, the injected amount of polymer solution usually ranged from 180 to 380 mg/L·PV. However, much larger amounts of polymer solution have been attempted, the largest amount being 771 mg/L·PV, which therefore resulted in a higher incremental oil recovery and improved economics [12].

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Author details

Bing Wei

Address all correspondence to: bwei@swpu.edu.cn

State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan, China

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