Experimental Study on Injection and Plugging Effect of Core–Shell Polymer Microspheres: Take Bohai Oil Reservoir as an Example

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Cite This: ACS Omega 2020, 5, 32112–32122

ABSTRACT: To meet the technical requirements of deep fluid diversion in Bohai oilfield, the swelling property, plugging effect, transport characteristics of polymer microspheres, and fluid diversion effect in heterogeneous cores are studied in this paper. There are two kinds of polymer microspheres including core–shell microspheres and traditional microspheres. The instruments used in this study include a biomicroscope, a metallurgical microscope, a scanning electron microscope, and core displacement experimental devices. The results of microscopes indicated that the core–shell microspheres were successfully synthesized, and the microspheres had good hydration expansion effect. The expanded microspheres could attract each other through the electrostatic force of anions and cations to achieve the purpose of coalescence. Compared with traditional microspheres (initial particle size is 3.8 μm), the initial particle size of the synthesized core–shell microspheres is close to 3.3 μm, but the particle size distribution is more concentrated, so the injection performance is close to that of traditional microspheres (initial particle size is 3.8 μm). After 8 days of hydration expansion, although the expansion multiple is small, it can coalesce and enhance the plugging effect, which can adapt to a wider range of permeability, ranging from 200 × 10⁻³ to 3000 × 10⁻³ μm² (200 × 10⁻³−1500 × 10⁻³ μm² for traditional microspheres). Under the same conditions (heterogeneous core), compared with the traditional microspheres, the core–shell microspheres have the characteristics of coalescence. Therefore, its fluid diversion effect is better, and the oil recovery is increased by 5.5%. Nevertheless, there is the "end effect" during the injection process, which weakens the steering effect of deep liquid flow. The results show that the "end effect" can be effectively reduced by alternate injection of microspheres and water. Meanwhile, the effect of deep fluid diversion is improved, and the increase of oil recovery is increased by 2.06%.

1. INTRODUCTION

With the oilfield entering the high water cut development stage, reservoir heterogeneity is stronger, and water flooding and water channeling are particularly serious. In the process of injection of the conventional profile control and flooding agent, it usually enters the low permeability layer, causing damage to it, which makes it difficult to get effective exploitation in the later stage. The particle size distribution of polymer microspheres is relatively concentrated, and it is difficult to enter the low permeability layer. When the polymer microspheres enter into the medium and high permeability layer, it has the abilities of hydration, expansion, deep profile control, and flooding. At the same time, it possesses the advantage of “blocking but not dying”. Therefore, it has been widely concerned by experts and scholars at home and abroad.1−15 Zhao et al. has studied the effects of the shape and size of polymer microspheres, the matching relationship between particle size and pore throat size, particle elasticity, seepage velocity, and particle concentration on migration and plugging in porous media.16−18 Nie et al. used capillary flow experiment, microscopic vision model, nuclear pore membrane filtration experiment, and sand filling model to explore the plugging mechanism of microspheres in porous media, and selected artificial cores with different particle sizes, and permeability for the oil displacement test.19,20 Conventional polymer microspheres only rely on hydration expansion to plug the reservoir, and the effect of fluid diversion is very limited. The core–shell microspheres may be grafted, interpenetrating or ionic bonding between the core and the shell, and can also be adsorbed on the formation, so as to increase the deep fluid diversion effect of the polymer microspheres, which has a good development prospect. At present, solid microspheres can be used in profile control and flooding. The core materials of solid microspheres are SiO₂, Fe₃O₄, TiO₂, etc., which have no swelling property.21−23 The
profile control and flooding effect are not good. Based on the theory of physical chemistry, polymer materials and reservoir engineering, core–shell microspheres with positive core and negative shell was synthesized by means of instrument detection, chemical analysis, and physical simulation. Its core is polymer gel, which can slow swelling, and its shell is polymer thread. The hydration expansion, injection performance, plugging, and profile control effect of core–shell microspheres are emphatically studied and compared with conventional hydrated expanded polymer microspheres, which provide experimental basis for the selection of microspheres in the target reservoir.

2. EXPERIMENTAL CONDITIONS

2.1. Materials. The synthetic microspheres medicaments include acrylamide (AM), N,N-methylene bisacrylamide (MBA), polyvinylpyrrolidone (PVP), dimethyldiallylammonium chloride (DMDAAC), 2-acylamide-2-methylpropanesulfonic acid (AMPS), azodiisobutyronitrile (AIBN), water-free ethanol, SP-80, and NaOH, and these were obtained from Tianjin Kemeo Chemical Reagent Co., Ltd.

