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[1]Haobin Shi,
Master's student, e-mail: 2842117353@qq.com
[1,2]*Hongbin Yang,
Associate Professor, *e-mail: hongbinyang@upc.edu.cn
[1]Xin Chen,
Master's student, e-mail: xin_baobei77@163.com
[1]Liang Peng,
Master's student, e-mail:1539552876@qq.com
[1]Shuhe Zhang,
Master's student, e-mail:1009383847@qq.com
[3]Wanli Kang,
Professor, e-mail: kangwanli@126.com
[4]Abdusamig Kadirov,
Professor, e-mail: abdusamig@rambler.ru

[1]School of Petroleum Engineering, China University of Petroleum (East China),
Qingdao, PR China
[2]Shandong Key Laboratory of Oil and Gas Field Chemistry, China University of Petroleum
(East China), Qingdao, PR China
[3]XinJiang Keli New Technology Development Co.Ltd, Karamay, PR China
[4]Department of Physical Chemistry, National University of Uzbekistan, Tashkent, Uzbekistan

A REVIEW ON ANTI-ADSORPTION BEHAVIORS OF PARTIALLY HYDROLYZED POLYACRYLAMIDE IN RESERVOIR FORMATIONS

Abstract

Polymer flooding is one of the key technologies for enhancing oil recovery. Partially Hydrolyzed Polyacrylamide (HPAM) is widely used due to its excellent viscosity-increasing properties. However, the adsorption and retention behavior of HPAM in reservoir porous media presents a dual effect: on one hand, it improves sweep efficiency by increasing flow resistance; on the other hand, it leads to a loss in effective polymer concentration and viscosity, reducing displacement efficiency and increasing costs. Therefore, a systematic understanding and control of HPAM adsorption behavior are crucial for improving the effectiveness of polymer flooding. This work systematically reviews seven main measurement methods for HPAM adsorption quantity, comparing their applicable conditions and limitations. It summarizes the key factors influencing HPAM adsorption and retention behavior from three aspects: polymer properties, rock mineral characteristics, and reservoir environmental conditions. Furthermore, it outlines chemical anti-adsorption methods, represented by competitive adsorption and nanofilm protection, along with their mechanisms. Finally, future research directions are proposed, focusing on building adsorption prediction models, deepening the understanding of adsorption mechanisms under multi-field coupling conditions, and developing novel functional polymers with anti-adsorption capabilities.

Keywords: partially hydrolyzed polyacrylamide, adsorption retention, factors influencing adsorption, anti-adsorption, enhanced oil recovery.

1. Introduction

In the process of Enhanced Oil Recovery (EOR), specifically in chemical flooding, polymer flooding has become a vital technique. Among the polymers used, Partially Hydrolyzed Polyacrylamide (HPAM) is extensively applied due to its excellent water solubility and thickening capability [1]. When high-molecular-weight polymers enter the formation, retention occurs through mechanisms including adsorption on mineral/rock surfaces, mechanical entrapment, and hydrodynamic retention, with adsorption being the primary mechanism. This widespread adsorption retention has both advantages and disadvantages. The beneficial aspect is that polymer adsorption and retention can plug large pore throats, thereby enlarging the sweep volume to some extent and consequently improving oil recovery [2]. Simultaneously, a higher retention amount leads to greater resistance factor and residual resistance factor. Studies show that a higher resistance factor enhances the polymer's mobility control capability, favoring the enlargement of the swept volume in the oil layer. A higher residual resistance factor is more conducive to increasing the displacement pressure and sweep volume during subsequent water flooding, thus achieving higher displacement efficiency. Additionally, adsorption retention increases the flow resistance of water molecules and polymer molecules in the aqueous phase, selectively reducing water phase permeability to achieve mobility control objectives, thereby expanding the sweep volume to a certain extent. Furthermore, the adsorbed film formed on the rock surface can prevent pore throat blockage caused by the migration of dispersed, mobile particles [3]. The detrimental aspects include the reduction of the effective polymer solution concentration due to adsorption retention, leading to decreased viscosity and weakened viscoelastic effects, which ultimately reduces the microscopic displacement efficiency and increases operational costs [4, 5]. Moreover, polymer adsorption and retention during flow in porous media can reduce permeability, and in severe cases, cause formation damage. Blockage by polymers and cross-linked polymers, in particular, can make it difficult for subsequent polymer solutions to enter formation pores, potentially leading to a significant decrease or even cessation of well production [6]. Furthermore, after years of development, various polymer-based profile control technologies have emerged, such as high-concentration polymer flooding, weak gel flooding, and pre-formed particle gel (PPG) technologies. These technologies aim to increase recoverable resources by plugging major flow channels. However, adsorbents and polymers may be adsorbed or retained during migration through porous media, affecting their gelation performance in areas far from the well-bore [7].

