The research status and summary of adsorption and retention mechanism of polymer

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Abstract. The polymer flooding technology has been established a relatively scientific and complete technical theory system, after decades of development. Theoretical and field applications have shown that the key to profile control and flooding is adsorption and retention of polymer in reservoirs. When the polymer flows through the porous medium of the reservoir, it will be adsorbed and trapped in the pores of the cores, resulting in serious decrease in the permeability of water in the porous medium of the reservoir, while only a slight decrease in the permeability of oil, increasing the mobility of crude oil, effectively increasing the injected water swept volume, and thereby improving the comprehensive economic benefit of water-flooding development reservoir. In order to further understand the adsorption and retention mechanism of polymer, guide the oilfield production, and achieve the purpose of low injection of polymer and the high production of oil, in this paper, we conducted a lot of research on the adsorption and retention mechanism of polymer at home and abroad. The comprehensive analysis shows that electrostatic and mechanical trapping are the main causes of adsorption and retention, followed by polymer concentration, degree of hydrolysis, rock wettability and formation mineralized water composition.

1. Introduction
In the oilfield development, the polymer can be used to control the mobility of reservoir fluid because of its residual or “loss” when it flows through porous media[1-7]. There are many theories that the main reasons of its residual or “loss” is the adsorption and retention of polymer in porous media in reservoirs. Some polymers can significantly reduce the permeability of water in reservoir porous media, while the permeability of oil decreases only slightly[8-13]. So this kind of polymer is often used for mobility control in the process of oilfield development. The decreasing of injection fluid mobility will contribute to the increasing of the mobility of oil in reservoir porous media, which can effectively improve water flooding sweep efficiency[14-16].

The polymer adsorption and retention is the main reason for the profile control and flooding of polymer. Laboratory experiments have shown that there are many reasons for the adsorption and retention of polymer: (1) It is mainly caused by surface adsorption in the static experiment. The polymer molecules interact with the rock surface and bond to the rock surface by physical adsorption. In other words, the physical adsorption is electrostatic interaction and hydrogen bonding. (2) In the dynamic experiment, the adsorption and retention of polymer is mainly caused by adsorption, mechanical trapping and hydrodynamic trapping[17].
2. Mechanism of Polymer Adsorption

2.1. Electrostatic interaction

In polyacrylamide molecules, since the C-C bond is essentially non-polar and the C-H bond is weak, the polyacrylamide molecules have only physical forces such as Van Der Waals forces[1]. However, the polyacrylamide can be hydrolyzed, under the action of base, to produce partially hydrolyzed polyacrylamide. When the partially hydrolyzed polyacrylamide is dissolved in water, the sodium-carboxy group(—COONa) can be ionized to produce negatively charged polyions. And the negatively charged group(—COO-) is in ionization equilibrium with the sodium-carboxy group(—COONa). When the partially hydrolyzed polyacrylamide is ionized, the carboxyl group is negatively charged, and the carboxyl group may be adsorbed to minerals by electrostatic interaction. For clay minerals with layered structure, the clay minerals are composed of silicon-oxygen tetrahedral plates and aluminum-oxygen octahedral plates alternately in accordance with certain laws, and the adjacent crystal layers have Van Der Waals forces, hydrogen bonds, electrostatic attraction and other forces. Under natural conditions, ions of equal radius with different charges are exchanged with each other, making such minerals mostly negatively charged. For example, when Si$^{4+}$ is replaced by Al$^{3+}$, it has a negative charge, which is determined by internal structure of the substance and it’s independent of the concentration of the solution.

In addition, hydroxyl ions formed by the breaking of Si-O and Al-O bonds at the end of the mineral can electrify the side (or end) of the mineral particles, which is related to the concentration or pH of the solution. Under acidic conditions, the clay mineral chip has a positive charge at the end and a negative charge on the surface. Under alkaline conditions, the charge distribution of clay mineral particles is uneven because of the negative charge on the end and surface of the clay mineral chip. When clay particles are charged at zero point, they may be charged on both the end surface and the inner surface, and have adsorbsability, while other minerals do not have this adsorption property at zero point charge. For other minerals, surface charge are positively charged at low pH and negatively charged at high pH. There are two reasons for this: (1) selective dissolution of minerals; (2) the hydrolysis of surface material resulting from the dissociation of hydroxide by solutions of different pH.

The above analysis is the cause of electrostatic adsorption and Van Der Waals forces on the surface of the polymer and minerals.