Polymer microspheres include core–shell microspheres (core–shell type), which are synthesized in the laboratory, and traditional microspheres (hydration expansion type) are provided by CNOOC Tianjin Branch. Experimental water is simulated injection water from Q oilfield of Bohai Sea, and the total salinity is 2893.7 mg/L. The ion composition (unit mg/L) is Ca²⁺ 7.5, Mg²⁺ 75.1, K⁺Na⁺ 921.7, Cl⁻ 737.5, SO₄²⁻ 126, CO₃²⁻ 1077.7, and HCO₃⁻ 61.6. The experimental oil is a mixture of Q oilfield crude oil and light hydrocarbon, and its viscosity is 75 mPa·s at 65 °C. According to the porosity and permeability structure of Q oilfield in Bohai Sea, the artificial core is a quartz sand epoxy resin cemented artificial core.24–26 A columnar core is used for the core fluidity test of polymer microspheres and matching relationship between microspheres size and core pore throat size (diameter × length = 2.5 cm × 10 cm). Homogeneous square core with four pressure measuring points is designed for transport characteristics of polymer microspheres (width × height × length = 4.5 cm × 4.5 cm × 60 cm). Homogeneous square core is intended for the study on fluid diversion effect of polymer microspheres (width × height × length = 4.5 cm × 4.5 cm × 30 cm). The core permeability is shown in the analysis table of relevant experimental results.

The schematic diagram of experimental cores is shown in Figure 1.

2.2. Apparatus. The main equipment used for the experiment included an HJ-6 multihed magnetic stirrer, an HW-III A thermostat, an HH-S2 temperature water bath, an L2030 metallurgical microscope (Beijing optoelectronics, Huilong Technology Center), a BDS400 inverted biomicroscope (Chongqing Aote Optical Instrument Co., Ltd), and an Hitachi S-3400n scanning electron microscope (Hitachi Corporation of Japan). Four-necked flask, condensing tube, drip funnel, etc. were also used in the experiment.

An L2030 metallurgical microscope was used to observe the initial appearance morphology of core–shell microspheres. A BDS 400 inverted biomicroscope was used to observe the appearance morphology of core–shell microspheres and traditional microspheres after 192 h. Figure 2 shows the synthesis experiment device diagram.

Figure 1. Schematic diagram of experimental cores.

Figure 2. Synthesis experiment device diagram.
The milk white cationic core microspheres were obtained. During this process, the flask is always filled with nitrogen. After a certain amount of AM, AMPS, MBA, PVP, AIBN, and TW-80 are dissolved in ethanol, the shell reaction solution is obtained and put into the separating funnel. The shell reaction solution was added to a four-necked flask drop by drop, and the drop was finished in about 30 min. The solution was kept at 65 °C and stirred continuously. The reaction was completed 3 h later. When the solution was cooled to room temperature (25 °C), core−shell polyacrylamide microspheres emulsion was prepared. Core−shell polyacrylamide microspheres emulsion is added to water during the sample preparation.

2.3.2. Relationship between Particle Size and Distribution of Microspheres and Time. The hydration expansion properties of polymer microspheres were measured by inverted biomicroscopy. The calculation formula of expansion ratio is as follows

\[ E = \frac{(D_2 - D_1)}{D_1} \]  

(1)

Where \( E \) is the expansion ratio; \( D_1 \) is the median particle size (initial), \( \mu m \); and \( D_2 \) is the median particle size (after 192 h of expansion), \( \mu m \).

2.3.3. Matching Relationship between Microspheres Size and Core Pore Size. Experimental steps for the matching relationship between microspheres size and core pore size were conducted as follows:

1. After the core was saturated with water, experiment’s water was injected into the core until the pressure difference was stable, and the theoretical pressure difference \( (\delta P_1) \) was then calculated.
2. Microspheres solution equal to 5 times the pore volume was injected into the core, and the pressure difference \( (\delta P_2) \) was recorded. The injection to the core was stopped at 0.5 cm of the core top surface to avoid the “end effect”.
3. After placed in a thermostatically controlled oven at 65 °C for 8 days, water equal to 5 times the pore volume was injected into the core until the pressure became constant. The pressure difference \( (\delta P_3) \) was recorded.
4. The resistance coefficient \( (F_R) \) and the residual resistance coefficient \( (F_{RR}) \) were calculated.

\[ F_R = \frac{\delta P_2}{\delta P_1}, \quad F_{RR} = \frac{\delta P_3}{\delta P_1} \]  

(2)

(5) The plugging rate \( (\beta) \) was calculated. It is generally considered that the plugging rate lies between 40 and 60%, which shows an acceptable liquid flow division effect; additionally, it is considered that the plugging rate is more than or equal to 50% of the plugging efficiency \( \beta \).

\[ \beta = \frac{(\delta P_3 - \delta P_1)}{\delta P_1} \]  

(3)

The liquid injection rate was 0.9 mL/min.

