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Preparation and characterization of polymer gel microspheres assembled layer by layer for profile control and water shutoff

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A new temporary plugging agent was developed to solve the problem of insufficient plugging performance of existing gel profile control and water shutoff. The organic material with temperature sensitivity and phase change function is assembled on the surface of the matrix material with high stability and good plugging performance by multi-layer assembly technology, and the composite gel profile control agent with multi-level structure is prepared. Research shows that the prepared profile control agent has a certain salt tolerance, and the inhibitory effect of $CaCl_2$ is greater than that of NaCl. When the $C_{25}H_{52}$ content is 3.6%, the multi-layer assembled profile control agent prepared by it has the best water absorption performance. When the temperature is 60 °C, the multi-layer assembled paraffin profile control agent prepared has the best water absorption effect.

Keywords: Composite gel profile control agent, multi-layer assembly, polydopamine, paraffin.

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INTRODUCTION

Due to the complex situation of oil reservoirs in our country, the burial depth of crude oil reservoirs has gradually deepened, and the reservoir conditions have become more complex. Currently, commonly used profile control agents have problems such as low-pressure strength, poor temperature and salt resistance, and short profile control time, which seriously limit the production efficiency of oil fields[1–4]. To adapt to complex formation conditions, it is urgent to develop a profile control agent with good profile control and water plugging effect and strong environmental adaptability. Therefore, the profile control agent is required to have temperature controllability, and has no plugging effect when the temperature is low to facilitate the transportation of the profile control agent. In the target area with high temperature, the profile control agent will absorb water and expand the plugging pores. In addition, the profile control agent is required to have a certain strength. After the pressure difference reaches a certain value, the profile control agent will not be broken, and only for elastic deformation, the profile control agent will move towards deeper pores in the formation to achieve the best plugging effect[5–7]. Due to the high temperature and high salinity in deep formations, profile control agents have certain temperature and salt resistance. In recent years, the development of multi-layer assembly technology can effectively solve the problems of profile control agents. The use of template layer by layer assembly technology[8–10] combined with the high compressive strength, good dispersibility, and temperature resistance of inorganic materials and the strong swelling and deformation ability and stable properties of organic materials to synthesize a new profile control agent with strong environmental adaptability and good temperature and pressure resistance has become a research focus and hotspot.

At the end of the 20th century, foreign countries innovatively developed a gel profile control agent[11]. This profile control agent has high water absorption expansibility and time delay, and is named “Bright Water”. Li et al.[12] crosslinked various types of acrylamide with various ions in different proportions at high temperatures to obtain a high-temperature-resistant temporary plugging agent system. Guy et al.[13] developed a gel profile control agent with good stability, no harm to the environment, and adjustable size. The profile control agent is less affected by the environment. It not only has good migration characteristics in the reservoir formation, but also plays a role in water plugging and profile control in the oilfield, and can be adapted to the formation with poor environmental conditions. Zhu et al.[14] synthesized a series of reversible gel polymers by aqueous solution polymerization, and tested the effects of polymer amount, NaCl concentration, and shear rate on polymer solution. The results showed that temperature-sensitive gel can be used as a temporary water plugging agent to improve oil recovery. Du et al.[15] elaborated on the development history of RAM-type profile control agents, studied the basic theory and analyzed the influence of various factors on the experiment. At present, water shutoff materials are developing towards the direction of nano multi-layer composite. Through multi-layer assembly technology, a composite gel temporary plugging agent is synthesized. Through the control of different materials and proportions, a temporary plugging agent with excellent water shutoff effect and environmental adaptability is explored and developed. This research and development is of great significance to the development of oil exploration and development in China.