Although research on polymer adsorption is abundant, a systematic integration focusing on measurement methods, influencing factors, and reservoir anti-adsorption measures is currently lacking. Therefore, this work first systematically introduces the measurement methods for polymer adsorption, providing a comparative analysis of their advantages and disadvantages. Subsequently, it summarizes the factors influencing the adsorption and retention of polyacrylamide. Finally, it reviews several types of chemical anti-adsorption methods. The research outcomes can provide guidance for field applications concerning polymer concentration measurement, polymer molecular structure design, and concentration selection.

2. Measurement Methods for Polymer Adsorption Quantity

The adsorption quantity of a polymer is calculated based on the difference between the initial polymer concentration at the injection point and the concentration at the production end. The core of this calculation lies in measuring the polymer concentration in the produced fluid. Therefore, determining the polymer solution concentration is fundamental for analyzing adsorption issues in polymer flooding technology. The primary methods for quantifying HPAM concentration include turbidimetry, ultraviolet (UV) spectrophotometry, starch-cadmium iodide method, kinematic viscosity method, ultrafiltration membrane drying method, molecular size exclusion chromatography (SEC), and fluorescence spectrophotometry [5].

2.1 Turbidimetry

Turbidimetry is an analytical method that determines sample concentration or particle count by measuring the degree of light scattering by suspended particles in a liquid. Its principle involves the reaction of glacial acetic acid with sodium hypochlorite to generate Cl_2, which then reacts with HPAM to form insoluble chloramide, causing turbidity in the solution. Under certain conditions, the turbidity value exhibits a linear relationship with the mass concentration of HPAM. The turbidity of the test solution is measured using a turbidimeter or spectrophotometer, and the HPAM concentration is determined from a pre-established standard calibration curve [8].

The main advantages of turbidimetry are its speed, simplicity, and low cost. However, this method requires a relatively large sample volume and is susceptible to interference from heavy metal ions and anionic surfactants, limiting its application. Additionally, factors such as the molecular weight, degree of hydrolysis, and molecular aggregation state of HPAM can influence the results. Given these characteristics, this method is suitable for preliminary field screening, process monitoring, and rough estimation of polymer concentration loss [9].

2.2 UV Spectrophotometry

UV spectrophotometry is based on the ultraviolet absorption of polymers, whose main chains consist of acrylamide and acrylic acid units, at a wavelength of 202.2 nm. Within a concentration range of 10–250 mg/L, the absorbance (E) shows a good linear relationship with concentration. The absorbance of the test solution is measured using a spectrophotometer, and the polymer concentration is calculated by comparison with a standard curve of known concentrations.

This method is simple, rapid, non-toxic, low-cost, and allows for sample recovery, making it an ideal laboratory technique. However, UV spectrophotometry has low sensitivity and is not suitable for low-concentration polymer solutions. Furthermore, it performs poorly in terms of linearity and stability for samples prepared with produced water from oil wells, primarily because organic impurities in the wastewater also absorb UV light. Therefore, when using UV spectrophotometry to determine HPAM concentration, strict requirements must be placed on water quality. If the water contains substances that absorb light around 200 nm, this method should not be used. Consequently, it is only applicable in laboratory settings and not suitable for direct detection of polymer concentration in oilfield produced water [10].

2.3 Starch-Cadmium Iodide Method

The reaction mechanism of this method involves bromine reacting with amide groups to generate N-bromoamide, which hydrolyzes to form hypobromous acid. Excess bromine is reduced and removed using sodium formate. Upon adding the starch-cadmium iodide reagent, I^- is oxidized by hypobromous acid to I_2, which then forms I_3^- with I^-. I_3^- reacts with starch to form a blue starch-triiodide complex. The absorbance is subsequently measured using a UV spectrophotometer. A standard curve of concentration versus absorbance is plotted using a series of standard solutions with known concentrations. The accurate HPAM content in the test sample is then calculated based on its absorbance. The detection wavelength for the starch-cadmium iodide method ranges from 574 to 590 nm, with a buffer solution pH of 5.0. This colorimetric method offers high detection sensitivity and can accurately measure HPAM concentration in colored samples containing surfactants and dissolved crude oil. It is suitable for analyzing core effluent and large batches of routine samples [9].

2.4 Kinematic Viscosity Method

This method involves conducting simultaneous test and reference group experiments during static adsorption processes. A standard curve of reduced specific viscosity versus mass concentration is established using the reference group. The polymer concentration in the test group is then determined by measuring the solution viscosity and referring to the standard curve. This method controls the specific viscosity increment between 0.2 and 1.5, where the relationship between reduced specific viscosity and mass concentration is linear. The relative standard deviation (RSD) for precision is 0.61%, and for repeatability, it is 0.043%. The kinematic viscosity method features simple procedures, low cost, no need for chemical reagents, and applicability to complex systems containing polymer solutions for static adsorption concentration loss measurement. Its drawbacks include significant influences from molecular weight, degree of hydrolysis, pH, temperature, salinity, and shear history, leading to low measurement accuracy. This method is often used as a reference for polymer concentration detection, primarily for the preliminary determination of concentration loss in static adsorption [11].