2.3.4. Transport Characteristics of Polymer Microspheres. The experimental steps are as follows:

1. At room temperature (25 °C), the core is saturated with simulated water after vacuum pumping, and the porosity is calculated.
2. Water was used to measure permeability at reservoir temperature (65 °C), and the pressure between each pressure measuring point was recorded.
3. The 1.2 pore volume (PV) microspheres solution was injected into the core from the first injection port, and the pressure of each pressure measuring point was recorded.
4. After the core is placed at the reservoir temperature for 192 h, subsequent water is injected until the pressure is stable, and the pressure at each pressure measuring point at the end of subsequent water is recorded.

The liquid injection rate was 0.9 mL/min.

2.3.5. Oil Displacement Experiment of Polymer Microspheres with Parallel Cores. Experimental steps to evaluate oil recovery on the parallel core were conducted as follows:

1. Dried cores were weighed before and after being saturated with water at 25 °C. Pore volume (PV) and porosity were calculated according to the weight difference.
2. Each core was placed in the core holder and saturated with crude oil and aged at 65 °C for 24 h to prepare it for use. Oil saturation of each sample was then calculated.
3. Water was injected into the core, the produced liquid was collected until the water content was 98%, and the water drive recovery was calculated according to the crude oil proportion in the produced liquid.
(4) Microspheres solutions equal to 0.2 times the pore volume were injected into the core and placed in a thermostatically controlled oven at 65 °C for 8 days.
(5) Water was injected into the core until the water content was 98%. The water flooding recovery was calculated according to the crude oil proportion in the produced liquid.
The injection speed was 1.2 mL/min.

3. RESULTS AND DISCUSSION

3.1. Hydration Expansion Properties of Microspheres.
The test results of the relationship between the particle size and particle size distribution and hydration time in the 3000 mg/L microspheres solution are shown in Figure 4. After 192 h, the morphology of microspheres is shown in Figure 5.

The test results of the relationship between the size and the distribution of microspheres and the hydration time in two kinds of microspheres solutions with concentration ($C_m$) of 3000 mg/L are shown in Figure 4 and Figure 5. The particle size distribution of the core–shell microspheres was approximately normal. The median initial particle size is 3.30 μm, which is 13.40 μm after hydration for 192 h, and the expansion ratio is 3.06 times. The initial particle size of traditional microspheres mainly concentrated between 1.24 and 5.03 μm, and the initial particle size was larger, and the median particle size was 3.80 μm. After 24 h hydration, the particle size difference was small. After 192 h of hydration, the increase of particle size became slower. The particle size of microspheres was mainly distributed between 10.62 and 34.22 μm, the maximum particle size was 38.53 μm, the median particle size was 28.02 μm, and the expansion ratio was 6.40. After comparing the two kinds of microspheres, it was found that the initial particle size of core–shell microspheres was slightly smaller, but the distribution was relatively concentrated. After 8 days, the expansion ratio was small, but there was coalescence.

Core–shell microspheres solution ($C_m = 3000$ mg/L) was prepared by injecting water from Q oilfield in Bohai Sea. The appearance morphology of core–shell microspheres (initial) was observed by metallographic microscope, as shown in Figure 6.

It can be seen from Figure 6 that the core–shell microspheres are core–shell structure.

3.2. Microstructure Characteristics of Polymer Microspheres.
The SEM observation results of micromorphology characteristics of purified polymer microspheres are shown in Figure 7. It can be seen from Figure 7 that the core–shell microspheres and traditional microspheres are spherical. The particle sizes of core–shell microspheres and traditional microspheres were from 1.35 to 4.08 μm and from 0.93 to 6.08 μm, respectively. Compared with the results of biomicroscopy, the results of core–shell microspheres and traditional microspheres are close.

3.3. Core Fluidity Test of Polymer Microspheres.
3.3.1. Resistance Coefficient and Residual Resistance Coefficient.
The experimental results of resistance coefficient, residual resistance coefficient, plugging rate, and permeability of core–shell microspheres and traditional microspheres are shown in Tables 1 and 2.
Figure 7. SEM observation results of purified polymer microspheres.

(b) Traditional microspheres

(a) Core-shell microspheres
It can be seen from Tables 1 and 2 that with the increase of core permeability, the resistance coefficient of microspheres decreases gradually, and the residual resistance coefficient increases first and then decreases. The analysis shows that with the increase of core permeability, the pore throat size increases, the compatibility between microspheres and core pore throat becomes better, the retention capacity decreases, the seepage resistance decreases, and the resistance coefficient decreases.