Dopamine is a biological neurotransmitter that can form a polydopamine thin layer covering the surface of the substrate material after undergoing oxidative cross--linking reaction under aqueous solution conditions. This can ensure the stability of the substrate material during the transportation process in the formation, and prevent it from swelling and blocking pores due to water absorption. It has excellent transportation characteristics. At the same time, research has shown that modifying hy-

drophobic groups on polydopamine composite thin layers can improve the sweep efficiency of temporary plugging agents in water plugging and oil recovery processes. Because paraffin has the characteristics of low-temperature hydrophobic and high-temperature ablation[16], decoration of paraffin on the surface of polydopamine composite thin layer can also further improve the delayed swelling effect of composite gel temporary plugging agent, and solve the problems of poor transportation performance, pressure resistance and temperature resistance of traditional water plugging gel. In this paper, the effects of temperature, salinity, and time on the water absorption of composite gel were studied under the conditions of monolayer assembly of polydopamine composite thin layer and multilayer assembly of paraffin.

EXPERIMENTS AND TESTING

To improve the plugging effect of composite gel temporary plugging agent, composite gel temporary plugging agent is synthesized through nanocomposite technology, and then smart materials with thermal response and infiltration transformation are assembled on its surface to prepare polymer composite gel with multiple functions. As dopamine undergoes oxidative cross-linking reaction in aqueous solution, it will attach to the surface of solid materials to form a polydopamine composite thin layer[17–18], which can be used for the initial assembly of composite gel to improve the transportation performance of matrix materials.

Paraffin ($C_{25}H_{52}$) has the characteristics of low-temperature water delivery and high-temperature ablation. Reassembling $C_{25}H_{52}$ on the surface of the polydopamine composite thin layer can not only hydrophobic modify the composite gel, improve its transport capacity in the core, but also adapt to complex formation conditions. When the paraffin is well coated on the surface of the formation, it is easy to transport the temporary plugging agent of the composite gel. When entering the deep layer of the formation, the paraffin will be dissolved due to the temperature rise, which is convenient for the temporary plugging agent of the composite gel to be successfully gelled (Fig. 1).

Experimental Materials

The chemical reagents and instruments required for this experiment are shown in Table 1.

Synthesis of composite sealing agent

Using nanocomposite technology[20], composite gel temporary plugging agent was prepared with acrylamide, acrylic acid, and montmorillonite as the main raw materials.

First, the acrylic acid aqueous solution with neutralization degree of 80% was obtained by neutralization reaction of 5.4 g acrylic acid, 15 mL distilled water, and 1.8 g sodium hydroxide. Then, 5.3 g acrylamide, 7 g carboxymethyl starch sodium, 10g bone glue, 0.46 g sulfonated asphalt, montmorillonite, 0.1 g sodium nitrate, and 0.8 g potassium persulfate were added to