2.5 Ultrafiltration Membrane Drying Method

This method primarily utilizes a Millipore tangential flow ultrafiltration system to ultrafilter and concentrate the test water sample. The sample is first filtered through a membrane package with pores small enough to allow only small molecules to pass, thereby retaining HPAM molecules with larger hydrodynamic radii. By repeatedly diluting and washing the concentrated test solution to purify the HPAM, followed by evaporation, drying, and weighing, the HPAM concentration can be accurately determined. This method is unaffected by variations in polymer molecular weight and degree of hydrolysis, allowing for accurate determination of polymer mass concentration in produced fluids with high precision. However, the procedure is relatively complex and requires ultrafiltration concentration materials, making it costly for many operators [9, 12].

2.6 Molecular Size Exclusion Chromatography

The Molecular Size Exclusion Chromatography (SEC) method is an integrated separation and detection analytical technique. Polymers are separated from small molecule impurities on a chromatographic column with specific pore sizes, and the absorption peak is measured using an ultraviolet (UV) detector. The HPAM concentration is determined based on the proportional relationship between concentration and peak height. Commonly used columns are surface-modified Gly-CPG with controlled pore sizes, on which HPAM adsorption is minimal. Using special eluent systems in standard gel chromatography columns can also eliminate HPAM adsorption. Small molecules in the test sample, such as petroleum sulfonates, crude oil, isopropanol, sodium chloride, and sodium hexametaphosphate, can be effectively separated by SEC without interfering with HPAM concentration measurement. Therefore, severely contaminated and complex samples, such as field-produced emulsions containing surfactants and colored samples containing dissolved crude oil, can be accurately measured using SEC. The analysis speed of the SEC method is moderate, typically processing 3□5 samples per hour. Factors affecting HPAM hydrodynamic volume, such as water salinity, divalent cations, and HPAM hydrolysis under high-temperature alkaline conditions, can influence this method, but they can be mitigated by selecting chromatographic columns with appropriate pore sizes. Additionally, when the HPAM molecular weight distribution is very broad, some molecules might enter the pore structure of the packing material, leading to peak tailing[13].

2.7 Fluorescence Spectrophotometry

This method utilizes the Hofmann rearrangement reaction to convert HPAM into amine derivatives. In the presence of phthalaldehyde and mercaptoethanol, amide derivatives are converted into compounds that emit strong light. Measurements using fluorescence spectrophotometry show a linear relationship within the concentration range of 0–6 mg/L, with an RSD of 5%. HPAM concentrations as low as 20 μg/L can be effectively detected. Interference occurs when concentrations of NaCl, $CaCl_2$, and $AlCl_3$ exceed 1×10^{-3} mol/L. The prominent feature of this method is its ability to detect trace amounts of HPAM, and it can be used for measuring anionic, cationic, and non-ionic PAMs. Since the rearrangement reaction proceeds relatively slowly, the measurement process is time-consuming. Thus, it is commonly used for concentration detection when sample quantities are limited [13].

Among the seven measurement methods listed above, the SEC method and the starch-cadmium iodide method exhibit fewer interfering factors and high accuracy, making them widely used in both laboratory research and field sample analysis in oilfields. The kinematic viscosity method is often employed as a reference method for polymer concentration detection, valued for its speed and simplicity in the preliminary determination of static adsorption concentration loss. Turbidimetry offers relatively high accuracy and fewer interfering factors, leading to its relatively widespread application in oilfields. UV spectrophotometry is only suitable for measuring HPAM concentration in pure systems. Produced fluids from field polymer flooding and compound flooding are complex in composition, generally have high salinity, and are often colored due to dissolved crude oil or emulsification. The SEC method, with its function of separating small molecules, is particularly suitable for analyzing such samples. The advantages and disadvantages of each method are summarized in Table 1 below.

Table 1 – Methods for Determining Polymer Adsorption Quantity [8–13]