The permeability limits of core−shell and traditional microspheres are 200 × 10^{-3} μm^2. The analysis shows that when the core permeability is too low, the "end effect" is serious during the injection of polymer microspheres. At this time, only a small number of microspheres enter the porous media, resulting in slow expansion, and the residual resistance coefficient and plugging rate are small. When the permeability reaches the minimum value that the microspheres can pass through, most of the microspheres can be injected into the porous media, and the sealing effect is the best after the microspheres expand slowly. However, when the core permeability continues to increase, the plugging effect of polymer microspheres decreases, and the residual resistance coefficient and plugging rate decrease. The results show that the core−shell microspheres have good plugging effect from 200 × 10^{-3} to 3000 × 10^{-3} μm^2.

Compared with the core−shell microspheres and the traditional microspheres, the initial particle size of the two microspheres is close, but the core−shell microspheres are more concentrated. In theory, the residual resistance coefficient and plugging rate of the core−shell microspheres should be larger than that of the core−shell microspheres. However, a large number of cationic materials exist in the core of core−shell microspheres, and the expansion degree is far greater than that of the shell material, resulting in the gradual fracture of the anion shell, the exposure of the cationic material, and the cross-linking and coalescence with the adjacent shell of the microspheres (Figure 8), at the same time, the cation can also adsorb and stay with the formation.30,31 Therefore, the residual resistance coefficient and plugging rate

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**Table 1. Resistance Coefficient, Residual Resistance Coefficient, and Plugging Rate (Core−Shell Microspheres)**

| permeability (10^{-3} μm^2) | 48  | 100 | 200 | 339 | 521 | 995 | 2037 | 3025 | 3500 |
|-----------------------------|-----|-----|-----|-----|-----|-----|------|------|------|
| resistance coefficient      | 5.00| 4.47| 3.41| 3.19| 2.43| 2.35| 2.05  |      |      |
| residual resistance coefficient | 8.27| 9.66| 11.01| 8.25| 6.56| 4.6 | 3.19 | 2.55 | 2.26 |
| plugging rate (%)           | 87.88| 89.62| 92.58| 89.68| 86.94| 83.29| 73.06 | 69.71 | 45.28 |

**Table 2. Resistance Coefficient, Residual Resistance Coefficient, and Plugging Rate (Traditional Microspheres)**

| permeability (10^{-3} μm^2) | 48  | 113 | 226 | 362 | 509 | 1011| 1455 | 1787 | 48   |
|-----------------------------|-----|-----|-----|-----|-----|------|------|------|------|
| resistance coefficient      | 4.41| 4.04| 3.00| 2.10| 1.81| 1.64 |      |      |      |
| residual resistance coefficient | 2.83| 3.8 | 5.48| 4.75| 3.42| 2.72 | 2.13 | 1.69 | 2.83 |
| plugging rate (%)           | 64.61| 73.71| 81.76| 78.96| 70.73| 63.29| 53.12 | 40.76 | 64.61 |

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Figure 8. Expansion and coalescence of core−shell microspheres.

Figure 9. Migration process of microspheres in porous media.
of core–shell microspheres were significantly higher than those of traditional microspheres. In addition, the traditional microspheres have strong expansion performance and strong elasticity, which lead to the weak retention capacity in the porous media and easier to pass through the pore throat. In the same case, the core–shell microspheres have weak expansion performance, strong rigidity, weak migration ability, and strong retention capacity in porous media after coalescence (Figure 9), which also makes the residual resistance coefficient and plugging rate of core–shell microspheres significantly higher than those of traditional microspheres.

3.3.2. Dynamic Characteristics. It can be seen from Figure 10 that the injection pressure tends to be "increased and stable" when the pore throat size of the core matches the particle size of the microspheres. Therefore, by observing the change trend of injection pressure, it can be determined that the lowest permeability of the two types of microspheres can enter the core is about $200 \times 10^{-3} \mu m^2$. According to the injection pressure, the residual resistance coefficient and plugging rate can be calculated, and the maximum core permeability value of the microspheres can effectively play the role of retention and fluid diversion can be determined. The initial particle size of the two kinds of microspheres is close, so the injection performance is similar. Because the core–shell microspheres can coalesce $^{30,31}$ after slow expansion, the subsequent water flooding pressure is higher and the plugging effect is better under the same permeability conditions. Combined with Tables 1 and 2, it can be seen that when the compatibility of microspheres is poor, the injection pressure will continue to increase. This is mainly due to the retention of polymer microspheres at the end face of the core, resulting in the "end effect". Only a part of the microspheres with smaller particle size enter the core.

The relationship between injection pressure and pore volume number of core–shell microspheres ($C_m = 3000 \text{ mg/L}$) and traditional microspheres solution ($C_m = 3000 \text{ mg/L}$) are shown in Figure 10.