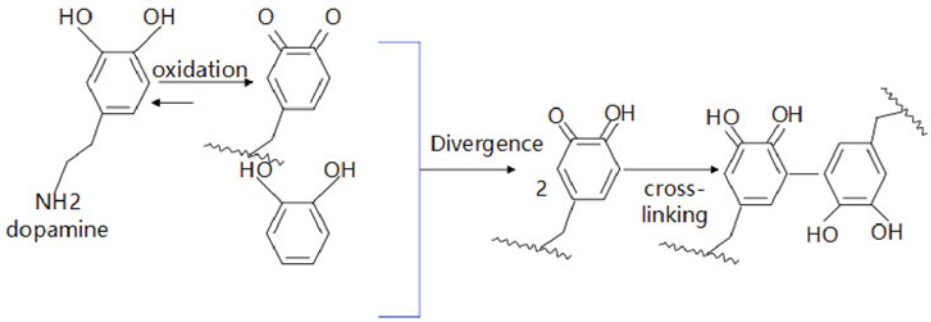

Figure 1. Crosslinking process of dopamine in aqueous solution

Table 1. Chemical reagents required for the experiment

Raw material name	Specifications	Manufacturer
Cyclohexane	Pure analysis	Tianjin Fuyu Fine Chemical Co., Ltd
Anhydrous ethanol	Pure analysis	Anhui Ante Food Co., Ltd
Acrylamide	Pure analysis	Tianjin Guangfu Institute of Fine Chemicals
Acrylic acid	Pure analysis	Tianjin Damao Chemical Reagent Factory
Sodium hydroxide	Pure analysis	Tianjin New Fine Chemical Industry Development Center
Aluminum nitrate	Pure analysis	Tianjin BASF Chemical Co., Ltd
Potassium persulfate	Pure analysis	Tianjin Employee Chemical Reagent Co., Ltd
Tetrahydrofuran	Pure analysis	Tianjin DeEn Chemical Reagent Co., Ltd
Liquid paraffin	Pure analysis	Shanghai Yongsheng Reagent Factory
Sodium chloride	Pure analysis	Jining Baiyi Chemical Co., Ltd
Calcium chloride	Pure analysis	Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd
Deionized water	–	Self-control
Organic montmorillonite	Industrial products	Beijing Lianke Nanoplastic Co., Ltd
Sodium carboxymethyl starch	Industrial products	Beijing Lianke Nanoplastic Co., Ltd
Bone glue	Industrial products	Beijing Lianke Nanoplastic Co., Ltd
Sulfonated asphalt	Industrial products	Beijing Lianke Nanoplastic Co., Ltd
Dodecanol	Pure analysis	Tianjin Fuchen Chemical Reagent Factory
Hexadecyl methyl ammonium bromide	Pure analysis	Tianjin Fuchen Chemical Reagent Factory
Paraffin wax	Industrial grade	Shanghai Hualing Rehabilitation Machinery Factory

prepare the prefabrication solution. The prefabrication solution was poured into the mold to raise the temperature by 90 °C to obtain blocky gel, and then the first assembly was carried out in dopamine solution to form a polydobutamine composite layer. After drying, the prefabrication solution was placed in polycaprolactone and Polycaprolactone composite gel temporary plugging agent and paraffin composite gel temporary plugging agent were prepared by secondary assembly in paraffin solution (Fig.2).

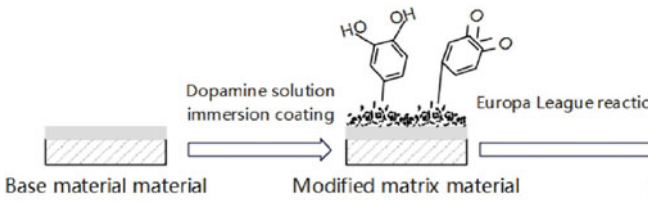

Figure 2. Surface process of dopamine-coated modified materials

Performance Testing

Infrared testing

The prepared sample was fully swollen, filtered, and dried in distilled water, and the infrared spectrum curve of the sample was tested using an FTIR-650 spectrometer (resolution 1.5 cm^{-1}, spectral range 4000–400 cm^{-1}).

Strength testing

Carry out the strength test and breakthrough pressure test respectively, take many equal portions of samples of temporary plugging agent of polycaprolactone composite gel and paraffin composite gel, spread them evenly in the crushing chamber of the press, apply pressure to the samples to measure the breaking rate of samples under different pressure conditions, and judge their compressive strength according to the size of broken particles. Put several equal portions of temporary plugging agent samples of polycaprolactone composite gel and paraffin composite gel into the pressure test tube, simulate the plugging formation state through the flow tester, and measure the strength performance of the plugging agent.

Water absorption rate test

Take several samples of temporary plugging agent of polycaprolactone composite gel and paraffin composite gel and weigh them as M_0. Put the sample into the waterproof bag and seal the mouth of the bag and weigh it as M_1. Put the beaker into the water bath pan and add 100 mL physiological saline. Set the temperature of the water bath pan as the temperature of the measured stratum. Put the sealed bag containing the sample into the beaker. Measure the weight of the meter after taking out the sealed bag and draining the water every other period of time until the weight of the meter is M_2 until the suction balance.

Aging time and viscosity testing

Accurately weigh 0.3 g of the sample and place it in 100 mL of physiological saline at a temperature of 60 °C. When sealing the device, the sample naturally dissolves. Record the time required for complete ablation of the sample as the aging time, and measure the viscosity of the dissolved solution using an SBN-1 viscometer.

RESULTS AND DISCUSSION

Infrared test results

The samples of polycaprolactone composite gel temporary plugging agent and paraffin composite gel temporary plugging agent were analyzed respectively, and the morphology of each wave peak and trough was analyzed through the prepared FTIR to verify the sample state.