Method Name	Advantages	Disadvantages	Applicability
Turbidimetry	Rapid, simple, low cost.	Susceptible to interference from heavy metal ions, anionic surfactants, molecular weight, and degree of hydrolysis.	Suitable for preliminary field screening, process monitoring, and rough estimation of polymer concentration loss.
UV Spectrophotometry	Simple, rapid, non-toxic, low cost, sample recovery possible.	Low sensitivity, not suitable for low-concentration solutions; requires high water quality, organics in produced water cause severe interference.	Ideal laboratory method, but only applicable to clean systems with known makeup water composition.
Starch-Cadmium Iodide Method	High sensitivity, strong resistance to interference.	Complex and time-consuming procedure.	Suitable for precise analysis of core effluent and large batches of routine samples.
Kinematic Viscosity Method	Simple operation, low cost, no chemical reagents needed, applicable to complex systems.	Highly influenced by MW, HD, pH, temperature, salinity, shear history; low precision.	Often used as a reference method for preliminary determination of static adsorption concentration loss.
Ultrafiltration Drying Method	High precision, unaffected by polymer MW and HD.	Complex operation, time-consuming, requires specialized ultrafiltration equipment, high cost.	Accurate determination of polymer mass concentration in produced fluids; suitable for high-precision requirements.
Size Exclusion Chromatography (SEC)	Integrated separation and detection, excellent anti-interference ability, can handle complex/s contaminated samples.	Moderate analysis speed; salinity, divalent cations can affect separation, requires column optimization.	Suitable for complex field samples.
Fluorescence Spectrophotometry	Extremely high sensitivity, very low detection limit (down to µg/L level), applicable to various ionic PAMs.	Rearrangement reaction is slow, measurement is time-consuming; high concentrations of inorganic salts ($>1x10^{-3}$ mol/L) cause interference.	Mainly used for trace polymer detection, suitable for scenarios with limited sample volume and low concentration.

3. Factors Influencing the Adsorption Retention Quantity of HPAM

The adsorption behavior of Partially Hydrolyzed Polyacrylamide (HPAM) is primarily controlled by three categories of factors: the polymer itself, rock mineral characteristics, and reservoir conditions. The intrinsic properties of HPAM include its molecular structure, molecular weight, degree of hydrolysis, and concentration. Rock mineral characteristics encompass mineral type, surface properties, surface charge, structure, and wettability. Reservoir conditions involve temperature, pressure, and the types and ionic strength of electrolytes in the liquid phase. These factors collectively influence the adsorption and retention of HPAM during its flow through the reservoir formation [4].

In recent years, significant attention has been paid to the factors influencing HPAM adsorption in formations, and extensive research has been conducted. However, a holistic understanding of its adsorption and retention behavior remains somewhat fragmented. Therefore, this review systematically collates and summarizes existing findings in this field.

3.1 Polymer Properties

During polymer flooding, factors such as polymer concentration, particle size, and dissolution rate can lead to polymer adsorption, loss, and retention within the formation [14].

Zhang et al. investigated the influence of HPAM concentration on its own adsorption retention in formations [15]. Their study indicated that within a certain concentration range, the adsorption quantity of HPAM increases with increasing solution concentration. Following this trend, once the concentration exceeds a critical value, the adsorption quantity increases abruptly; below this critical value, the relationship between adsorption quantity and solution concentration is less pronounced. If high molecular weight polymers adsorb onto the rock surface, numerous polymer chains come into contact with the rock. Although the adsorption amount per individual chain might be low, the adsorption of molecular aggregates is typically higher. Consequently, the adsorption isotherm of HPAM exhibits characteristics of strong adsorption: the adsorption density increases rapidly with concentration in the low-concentration region and can reach a plateau in the high-concentration region. The study also found that if the porous medium is first saturated by exposure to a dilute polymer solution, subsequent exposure to a higher HPAM concentration does not result in significant additional adsorption.

Yang Jiping et al. explored the relationship between the degree of hydrolysis and the adsorption quantity of HPAM on kaolinite and montmorillonite [1]. They discovered that the adsorption quantity of HPAM on both kaolinite and montmorillonite decreases with an increasing degree of hydrolysis, reaching a minimum at around 25–30% hydrolysis. Beyond this point, the adsorption quantity increases again with further increases in hydrolysis. Additionally, the amount of polymer adsorbed on montmorillonite was greater than on kaolinite. This is attributed to the significantly larger specific surface area of montmorillonite compared to kaolinite, leading to higher adsorption under the same conditions.

Hu Jingbang et al. studied the relationship between polymer adsorption retention and HPAM concentration within the range of 0–1500 mg/L [16]. They found that the dynamic adsorption retention amount increases with increasing HPAM concentration. The relationship between HPAM concentration and dynamic adsorption quantity can be approximately described by a straight line, with an average relative error of 5.8%, although the rate of increase is not substantial. This is because, at higher polymer concentrations, mechanical entrapment occurs more readily, increasing the number of molecules retained at trapping sites, thereby increasing the retention amount. In this scenario, the increase in adsorption amount itself is modest, so the overall increase in retention is determined by the entrapment amount.

3.2 Rock Mineral Characteristics

Rock mineral characteristics, including mineral type, surface properties, surface charge, structure, and wettability, are crucial factors influencing HPAM adsorption and retention behavior. The interfacial interaction mechanisms between different minerals and HPAM molecules vary significantly, directly determining the dynamic retention of the polymer in the formation and the resulting displacement efficiency. Therefore, studying the influence of mineral characteristics on adsorption behavior is of great importance.