3.4. Matching Relationship between Microspheres Size and Core Pore Throat Size. The matching relationship between microspheres size and core pore throat is shown in Table 3.

It can be seen from Table 3 that the ratio of throat diameter and microspheres size of the two microspheres is close to that obtained by the "bridging" principle. $^{32,33}$ After hydration and slow expansion, the "throat diameter/particle size" of core–shell microspheres is larger due to the phenomenon of coalescence and cross-linking. However, the "throat diameter/particle size" of the traditional microspheres was close to 1. In other words, the elasticity of microspheres is enhanced after slow expansion (the microspheres only rely on slow expansion plugging). To have good plugging effect (the plugging rate is greater than 50%), the "throat diameter/particle size of microspheres" should be less than 1.13.

3.5. Transport Characteristics of Polymer Microspheres. At the end of microspheres flooding and subsequent water flooding of core–shell microspheres and traditional microspheres, the test results of pressure difference in each interval of core are shown in Table 4, and the relationship between pressure at injection point and each pressure measuring point and pore volume is shown in Figure 11.

Table 4 and Figure 11 indicate that the pressure at each point of core–shell microspheres is higher than that of traditional microspheres. The main reason is that the particle size distribution range of traditional microspheres is large, and the retention capacity of smaller microspheres in the core is weak. Only the microspheres with larger particle size have better retention capacity in porous media. The size distribution of core–shell microspheres was concentrated. There are a lot of microspheres that can retain in the core. Also, the retention capacity of the microspheres with slow expansion coalescence is stronger than that of the microspheres with slow expansion. Therefore, the injection pressure of core–shell microspheres is high. Compared with core–shell microspheres, the $P_2$ and $P_3$ of traditional microspheres increased earlier. This is due to the weaker retention and stronger migration ability of microspheres with smaller particle size of traditional microspheres.
In the microspheres injection stage, compared with core−shell microspheres, the $\delta P_{0-1}$, $\delta P_{1-2}$, and $\delta P_{2-3}$ of traditional microspheres are larger, while the $\delta P_{3-\text{export}}$ is smaller. This indicates that the transport ability of traditional microspheres is poor, and it is mainly retained in front of the core, and there are less microspheres or smaller particle size migrating to the back of the core.

3.6. Study on Fluid Diversion Effect of Polymer Microspheres. Core−shell microspheres solution and traditional microspheres solution ($C_m = 3000$ mg/L) of were prepared with simulated injection water from Q oilfield in Bohai Sea. The core displacement experiment results of core−shell microspheres and traditional microspheres are shown in Table 5, and the dynamic characteristic curve is shown in Figure 12.

It can be seen from Table 5 and Figure 12 that compared with "project 1" (traditional microspheres), the injection pressure of microspheres in "project 2" (core−shell microspheres) in the subsequent water flooding stage is higher, the water cut decreases greatly, and the oil recovery increases greatly. This is because the core−shell microspheres polymerize and cross-linked in the high permeability layer, resulting in greater seepage resistance, leading to a greater increase in the low permeability layer diversion ratio, better fluid diversion effect, and greater increase in oil recovery. At the same time, in "project 2", the recovery rate of the high permeability layer is also increased greatly, which is mainly due to the heterogeneity of the homogeneous core in the high permeability layer. Coalescence microspheres can be retained in pore throat, forcing subsequent water into small pores, thus displacing

| stage                  | injection pressure (MPa) | pressure difference (MPa) |
|------------------------|--------------------------|----------------------------|
|                        | $P_0$ (injection end)    | $P_1$ | $P_2$ | $P_3$ | $\delta P_{0-1}$ | $\delta P_{1-2}$ | $\delta P_{2-3}$ | $\delta P_{3-\text{export}}$ |
| core−shell microspheres| microspheres flooding    | 0.0120 | 0.0057 | 0.0030 | 0.0013 | 0.0063 | 0.0027 | 0.0017 | 0.0013 |
|                        | subsequent water flooding| 0.0121 | 0.0066 | 0.0036 | 0.0016 | 0.0055 | 0.0030 | 0.0020 | 0.0016 |
| traditional microspheres| microspheres flooding    | 0.0115 | 0.00514| 0.0023 | 0.0005 | 0.0064 | 0.0028 | 0.0019 | 0.0005 |
|                        | subsequent water flooding| 0.0112 | 0.00538| 0.0025 | 0.0006 | 0.0058 | 0.0029 | 0.0019 | 0.0006 |