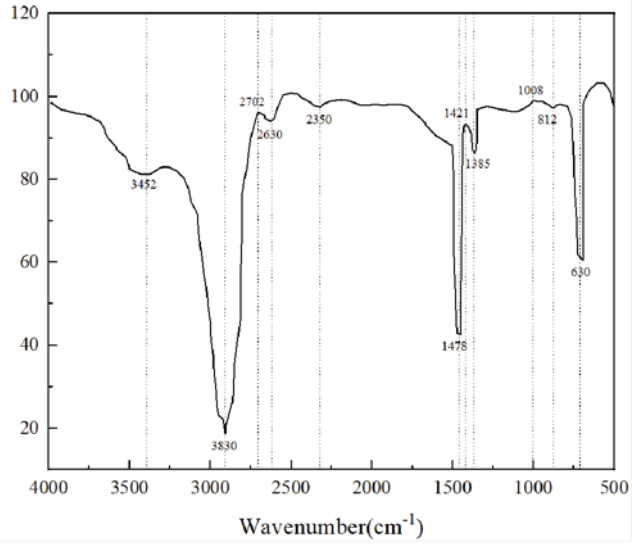

Figure 3. Infrared Spectra of Paraffin Compound gel Temporary Plugging Agent

Figure 3 shows the stretching vibration of water N-H and O-H absorbed by the temporary plugging agent at 3452 cm^{-1}. 3830 cm^{-1} represents the C-H stretching vibration of CH_2 and CH. 2702 cm^{-1} represents the stretching vibration of the O-H bond of the associative COOH. 2630 cm^{-1} represents the C=O stretching vibration in $CONH_2$. 2350 cm^{-1} represents the stretching vibration of C-O in O=C-O. 1478 cm^{-1} represents the bending vibration of O-H and N-H. 1421 cm^{-1} represents the stretching vibration of C-O in C-O-C. 1385cm^{-1} represents the stretching vibration of C-O in COH. 1008 cm^{-1} represents the C-O stretching vibration in C-O-C. 812 cm^{-1} represents the bending vibration of C=C. 630 cm^{-1} represents the oscillation of O-H in H_2O. Therefore, it is confirmed that paraffin wax has been successfully assembled and coated on the surface of the polydopamine composite thin layer of the matrix material.

Strength Performance

The surface of the samples was tested with only a thin layer of polydopamine composite coating and multiple layers of assembled paraffin wax for comparison. The results of the fragmentation rate and breakthrough pressure tests are shown in Figure 4.

Water absorption performance

Measure the influence of the amount of paraffin used to modify only the polydopamine composite thin layer and multi-layer assembly on the water absorption of the composite temporary plugging agent. Because the formation temperature and mineralized substances

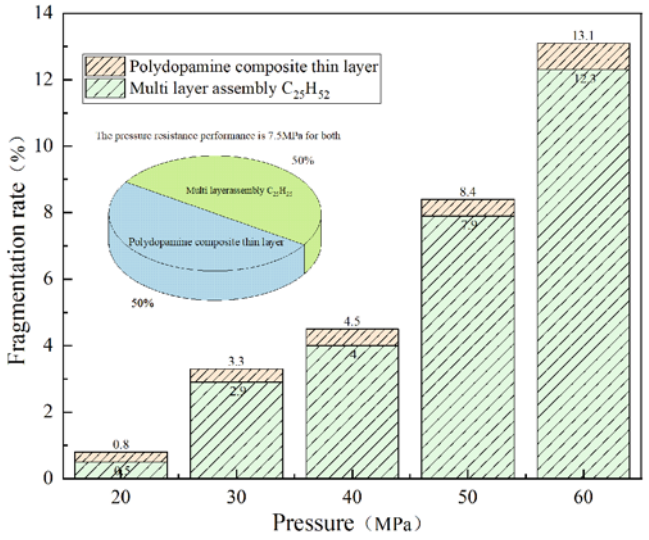

Figure 4. Results of Crushing Rate and Breakthrough Pressure Test

have a great influence on the temporary plugging agent, test the relationship between the influence of different temperatures and salinity on the water absorption of the composite gel. The test results are shown in Figure 5.