Liu Xiao et al. investigated the adsorption of HPAM on different minerals [4]. Their results showed that the adsorption quantity of HPAM on minerals reaches saturation after a certain time, with no significant increase observed after 10 hours. The time required to reach equilibrium adsorption ranged from 20 to 70 hours, with clay minerals requiring longer times. The order of adsorption quantity on various solid materials was: gypsum > montmorillonite > kaolinite > chlorite > biotite > muscovite > dolomite > calcite > plagioclase > microcline > quartz. The adsorption quantity on gypsum could reach 0.36 mg/g.

Li Jun et al. studied the effect of initial concentration on HPAM adsorption on shale and sandstone [17]. They found that the adsorption quantity on rock surfaces increases with increasing

HPAM solution concentration. This is because a higher polymer concentration means more macromolecular chains are present in the solution, increasing the probability of contact with the rock surface, thus leading to more adsorption. Simultaneously, the adsorption quantity of HPAM on shale was significantly greater than on sandstone across different concentrations, with adsorption quantities ranging from 0.12 to 1.05 mg/g on shale and 0.06 to 0.51 mg/g on sandstone.

Li Yiqiang et al. observed that the presence of varying clay content in clean sand increases the adsorption quantity [3]. Under reservoir conditions at 45°C, the adsorption of HPAM in oil-free quartz sand increased with concentration, exhibiting an "S"-shaped adsorption isotherm. The maximum adsorption occurred around a solution concentration of 1200 mg/L. The adsorption quantity was only 0.953 mg/g in quartz sand without kaolinite but increased to 1.725 mg/g when the kaolinite content reached 5%. Furthermore, the presence of kaolinite in the porous medium significantly increased HPAM retention due to its specific lattice structure. When the kaolinite content increased from 2% to 5%, the retention amount increased from 0.584 mg/g to 0.794 mg/g. Additionally, under identical temperature and kaolinite content conditions, the adsorption amount of HPAM in quartz sand was far greater than the retention amount in the porous medium.

3.3 Reservoir Conditions

Reservoir conditions include temperature, pressure, wettability, and the types and ionic strength of electrolytes in the liquid phase. A deep understanding of the multi-scale regulatory role of reservoir conditions on adsorption behavior is essential for studying polymer adsorption and retention in oil reservoirs.

YANG L, et al. indicated that the adsorption of HPAM on reservoir rocks largely depends on the wettability of the rock surface [15]. The adsorption amount on water-wet models was much higher than on oil-wet models.

Hu Jingbang et al. investigated the effect of salinity (2000–10000 μg/mL) on the dynamic adsorption retention of HPAM in porous media [16]. They found that within this salinity range, the dynamic adsorption quantity initially decreased rapidly with increasing salinity and then tended to stabilize. The study also noted that the saturated dynamic retention quantity is the sum of the dynamic adsorption quantity and the amount of polymer retained in the accessible pore volume of the core. While increased salinity reduces dynamic adsorption, the concomitant shrinkage of HPAM molecular size increases the accessible pore volume of the core, leading to an increase in the amount of polymer retained therein. Consequently, the saturated retention quantity changes more gradually with salinity. Furthermore, permeability also significantly affects HPAM adsorption retention: lower permeability leads to greater dynamic adsorption quantity. Under constant injection rate, the retention mechanisms are primarily adsorption and mechanical entrapment. Low-permeability cores have smaller pore throat radii, resulting in stronger mechanical entrapment. Although their smaller accessible pore volume and adsorption surface area lead to lower pure adsorption, the total dynamic adsorption quantity remains high. As permeability increases, the inaccessible pore volume decreases and the adsorption surface area increases, potentially increasing the adsorption component. However, due to the enlargement of pore throat radii, mechanical entrapment decreases significantly, causing the total dynamic adsorption quantity to drop rapidly.

3.4 Chemical Additives

Besides polymer properties, rock mineral characteristics, and reservoir conditions, chemical additives represent another important factor influencing the adsorption and retention behavior of HPAM.

Li Yiqiang et al. pointed out that the presence of surfactants can reduce the retention of HPAM in porous media. As surfactant concentration increases, HPAM retention decreases [5]. This is attributed to competitive adsorption between the surfactant and polymer on the rock surface.

Zhou Yangfan confirmed that the introduction of surfactants suppresses the adsorption of HPAM on rock surfaces [21]. Their experiments, conducted at 45°C using distilled water to prepare HPAM-surfactant mixed solutions, showed that the adsorption isotherm of HPAM on oil-free formation sand was "L"-shaped, and the equilibrium adsorption quantity in the composite system was significantly lower than in the polymer-only system. This phenomenon stems from the competitive adsorption between the polymer and surfactant, thereby reducing the adsorption amount of HPAM.