Table 5. Experimental Data of Recovery Rate

| parameter | recovery ratio (%) |
|-----------|--------------------|
| water flooding finished | microspheres flooding finished | subsequent water flooding finished | growth rate |
| 1 (traditional microsphere) | high | 446 | 70.80 | 35.98 | 40.10 | 45.67 | 9.69 |
| | low | 149 | 69.30 | 14.68 | 17.59 | 21.77 | 7.09 |
| | model as a whole | 70.12 | 26.42 | 30.00 | 34.94 | 8.52 |
| 2 (core−shell microsphere) | high | 440 | 70.50 | 35.71 | 39.80 | 48.98 | 13.06 |
| | low | 145 | 68.54 | 14.94 | 17.90 | 30.25 | 15.19 |
| | model as a whole | 69.65 | 26.31 | 29.89 | 40.50 | 14.02 |
| 3 (core−shell microspheres) | high | 452 | 70.71 | 35.15 | 40.51 | 51.21 | 15.96 |
| | low | 151 | 70.09 | 14.76 | 18.29 | 31.10 | 16.22 |
| | model as a whole | 70.43 | 25.91 | 30.44 | 42.10 | 16.08 |

"Represents the alternative injection of core−shell microspheres and water. The specific scheme is "0.067 PV microsphere + 0.07 PV water + 0.066 PV microsphere"."
residual oil. In addition, microspheres can accumulate repeatedly in the core, deform, and migrate. As a result, the micro pressure in the core is continuously transmitted forward, and the oil in the small pores in the "local area" is continuously displaced. The stronger the plugging effect of microspheres the greater the "local" micro pressure, the stronger the ability of displacement of remaining oil, and the greater the increase of oil recovery in the high permeability layer.

Compared with "project 2", the high permeability layer, low permeability layer, and comprehensive recovery rate of "project 3" increased by 2.9, 2.2, and 2.06%, respectively. This is mainly due to the alternative injection of microspheres and water. Water slug can effectively ameliorate the "end effect" caused by the retention of microspheres at the injection end of the core. It can significantly decrease the retention of microspheres in the region near the injection end, so that more microspheres can enter the interior of the high permeability layer. These microspheres stay, expand, coalesce, and migrate in the deep part of the high permeability layer, so as to increase the seepage resistance, further enhance the injection pressure and the effect of fluid diversion. When more microspheres enter into the high permeability layer, the migration of microspheres in the high permeability layer will promote the micro profile control and displacement effect. The remaining oil in the high permeability layer can be produced effectively, the oil saturation is further reduced and the recovery factor is further increased. In addition, the injection pressure rise is small due to the alternate injection of microspheres and water. Less microspheres will cause liquid flow diversion to the end face of the low permeability layer, thus reducing the pollution of the low permeability layer, which is conducive to improving oil recovery of the low permeability layer.

In summary, although the expansion multiple of traditional microspheres is 6.40 times, the profile control and displacement effect of traditional microspheres is still slightly poor, and the increase of oil recovery is less than 10%. To make polymer microspheres profile control and flooding have better fluid diversion effect, we must carry out research from these aspects: (1) The polymer microspheres have good adaptability to reservoir. According to the pore throat size of the reservoir, the appropriate microspheres should be selected. First, the polymer microspheres can enter the deep part of the reservoir, and then the microspheres can have good plugging effect or liquid diversion effect. (2) At the same time, if the polymer microspheres cross-linked or coalesced in the deep reservoir, it will have greater fluid diversion effect, forcing more water into the low permeability layer, thus ensuring better oil displacement effect. (3) The synthesis of polymer microspheres must be stricter. To ensure that the distribution of polymer microspheres is relatively concentrated, so as to reduce or eliminate the damage to the low permeability layer, the ratio of injection rate/pressure should be controlled to reduce the probability of microspheres entering the low permeability layer. (4) For highly heterogeneous reservoirs, it is very necessary to use gel to block up and then use microspheres to adjust and drive.
4. CONCLUSIONS

(1) The median initial particle size of the traditional microspheres was 3.80 μm, and expanded by 6.40 times after 8 days. The reservoir adaptability of traditional microspheres is between 200 × 10⁻³ and 1500 × 10⁻³ μm². The average initial particle size of the synthesized core–shell microspheres was 3.30 μm and expanded by 3.06 times after 8 days. Although the hydration expansion ratio of core–shell microspheres is small, the plugging effect is enhanced due to the aggregation and cross-linking of the microspheres after hydration. The core–shell microspheres have a wide range of reservoir adaptability, ranging from 200 × 10⁻³ to 3000 × 10⁻³ μm².

(2) Compared with the traditional microspheres, the core–shell microspheres have more concentrated particle size distribution, stronger transport in porous media, polymerization and cross-linking after hydration expansion, better fluid diversion effect, and higher recovery increase. It is suggested that the microspheres, which can be polymerized or cross-linked should be used in the field to achieve better EOR.