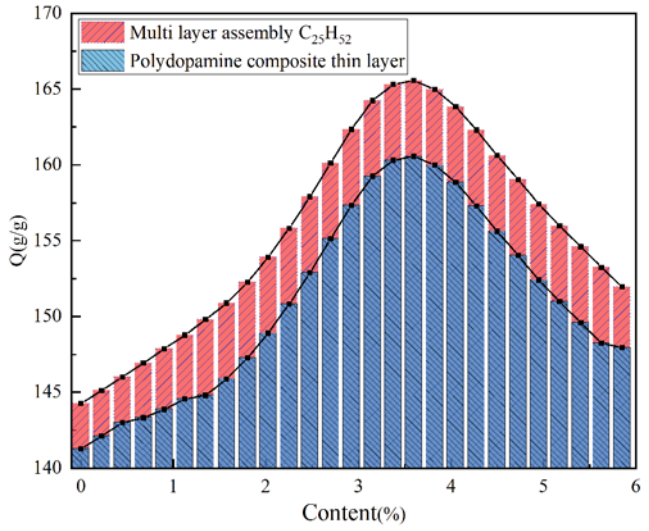

Figure 5. Relationship between Content and Water Absorption Rate (Q)

It can be seen from the analysis of Figure 5 that the water absorption ratio of the paraffin composite gel temporary plugging agent increases first and then decreases with the increase of the content.

For the paraffin composite gel temporary plugging agent, when the content of $C_{25}H_{52}$ is less than 3.6%, the paraffin is just coated, so the water absorption performance is weak. With the increase of the content of $C_{25}H_{52}$, the water absorption performance gradually increases. When the content of $C_{25}H_{52}$ is more than 3.6%, the breaking rate of the temporary plugging agent gradually increases, and the effective coating decreases, so the water absorption gradually decreases.

Figure 6 shows the relationship curve between water absorption performance of composite gel temporary plugging agent and temperature. Analysis of Figure 3–4 shows that for paraffin composite gel temporary plugging agent, when the temperature reaches 35 °C, the paraffin

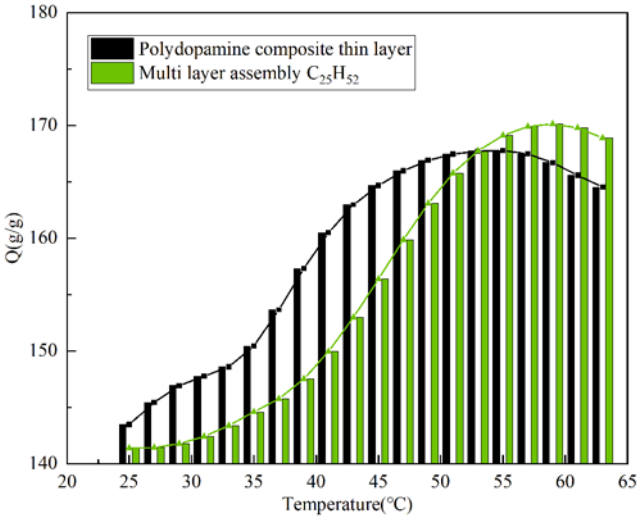

Figure 6. Relationship curve of water absorption performance with temperature change

film begins to dissolve, so the water absorption rate increases rapidly.

When the temperature reaches 53 °C, the matrix material begins to dissolve, and the water absorption rate decreases. Therefore, the water absorption ratio of paraffin composite gel temporary plugging agent is optimal at 53 °C.