2.2. Hydrogen bonding

In addition to electrostatic adsorption, hydrogen bond adsorption is also the cause of polymer adsorption. Under the condition of water invasion for a long time, hydroxyl group can be formed on the surface of the rock. The hydroxyl groups on the surface can be connected to the carboxylic acid roots in HPAM or to the amide groups in HPAM by hydrogen bonding. And a polymer chain contains a number of groups that from hydrogen bonds. The adsorption of these groups($\text{C–NH}_2$, $\text{C–O}$, $\text{C–OH}$) on the particle surface is only point contact, and macromolecular chains exist in solution as clusters. Besides, the amides and carboxyl groups of partially hydrolyzed polyacrylamide have hydrophilic properties. Under the double action of the two functional groups, the partially hydrolyzed polyacrylamide exhibits flocculation ability, which contributes to large number of hydrophilic groups on the clusters, to adsorb a large number of water. At the same time, the partially hydrolyzed polyacrylamide forms an adsorbed film in the reservoir pores, which reduces the seepage capacity of the oil-water channel, inhibits the flow of water, and changes the direction of water drive in the reservoir.
In the study of adsorption of polyacrylamide by ZrO$_2$, we found that the polymer was monolayer adsorption. And the adsorption capacity and equilibrium concentration can be expressed by Langmuir isotherm[18,19].

$$\frac{C}{x/m} = \frac{1}{K_1K_2} + \frac{C}{K_2} \tag{1}$$

Where $K_1$ and $K_2$ are equilibrium constant; $C$ is the equilibrium concentration of polyacrylamide (mg/g); $x$ is the adsorption capacity of polyacrylamide (mg); $m$ is the amount of adsorbent (g).

3. Mechanism of Polymer retention

3.1. Mechanical trapping effect
The mechanical trapping effect of polymer in pores is mainly due to the large size of polymer molecules relative to the pores, so that they cannot flow through the pores, leading to pores blockage. Although the adsorption of polymer molecules also can cause the decrease of pore permeability, the pores will not be completely blocked. The mechanism trapping of polymers is similar to the osmotic process that the extremely fine particles flow through a filling bed. But the polymer molecules in solution are flexible and can deform under shear stress.

As the Figure 1 shown, in the reservoir porous media, these are the location where polymer molecular clusters may be trapped. Although the adsorption of polymer molecular clusters occurs at the surface location, interactions between the adsorbed polymer and the polymer in solution may still occur. The force that traps the polymer is mechanical. The size of the compressed polymer molecules or the size of the polymer clusters can be trapped in the porous. There is a location in the fracture where the polymer molecular clusters can be trapped because the contact area between the adjacent sand grains is wedge-shaped. The location of the polymer compression indicates that these smaller pores can also allow polymer molecular clusters to penetrate them. For the cave location, this is a false location. When the polymer flows through the cave, the flow direction changes due to the tortuosity of the flow path or the decrease of the flow velocity, resulting in the retention of the polymer.

![Figure 1. Retention patterns of polymer molecular clusters in porous media.](image)

The study of Gogarty[20] and Smith[21] suggested that the retention of polymer in porous media can also occur due to the infiltration or mechanical trapping of polymer in porous media. The flow capacity of the polymer solution decreases when it passes through the filter medium with a pore size of 0.5~2.0 microns. The pore size distribution of Berea sandstone can be determined by mercury injection porosity as shown in Figure 2[1]. The shaded portion represents the volume of the portion of the core where the pore diameter is less than 1 micron.

Domingue and Willhite[22] determined the retention of HPAM with a molecular weight of 5 × 10$^6$ in a polytetrafluoroethylene (ptfe) cementing core with a very small adsorption. Palmer[23] used the
same polytetrafluoroethylene (ptfe) 3.5 Darcy unconsol|id bed for polymer retention experiments. A number of experimental studies have shown that mechanical capture of macromolecules can occur in a wide range of permeability and porosity, even in a very small adsorption.

![Figure 2. Pore size distribution of Berea sandstone.](image)

3.2. Hydrodynamic trapping effect
The concept of hydrodynamic trapping effect is put forward based on the phenomena observed in experiments[24]. In experiments, it was found that the retention of polymer increased as the flow velocity increased. However, there is a critical shear rate, which defines the optimal rate of polymer injection for better economic viability of the process[25]. And after the flow rate decreases or stops for a certain period of time, some of the retained polymer will be flowed out of the channel again, reducing the retention of polymer. Thus, we can know that the retention of the polymer in the core is related to the flow rate. In other words, some of the polymer trapped in the core is due to hydrodynamic trapping effect. In addition to the flow rate, the degree of hydrodynamic retention was greater when higher molecular weight polymers were injected[26].

4. Factors affecting polymer adsorption and retention
There are many factors influencing the adsorption and retention of polymer in reservoir pores. Factors such as polymer type, molecular weight, degree of hydrolysis, salinity, hardness, ionic strength of solvent water, composition and surface properties of rock particles, and ambient temperature all affect the size of static adsorption of polymer. Generally speaking, the increase of salinity in aqueous solution is favorable for adsorption[16]. The surface of carbonate rocks is easier to adsorb polymer molecules than that of sandstone, and the increase of temperature is favorable for adsorption.