(3) Due to the existence of a small amount of microspheres with large or very small particle size in the polymer microspheres solution, the polymer microspheres will also enter the low permeability layer under the condition of high injection pressure, which will cause hydration expansion and damage in the low permeability layer. Therefore, it is suggested that the injection rate/pressure should be controlled to reduce the probability of microspheres entering the low permeability layer.

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Notes
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■ ACKNOWLEDGMENTS

This work was supported by the “Seepage Characteristics and Liquid Flow Mechanism of Polymer Microspheres for Profile Control in Bohai Oilfield” (no. CCL2018RCPS0029RON).

■ REFERENCES

(1) Pekarek, K. J.; Jacob, J. S.; Mathiowitz, E. Double-walled polymer microspheres for controlled drug release. Nature 1994, 367, 258.
(2) Alaskar, M. N.; Ames, M. F.; Connor, S. T.; Liu, C.; Cui, Y.; Li, K.; Horne, B. N. Nanoparticle and microparticle flow in porous and fractured media—an experimental study. SPE J. 2012, 17, 1160–1171.
(3) Lu, X.; Cao, B.; Xie, K.; Cao, W.; Liu, Y.; Zhang, Y.; Wang, X.; Zhang, J. Mechanisms of polymer flooding in a heterogeneous reservoir and its improvement method. PETROL EXPLOR. DEV. 2021.
(4) Cao, W.; Xie, K.; Lu, X.; Liu, Y.; Zhang, Y. Effect of profile-control oil-displacement agent on increasing oil recovery and its mechanism. Fuel 2019, 237, 1151–1160.
(5) Cao, D.; Han, M.; Alshehri, A.; Also, A.; Shamsuddin, S. Field study on microsphere injection in sandstone reservoir. In PESC 2012, 17, 1160–1171.
(6) Lu, X.; Cao, B.; Xie, K.; Cao, W.; Liu, Y.; Zhang, Y.; Wang, X.; Zhang, J.; Liu, T. Field application and performance evaluation of polymer microsphere profile control in low permeability oil reservoir. In Abu Dhabi International Petroleum Exhibition & Conference; SPE: 197198, 2019.
(7) Lei, G.; Li, L.; Nasr-El-Din, H. New gel aggregates to improve sweep efficiency during waterflooding. In Abu Dhabi International Petroleum Exhibition & Conference; Society of Petroleum Engineers: 2011, J4, 120–128, DOI: 10.2118/129960-PA.
(8) Liu, H.; Wang, X.; Li, G.; Shang, H. An enhanced oil recovery technology continues to improve oil recovery efficiency. SPE Enhanced Oil Recovery Conference; SPE: 2011, 1, 752–759.
(9) Qian, Q.; Wang, L.; Tang, Y.; Liu, C.; Ma, C. Research and application of nano polymer microspheres diversion technique of deep fluid. SPE International Oilfield Nanotechnology Conference and Exhibition; SPE: 156958, 2019.
(10) Liu, H.; Wang, X.; Xie, K.; Wang, X.; Lu, X.; He, X.; Xu, G.; Li, X. Starch graft copolymer and polymer gel applied in Bohai oilfield for water plugging and profile control and their mechanisms. Geosyst. Eng. 2020, 23, 197–204.
(11) Cao, W.; Xie, K.; Cao, B.; Lu, X.; Tian, Z. Inorganic gel enhanced oil recovery in high temperature reservoir. J. Pet. Sci. Eng. 2021, 196, 107691.
(12) Cormack, P. A. G.; Davies, A.; Fontanals, N. Synthesis and characterization of microporous polymer microspheres with strong cation-exchange character. React. Funct. Polym. 2012, 72, 939–946.
(13) Khare, P.; Jain, S. K. Influence of rheology of dispersion media in the preparation of polymeric microspheres through emulsification method. AAPS PharmSciTech 2009, 10, 1295–1300.
(14) Jia, H.; Chen, H. The potential of using Cr$^{3+}$/salt-tolerant polymer gel for well workover in low-temperature reservoir: Laboratory investigation and pilot test. SPE Prod. Oper. 2018, 33, 569–582.
(15) Zhou, Y.; Lu, X.; Wang, R.; Liu, Y. Numerical simulation for optimizing injection – production parameters when using cyclic steam injection plus polymer gel flooding in an offshore heavy-oil field. Chem. Technol. Fuels Oils 2017, 53, 621–631.