It can be seen from the analysis of Figure 7 that compared with the polydopamine composite thin layer, the salt resistance of the multilayer assembly paraffin is

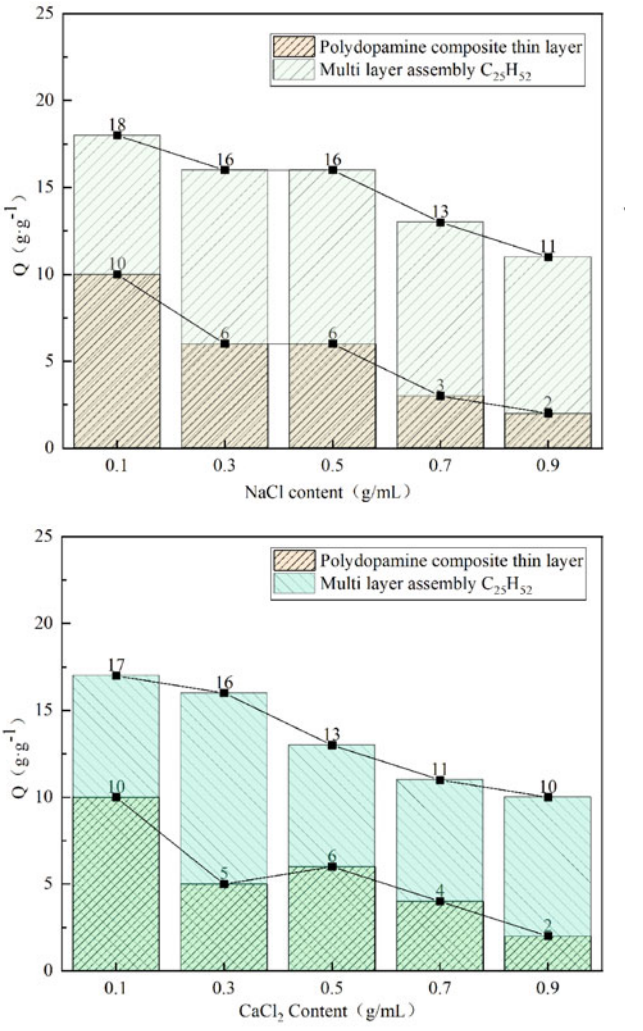

Figure 7. Comparison test of salt resistance performance

significantly improved. With the increase of NaCl content, the water absorption of the multilayer assembly paraffin gradually increases.

For $CaCl_2$, the water absorption gradually decreases with the increase in content, and the water absorption of the multilayer assembly paraffin decreases more rapidly. Therefore, the content of mineralized matter has a greater impact on the swelling performance of the composite gel, and $CaCl_2$ has a greater inhibitory effect.

Aging time and viscosity performance

From the analysis of Figure 8, it can be seen that with the increase of $C_{25}H_{52}$ content, the aging time of the temporary plugging agent shows a trend of first increasing and then decreasing. When the $C_{25}H_{52}$ content is greater than 3.6%, the aging time of the multi-layer assembled paraffin temporary plugging agent gradually decreases because the breakage rate increases when the $C_{25}H_{52}$ content is greater than 3.6%.

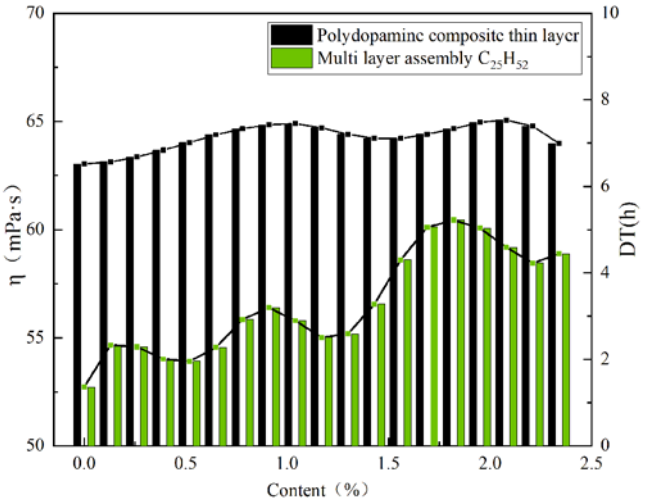

Figure 8. Relationship between Content, Aging Time (DT), and Viscosity (η) Changes

Therefore, the effective paraffin composite layer wrapped on the surface of the base material gradually decreases, and the aging time begins to decrease. The viscosity of multi-layer assembled polyethylene terephthalate and multi-layer assembled paraffin temporary plugging agent fluctuates with the increase of $C_{25}H_{52}$ content, so its impact on the system is relatively small[19–20].