4. Anti-adsorption Methods During Polymer Flooding

To efficiently utilize the oil displacement effect of polymers and reduce adsorption losses, the addition of chemical additives into the formation for anti-adsorption purposes is a common field practice. Based on literature review, three primary types of chemical anti-adsorption methods are currently employed. The first method involves using silane coupling agents as anti-adsorbents to modify the sandstone surface into a hydrophobic one, thereby reducing polymer adsorption. The second method utilizes chemicals like surfactants, which readily adsorb onto reservoir rock surfaces, to compete with the polymer for adsorption sites, thus achieving a reduction in polymer adsorption. The final method employs nano-film agents, which utilize electrostatic interactions between ions to deposit and reach saturation on the reservoir surface, forming a monomolecular film that alters the adsorption properties of the reservoir rock and reduces polymer adsorption.

The mechanism by which silane coupling agents reduce adsorption is as follows: After injection, the coupling agent first hydrolyzes to generate hydroxyl compounds. These hydroxyl compounds undergo etherification reactions with the silanol groups on the sandstone surface, forming Si-O-S groups. This reaction exposes the hydrophobic chains of the anti-adsorbent, thereby modifying the sandstone surface into a hydrophobic one, which in turn reduces the adsorption amount of the polymer.

Fu Meilong et al. addressed the issue of severe production decline in Henan Oilfield caused by polymer blockage in injection wells during polymer flooding [18]. They developed a silane coupling agent anti-adsorbent, with n-octyltriethoxysilane as the main agent, and acidic catalysts and alcoholic co-solvents as additives. The study primarily analyzed the effects of anti-adsorbent mass fraction, salinity, injected volume of anti-adsorbent, treatment duration, and injection mode on the polymer anti-adsorption rate. The results showed that the optimal injection mass fraction for the developed silane coupling agent anti-adsorbent was 0.5%. Within the salinity range of 1500–10000 mg/L, salinity had little effect on the anti-adsorption rate of this system. Under conditions of pH=3, temperature 80°C, core permeability 408.6 mD, salinity 2500 mg/L, anti-adsorbent mass fraction 0.5%, treatment time 12 hours, and polymer injection rate 0.5 mL/min, a larger injected slug volume resulted in lower dynamic adsorption of polymer on the rock surface and a higher polymer anti-adsorption rate. Considering both treatment effectiveness and economic cost, the optimal injected slug volume for the anti-adsorbent was determined to be 0.6 PV. When the treatment time exceeded 12 hours, the anti-adsorption rate was greater than 70%. Under conditions of pH=3, temperature 80°C, core permeability 286.12 mD (Core 5), salinity 2500 mg/L, anti-adsorbent slug volume 0.6 PV, anti-adsorbent mass fraction 0.5%, polymer injection rate 0.5 mL/min, and treatment time 12 hours, the optimal injection sequence was: displacing fluid + 0.6 PV anti-adsorbent slug + 1 PV cleaning agent.

Gao Shenling et al. studied the effects of permeability, temperature, pH, and salinity on the anti-adsorption rate of the silane coupling agent [19]. They found that when permeability was not less than 196 mD, the silane coupling agent maintained a high anti-adsorption rate for the polymer, staying above 70%. Higher temperatures led to lower dynamic adsorption of polymer on the rock surface. The increase in anti-adsorption rate diminished after 80°C, but the anti-adsorption rate remained above 70%. Higher fluid pH values resulted in lower anti-adsorption rates for the treatment agent. The optimal pH range for this anti-adsorbent system to reduce polymer adsorption was between 3 and 5, with the lowest anti-adsorption rate observed at pH=7. Due to the good salt tolerance of this anti-adsorbent system, different salinities had little effect on its anti-adsorption rate, which remained above 70%. A higher mass fraction of the anti-adsorbent system led to lower dynamic adsorption of polymer on the rock surface and a higher polymer anti-adsorption rate. When the mass fraction was not less than 0.5%, the anti-adsorption rate gradually stabilized above 70%.

Surfactants can compete with polymers for adsorption sites. Based on this principle, they can be used to suppress and reduce the adsorption retention of polymers in formation pores.

Guo Yongjun et al. examined the adsorption behavior of a water-soluble hydrophobically associating polymer (acrylamide/sodium acrylate/octadecyldimethyl allyl ammonium chloride copolymer) at the kaolinite/water interface [20]. They reported that the adsorption amount of the copolymer on kaolinite increased with equilibrium concentration, exhibiting characteristics of multilayer adsorption. Increasing the concentration of SDBS (sodium dodecyl benzene sulfonate) in the solution led to a monotonic decrease in the copolymer adsorption amount on kaolinite. Zhou Yangfan conducted experiments on the effect of surfactants on HPAM adsorption [21]. The results showed that under experimental conditions of 45°C, using distilled water to prepare polymer-surfactant mixed solutions, the adsorption isotherm on oil-free formation sand after reaching equilibrium was "L"-shaped. Due to competitive adsorption between the polymer and surfactant components, the adsorption amount of HPAM under the binary composite condition was significantly lower than in the single-component condition without surfactant. This aligns with the general rule that in multi-solute mixed solutions, the adsorption amount of each solute is less than that in its single-component solution. Therefore, the polymer-surfactant binary composite flooding method can be employed to reduce polymer adsorption issues in the formation.