(16) Zhao, S.; Pu, W. Migration and plugging of polymer microspheres (PMs) in porous media for enhanced oil recovery: Experimental studies and empirical correlations. Colloids Surf., A 2020, 597, 124774–124778.
(17) Hua, Z.; Lin, M.; Guo, J.; Xu, F.; Li, Z.; Li, M. Study on plugging performance of cross-linked polymer microspheres with reservoir pores. J. Pet. Sci. Eng. 2013, 105, 70–75.
(18) Cao, D.; Han, M.; Wang, J.; Alshehri, A. J. Polymeric microsphere injection in large pore-size porous media. Petroleum 2020, 6, 264–270.
(19) Nie, X.; Chen, J.; Cao, Y.; Zhang, J.; Zhao, W.; He, Y.; Hou, Y.; Yuan, S. Investigation on Plugging and Profile Control of Polymer Microspheres as a Displacement Fluid in Enhanced Oil Recovery. Polymers 2019, 11, 193.
(20) Lin, M.; Zhang, G.; Hua, Z.; Zhao, Q.; Sun, F. Conformation and plugging properties of crosslinked polymer microspheres for profile control. Colloids Surf., A 2015, 477, 49–54.
(21) Sun, C.; Xie, Y.; Ren, X.; Song, G.; Alkaedi, A.; Hayat, T.; Chen, C. Efficient removal of Cd(II) by core-shell Fe$_3$O$_4$@polydopamine microspheres from aqueous solution. J. Mol. Liq. 2019, 295, 111724.
(22) Fu, N.; Ren, X.-c.; Wan, J.-x. Preparation of Ag-Coated SiO$_2$@TiO$_2$ core-shell nanocomposites and their photocatalytic applications towards phenol and methylene blue degradation. J. Nanomater. 2019, 2019, 1–8.
(23) Jia, H.; Dai, J.; Huang, P.; Han, Y.; Wang, Q.; He, J.; Song, J.; Wei, X.; Yan, H.; Liu, D. Application of novel amphiphilic Janus-SiO$_2$ nanoparticles for an efficient demulsification of crude oil/water emulsions. Energy Fuels 2020, 34, 13977.
(24) Xie, K.; Lu, X.; Pan, H.; Han, D.; Hu, G.; Zhang, J.; Zhang, B.; Cao, B. Analysis of dynamic imbibition effect of surfactant in microcracks of reservoir at high temperature and low permeability. SPE Prod. Oper. 2018, 33, 596–606.
(25) Xie, K.; Lu, X.; Li, Q.; Jiang, W.; Yu, Q. Analysis of reservoir applicability of hydrophobically associating polymer. SPE J. 2016, 21, 1–9.
(26) Cao, W.; Xie, K.; Lu, X.; Chen, Q.; Tian, Z.; Lin, W. Self-suspending proppant manufacturing method and its property evaluation. J. Pet. Sci. Eng. 2020, 107251.
(27) Yang, J.; Xie, X.; Zhang, J.; Zhang, X.; Wei, Z. Injection parameters optimization of cross-linked polymer microspheres and polymer composite flooding system. Pet. Explor. Dev. 2014, 41, 794–797.
(28) Lian, P.; Jia, H.; Wei, X.; Han, Y.; Wang, Q.; Dai, J.; Wang, D.; Wang, S.; Tian, Z.; Yan, H. Effects of zwitterionic surfactant adsorption on the component distribution in the crude oil droplet: A molecular simulation study. Fuel 2021, 283, 119252.
(29) Jia, H.; Leng, X.; Wang, Q.; Han, Y.; Wang, S.; Ma, A.; Guo, M.; Yan, H.; Lv, K. Controllable emulsion phase behavior via the selective host-guest recognition of mixed surfactants at the water/oil interface. Chem. Eng. Sci. 2019, 202, 75–83.
(30) Sun, Z.; Wu, X.; Kang, X.; Lu, X.; Li, Q.; Jiang, W.; Zhang, J. Comparison of oil displacement mechanisms and performances between continuous and dispersed phase flooding agents. Pet. Explor. Dev. 2019, 46, 121–129.
(31) Sun, Z.; Lu, X.; Sun, W. The profile control and displacement mechanism of continuous and discontinuous phase flooding agent. J. Dispersion Sci. Technol. 2017, 38, 1403–1409.
(32) Xie, K.; Cao, B.; Lu, X.; Jiang, W.; Zhang, Y.; Li, Q.; Song, K.; Liu, J.; Wang, W.; Lv, J.; Na, R. Matching between the diameter of the aggregates of hydrophobically associating polymers and reservoir pore-throat size during polymer flooding in an offshore oilfield. J. Pet. Sci. Eng. 2019, 177, 558–569.
(33) Lu, X.; Wang, S.; Wang, R.; Wang, H.; Zhang, S. Adaptability of a deep profile control agent to reservoirs: Taking the lamadian oilfield in Daqing as an example. Pet. Explor. Dev. 2011, 38, 576–582.