ANALYSIS OF THE MECHANISM OF DEEP PROFILE ADJUSTMENT

The deep profile control technology in the process of oilfield exploitation and development is to use inorganic particles and organic polymers to form gel microsphere polymers, and use the characteristics of inorganic particles' water absorption and non organic polymers' strong hydrophobic performance, strong temperature and pressure resistance to form a new composite gel temporary plugging agent.

When the profile control agent is pumped into the formation by using the profile control technology, the profile control agent will move in the formation (Fig. 9). First, the profile control agent will be stored in a large amount in the high permeability area, because the resistance of the area is small, when the profile control agent is largely detained in the area, the aperture of the high permeability area will become smaller or even blocked, changing the direction of the formation fluid flow, making it reach the middle low permeability area, and improving the efficiency of oilfield exploitation.

Therefore, the performance of the organic polymer assembled on the outer layer of the profile control agent is very important. It needs a strong hydrophobic performance and a strong temperature and pressure resistance performance so that the profile control agent can overcome the influence of formation temperature and mineralization, and effectively cross the shallow area of the formation to reach the deep area to be blocked. When it reaches the deep area of the formation, the organic matter assembled on the outer layer of the profile control agent can collapse on its own, so that the inorganic polymer in the inner layer can fully leak in the formation water environment to absorb water and expand, thus forming a high-strength gel to achieve the water plugging effect.

CONCLUSION

Multi-layer assembled polyethylene terephthalate and multi-layer assembled paraffin temporary plugging agent were prepared by traditional polymerization methods and their properties were studied. The treatment agent can effectively improve the efficiency of profile control and water shutoff.

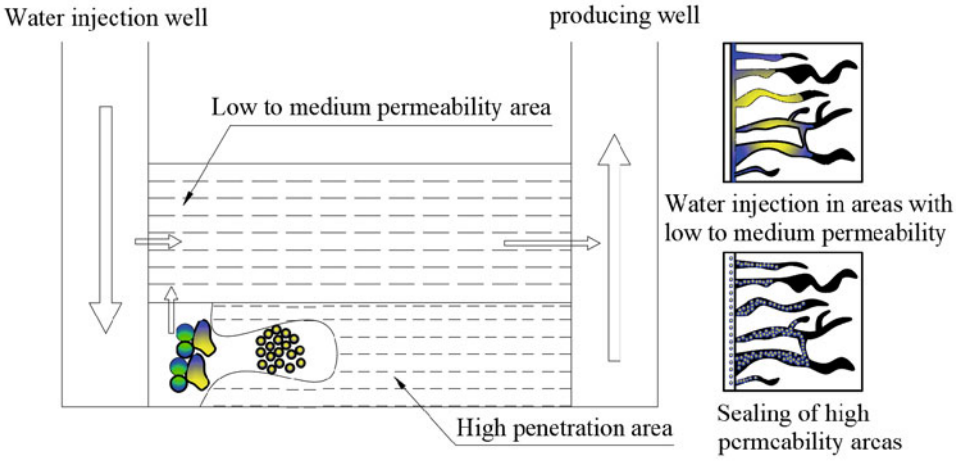

Figure 9. Deep profile control mechanism diagram

(1) Multi-layer assembled polydopamine composite thin layer was modified on the substrate, and then $C_{25}H_{52}$ was modified on the thin layer to prepare multi-layer assembled polyethylene terephthalate and multi-layer assembled paraffin temporary plugging agent.

(2) When the content of $C_{25}H_{52}$ is 3.6%, the multi-layer assembly temporary plugging agent prepared by it has the best water absorption performance.

(3) When the temperature is 53 °C, the multi-layer assembled paraffin temporary plugging agent prepared has the best water absorption effect.

(4) The prepared temporary plugging agent has a certain salt tolerance, but the mineral content has a significant impact on the water absorption effect of the temporary plugging agent, and the inhibitory effect of $CaCl_2$ is greater than that of NaCl.

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