Nano-film agents, after injection into the formation, utilize electrostatic interactions between ions to deposit and reach saturation on the reservoir surface, forming a monomolecular film that alters the adsorption properties of the reservoir rock. Because the film is extremely thin, it does not affect the permeability of the reservoir. When the polymer solution flows, the rock surface covered with the molecular deposition film makes polymer adsorption less likely, reducing flow resistance and thus preventing formation blockage caused by polymer adsorption and retention.

Xu Guomin et al. proposed a nano-film anti-adsorption technology [22]. Their research results indicated that after injection into the formation, the nano-film firmly adsorbs onto the rock surface through electrostatic interactions, forming a nano-scale ultra-thin film. This film combines strongly with the substrate, is resistant to flushing, and plays a significant role in reservoir protection. When polymer solutions flow over rock surfaces with this molecular deposition film, adsorption is less likely to occur, flow resistance is reduced, and thus formation blockage due to polymer adsorption and retention can be prevented.

5. Conclusions and Perspective

This work has systematically reviewed the research methods, influencing factors, and anti-adsorption techniques related to the adsorption behavior of Partially Hydrolyzed Polyacrylamide (HPAM) in reservoir formations. Although existing research has yielded substantial results, further efforts are required to achieve more efficient and economical polymer flooding technology. Based on the content of this review and current development trends, the following future research directions for polymer adsorption studies are proposed.

(1) Digitization of Adsorption Retention and Construction of Predictive Models. With the rapid development of artificial intelligence and big data, it has become feasible to construct predictive models for polymer loss based on factors such as polymer properties, rock mineral characteristics, and reservoir conditions. Utilizing machine learning algorithms to train on vast amounts of experimental and field data can create intelligent tools capable of quickly and accurately predicting polymer adsorption quantity under specific reservoir conditions. This will significantly optimize the design of flooding schemes and promote the intelligent development of polymer flooding technology.

(2) Research on Adsorption Mechanisms under Multi-Physics-Chemical Field Coupling. Current adsorption studies are often conducted under single-variable or idealized conditions. However, actual reservoirs are complex systems characterized by high temperature, high salinity, strong heterogeneity, and the presence of residual oil. Therefore, future research needs to strengthen the investigation of the dynamic adsorption and retention mechanisms of polymer molecules under multi-field coupling (e.g., temperature field, chemical field, stress field) and within micro-nano scale pores. Utilizing technologies such as micro-visualization models and molecular dynamics simulations to reveal the adsorption retention process at the pore scale will provide a more solid theoretical foundation for studying polymer adsorption behavior.

(3) Precision Design of Novel Functional Polymers with Anti-adsorption Properties. Future efforts should focus on precision design at the molecular level, such as developing self-responsive polymers that can adapt their configuration based on the formation environment. Concurrently, bio-based polymers or nano-composite polymers, owing to their unique environmental friendliness and high stability, also represent promising directions for improving oil displacement efficiency.

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[1]Хаобин Ши,
магистрант, e-mail: 2842117353@qq.com
[1,2]*Хунбин Ян,
доцент, *e-mail: hongbinyang@upc.edu.cn
[1]Син Чэнь,
магистрант, e-mail: xin_baobei77@163.com
[1]Лян Пэн,
магистрант, e-mail: 1539552876@qq.com
[1]Шухэ Чжан,
магистрант, e-mail: 1009383847@qq.com
[3]Ванли Кан,
профессор, e-mail: kangwanli@126.com
[4]Абдусамиг Қадыров,
профессор, e-mail: abdusamig@rambler.ru

[1]Мұнай инженериясы мектебі, Қытай мұнай университеті (Шығыс Қытай),
Циндао қ., ҚХР
[2]Шаньдун провинциясының мұнай және газ кен орындарының химиясы жөніндегі негізгі
зертханасы, Қытай мұнай университеті (Шығыс Қытай), Циндао қ., ҚХР
[3]XinJiang Keli New Technology Development Co. Ltd, Қарамай қ., ҚХР
[4]Физикалық химия кафедрасы, Өзбекстан ұлттық университеті,
Ташкент қ., Өзбекстан