4.1. Average molecular weight and degree of hydrolysis
With the increase of molecular weight, the adsorption capacity of polymer decrease of molecular weight. But the degree of hydrolysis has great influence on polymer adsorption. The lower the molecular weight of partially hydrolyzed polyacrylamide, the lower the degree of hydrolysis. Therefore, when the average molecular weight and degree of hydrolysis of partially hydrolyzed polyacrylamide increased, the volume of each molecule group increased, the density decreased, and the adsorption and retention in the porous media decreased. When the difference in average polymer molecular weight is not large, the density of polymer molecular clusters mainly depends on the number of carboxyl group on the molecular chain. Therefore, the adsorption capacity of polymer is mainly determined by the degree of hydrolysis, followed by the average molecular weight.
4.2. Polymer concentration
Within certain polymer concentration, the adsorption capacity of partially hydrolyzed polyacrylamide increases with the increase of polymer solution concentration. Under this pattern of change, after a certain concentration, the adsorption increases suddenly. And the dependence of adsorption on solution concentration is not obvious before that concentration. If the high molecular weight polymers are adsorbed on the rock surface, a large number of polymer chains will come into contact with the rock surface. Although the amount of adsorption of a single molecule chain is low, the amount of adsorption of a molecular clusters is usually high. Therefore, the isothermal adsorption of partially hydrolyzed polyacrylamide has strong adsorption characteristics. At low concentrations, the adsorption density increases rapidly with the increase of concentration; at high concentrations, the adsorption density can reach stable. As the same time, it was found that if a porous medium is first contacted sufficiently with dilute polymer solution to satisfy the retention, no significant additional retention occurs during exposure to higher HPAM concentrations[27].

4.3. Inorganic electrolyte
When the polyacrylamide is hydrolyzed in an aqueous solution, the repulsion between the anions causes the molecular clusters to expand and the molecular chains to become interwined. The monovalent and bivalent cations can inhibit the dissociation of carboxyl groups, resulting in ion shielding, which weakens the repulsion on the molecular chain, shrinks the group volume of molecular lines, and reduces the interwinding, resulting in an increase in the adsorption capacity of the polymer. The properties of inorganic electrolyte have great influence on polymer adsorption. The compression of bivalent cations to the molecular cluster is 10%~30% higher than that of alkali metal ions[28]. When polyvalent metal salts exist in solution, the adsorption capacity increases gradually with the increase of dissociation degree of ionic groups and cation valence state. The Na+ dissociated from the sodium-carboxy group in the polymer molecule is ion exchanged with the divalent ion the clay mineral. The divalent ions compress the polymer cluster’s bulk structure, increasing the adsorption capacity of polymer on mineral[29]. The adsorption effect of low concentration Ca2+ can improve polymer on silicon powder was much greater than that of low concentration Na+. However, at high salinity, the effect of Ca2+ concentration on polymer adsorption is much less than that of Na+.

4.4. Wettability
The adsorption of polyacrylamide on reservoir rocks depends largely on the wettability of the rock surface. Relevant studies show that the adsorption capacity of polymer on the water-wet model is much higher than that on the oil-wet model. Therefore, in the field applications, inject of polymer slugs below the oil-water contact may cause delays in the breakthrough polymer and the arrival of the associated reservoirs, which in turn may have significant detrimental effects on the economics of a commercial polymer project[30,31].

5. Conclusion
The adsorption and retention of polymer in reservoir core pores are affected by many factors. The study shows that polymer properties, formation water salinity and reservoir mineral types are important factors affecting polymer adsorption and retention. The electrostatic and mechanical trapping are the main causes of adsorption and retention, followed by polymer concentration, degree of hydrolysis, rock wettability and formation mineralized water composition. (1) With the increase of molecular weight, the adsorption capacity of polymer decrease of molecular weight. But the degree of hydrolysis has great influence on polymer adsorption. The lower the molecular weight of partially hydrolyzed polyacrylamide, the lower the degree of hydrolysis. (2) With certain polymer concentration, the adsorption capacity of partially hydrolyzed polyacrylamide increases with the increase of polymer solution concentration. (3) When the polyacrylamide is hydrolyzed in an aqueous solution, the repulsion between the anions causes the molecular clusters to expand and the molecular chains to become interwined. The monovalent and bivalent cations can inhibit the dissociation of
carboxyl groups, resulting in reducing the interwinding of the clusters and increasing in the adsorption capacity of the polymer. (4) The water-wet reservoir is favorable for adsorption and retention of polymer.

In the present studies, the main research methods for the mechanism of polymer adsorption and retention is core displacement experiment in laboratory. Based on the phenomena of core displacement experiment (injection pressure, polymer concentration in produced solution), the mechanism of polymer adsorption and retention in pore structure is indirectly understood. This method cannot directly observe the adsorption and retention process of the polymer, when it flows through the pores of the core, and it also requires a large amount of polymer and takes a long measurement time. In recent years, a novel technology, microfluidics, is used in the field of biomedicines. These methods drastically reduce sample volume (from litres to nanolitres) and measurement time (from several hours or days to 30 minutes or less) requirements, while maintaining or increasing accuracy offered by traditional methods. Perhaps, we can try to combine it with the traditional research methods of petroleum technology in the future, which will lead us to make a new understanding of some classical theories.

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