ҚАБАТ ЖАҒДАЙЛАРЫНДАҒЫ ЖАРТЫЛАЙ ГИДРОЛИЗДЕНГЕН ПОЛИАКРИЛАМИДТІҢ АНТИАДСОРБЦИЯЛЫҚ ҚАСИЕТТЕРІНЕ ШОЛУ

Аңдатпа

Полимерлі айдау – мұнай өндіруді арттырудың негізгі технологияларының бірі. Жартылай гидролизденген полиакриламид (HPAM) жоғары тұтқырлық түзуші қасиеттеріне байланысты кеңінен қолданылады. Алайда HPAM-ның қабаттың кеуекті ортасында адсорбцияланып, ұсталып қалуы екі түрлі әсер туындатады: бір жағынан, фильтрацияға кедергіні арттырып, қамту аймағын кеңейтеді; екінші жағынан, ерітіндідегі тиімді полимер концентрациясы мен тұтқырлығын төмендетіп, мұнай ығыстыру тиімділігін азайтады және технологиялық шығындарды көбейтеді. Осыған байланысты HPAM адсорбциясын терең түсіну және оны бақылау полимерлі айдаудың нәтижелілігін арттырудың маңызды шарты саналады. Бұл шолуда HPAM адсорбция мөлшерін анықтаудың жеті негізгі әдісі жүйеленіп, олардың қолдану ауқымы мен шектеулері салыстырмалы талданады. Сонымен қатар адсорбцияға әсер ететін басты факторлар – полимердің молекулалық сипаттамалары, жыныстың минералдық құрамы және қабат жағдайлары бойынша ғылыми қорытындылар сараланады. Химиялық антиадсорбциялық тәсілдер – бәсекелі адсорбция және нанопленкалық қорғаныс – олардың әрекет ету механизмдерімен бірге сипатталады. Сонымен қатар болашақ зерттеу бағыттары ұсынылады: адсорбцияны болжауға арналған модельдерді жетілдіру, көп өрісті әсерлер жағдайындағы адсорбция механизмдерін терең зерделеу және антиадсорбциялық қасиеттері жақсартылған жаңа функционалды полимерлерді әзірлеу.

Тірек сөздер: жартылай гидролизденген полиакриламид, адсорбция және ұсталып қалу, адсорбцияға әсер ететін факторлар, антиадсорбция, мұнай өндіруді арттыру.

[1]Хаобин Ши,
магистрант, e-mail: 2842117353@qq.com
[1,2]*Хунбин Ян,
доцент, *e-mail: hongbinyang@upc.edu.cn
[1]Син Чэнь,
магистрант, e-mail: xin_baobei77@163.com
[1]Лян Пэн,
магистрант, e-mail: 1539552876@qq.com
[1]Шухэ Чжан,
магистрант, e-mail: 1009383847@qq.com
[3]Ванли Кан,
профессор, e-mail: kangwanli@126.com
[4]Кадыров,
профессор, e-mail: abdusamig@rambler.ru

[1]Школа нефтяной инженерии, Китайский университет нефти (Восточный Китай),
г. Циндао, КНР
[2]Шаньдунская ключевая лаборатория химии нефтегазовых месторождений,
Китайский университет нефти (Восточный Китай), г. Циндао, КНР
[3]XinJiang Keli New Technology Development Co. Ltd, г. Карамай, КНР
[4]Кафедра физической химии, Национальный университет Узбекистана,
г. Ташкент, Узбекистан

ОБЗОР АНТИАДСОРБЦИОННЫХ СВОЙСТВ ЧАСТИЧНО ГИДРОЛИЗОВАННОГО ПОЛИАКРИЛАМИДА В ПЛАСТОВЫХ УСЛОВИЯХ

Аннотация

Полимерное заводнение является одной из ключевых технологий повышения нефтеотдачи. Частично гидролизованный полиакриламид (HPAM) широко используется благодаря своим превосходным вязкоувеличивающим свойствам. Однако процессы адсорбции и удерживания HPAM в поровом пространстве коллектора имеют двойственный эффект: с одной стороны, они повышают охват вытеснением за счет увеличения сопротивления фильтрации, с другой – приводят к снижению эффективной концентрации и вязкости полимера, уменьшают эффективность вытеснения и повышают затраты. Поэтому систематическое понимание и контроль адсорбционного поведения HPAM имеют решающее значение для повышения эффективности полимерного заводнения. В данной работе систематически рассмотрены семь основных методов измерения количества адсорбции HPAM, проведено сравнение их применимости и ограничений. Обобщены ключевые факторы, влияющие на адсорбцию и удерживание HPAM, с точки зрения свойств полимера, минералогических характеристик породы и условий пластовой среды. Кроме того, рассмотрены химические методы предотвращения адсорбции, такие как конкурентная адсорбция и нанопленочная защита, и раскрыты их механизмы. Наконец, предложены будущие направления исследований, включая создание моделей предсказания адсорбции, углубление понимания механизмов адсорбции при многополевой сопряженности и разработку новых функциональных полимеров с антиадсорбционными свойствами.

Ключевые слова: частично гидролизованный полиакриламид, адсорбция и удерживание, факторы, влияющие на адсорбцию, антиадсорбция, повышение нефтеотдачи.

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