Performance Evaluation and Plugging Characteristics of Controllable Self-Aggregating Colloidal Particle Profile Control Agent

Zhiguo Yang, Xiangan Yue, Minglu Shao, Yang Yue, Tianqi Yue

Abstract—In low permeability reservoirs, the reservoir pore throat is small and the micro heterogeneity is prominent. Conventional microsphere profile control agents generally have good injectability but poor plugging effect; however, profile control agents with good plugging effect generally have poor injectability, which makes it difficult for agent to realize deep profile control of reservoir. To solve this problem, styrene and acrylamide were used as monomers in the laboratory. Emulsion polymerization was used to prepare the Controllable Self-Aggregating Colloidal Particle (CSA), which was rich in amide group. The CSA microsphere dispersion solution with a particle diameter smaller than the pore throat diameter was injected into the reservoir to ensure that the profile control agent had good inject ability. After dispersing the CSA microsphere to the deep part of the reservoir, the CSA microspheres dispersed in static for a certain period of time will self-aggregate into large-sized particle clusters to achieve plugging of hypertonic channels. The CSA microsphere has the characteristics of low expansion and avoids shear fracture in the process of migration. It can be observed by transmission electron microscope that CSA microspheres still maintain regular and uniform spherical and core-shell heterogeneous structure after aging at 100 ºC for 35 days, and CSA microspheres have good thermal stability. The results of bottle test showed that with the increase of cation concentration, the aggregation time of CSA microspheres gradually shortened, and the influence of divalent cations was greater than that of monovalent ions. Physical simulation experiments show that CSA microspheres have good injectability, and the aggregated CSA particle clusters can produce effective plugging and migrate to the deep part of the reservoir for profile control.

Keywords—Heterogeneous reservoir; deep profile control; emulsion polymerization; colloidal particles, plugging characteristic.

I. INTRODUCTION

LOW permeability reservoirs have poor pore permeability, small pore throats, low permeability, and complex pore structures. During the water injection development process, there are problems such as serious water channeling and low recovery, and the development effect is not ideal [1]-[3]. Therefore, how to effectively prevent and control the scouring of injected water in low permeability reservoirs, expand the wave volume and drive the remaining oil are of great significance to improve the recovery of reservoirs [4], [5].

For low permeability reservoir dissection, there is often a situation that "what can be injected cannot be plugged" or "what can be plugged cannot be injected", thus affecting the effect of

dissection [6], [7]. After the microsphere dispersion system enters the oil layer, it can accumulate at the throat through adsorption, retention, bridge blocking and elastic blocking to produce blocking and resistance to the water flow, thus reducing the permeability of the water-splitting layer, causing the subsequent water to bypass the flow, rippling through the unsplitting area and tapping the remaining oil, thus achieving the purpose of preventing water-splitting and improving the recovery rate [8]-[11]. However, due to the low permeability and complex pore throat structure, the injectivity of microspheres is required to be high, at the same time, low permeability reservoirs are highly heterogeneous, fractures are developed, and microspheres of larger particle size are susceptible to shear during transport, which cannot achieve the expected indoor evaluation effect in the field. In order to effectively alleviate the contradiction between injection ability and deep dissection, polyacrylamide microspheres with controllable particle size and strong water absorption and swelling properties were developed. It starts from the matching relationship between microsphere size and reservoir pore throat, and injects undissolved microspheres into the formation, which can expand to several times the original size of elastic microspheres after water absorption and expansion, thus sealing the high permeability water flow channel, which to a certain extent alleviates the contradiction between microsphere injection ability and deep dissection [12]-[14]. For example, [15] used reverse-phase micro emulsion polymerization to synthesize nano-micron acrylamide microspheres as a dissection agent, which could swell from 0.733 μm to 3.291 μm at 60 ºC, and its water absorption and swelling multiplier could reach 90.5 times. Yu [16] reported temperature- and salt-resistant amphiphilic polyacrylamide microspheres, which could swell from 50 nm to 634 nm in particle size with a water absorption swelling multiple of more than 2000 after full dissolution in simulated water at 70 ºC. However, the excessive pursuit of maximizing the swelling performance of the microspheres leads to the easy shear fragmentation of the dissolved microspheres in the process of transporting to the deeper part, thus seriously affecting the dissection effect of the microspheres.

In order to solve the contradiction between microsphere injectivity and deep dissection, in this paper, CSA-seal, a nano-sized polymeric microsphere dissection agent with low swelling

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multiplier and controllable particle size, was prepared by emulsion polymerization using styrene and acrylamide as monomers and ammonium persulfate as initiator, and a self-aggregating seal of microspheres was proposed. CSA-seal microspheres with a particle size smaller than the diameter of the pore throat were injected into the reservoir to solve the problem of injection ability for the microspheres. When the dispersed microspheres migrate to the deep part of the reservoir, they will aggregate into large particle clusters under the action of physicochemical effects, and the particle clusters will block the channeling channels [17], [18]. This study provides an idea to effectively solve the contradiction between injection ability and deep sealing of microspheres in low permeability reservoirs.

II. EXPERIMENT

A. Experimental Reagents and Instruments

Experimental reagents included sodium chloride (NaCl), calcium chloride (CaCl$_2$), potassium chloride (KCl), magnesium chloride (MgCl$_2$), acrylamide (AM), styrene (PS), N,N'-methylenebisacrylamide (MBA), ammonium persulfate (APS) and vitamin C (Vc) with all of analytical purity grade, fatty alcohol polyoxyethylene ether sodium sulfate (AES), industrial grade, effective content 70%.

Experimental instruments included NanoBrook 90plus zeta potential laser particle size analyzer; Transmission Electron Microscope (JEM 2100 LaB6); Atomic Force Microscope (5500AFM).

B. Preparation of Polymeric Microspheres

Firstly, 12.5 g of acrylamide, 2.5 g of MBA, and 0.4 g of sodium fatty alcohol polyoxyethylene ether sulfate were dissolved in 400 mL of deionized water to prepare the aqueous phase, and stirred well. Secondly, 120 g styrene were added, then added 0.3 g APS catalyst after styrene pre-emulsified for 20 min. Finally, the mixed solution was poured into a four-neck flask. The reaction temperature of the control system was set to 70 ºC, the speed was 600 rpm, and the reaction was terminated by adding hydroquinone after 5 h. After cooling, filtering and washing, CSA was obtained.

C. Particle Size and Turgidity Performance Analysis

Aqueous dispersion solution of CSA microspheres with a mass concentration of 1000 mg/L was prepared using deionized water and placed in a constant temperature water bath at 60 ºC. The particle size of the microspheres was measured at regular intervals using a zeta-potential laser particle size analyzer, and the water absorption turgidity was calculated.

$$\text{turgidity} = \frac{V_1}{V_0}$$

where V_0 was the particle size of CSA-seal microspheres before dissolution, nm, V_1 was the size after swelling, nm.

D. Thermal Stability Analysis

The aqueous dispersion of CSA microspheres with a mass concentration of 1000 mg/L was placed in an aging tank and then placed in a 100 ºC thermostat, and the morphology of the microspheres was observed by JEM 2100 LaB6 transmission electron microscope after 1, 3 and 5 weeks of aging to evaluate their thermal stability.

E. Self-Aggregation Performance

Under stirring conditions, 1000 mg/L microsphere emulsion was prepared with simulated water, then it was sealed in a 100 mL blue-capped test bottle, ultrasonically dispersed for 5 minutes and placed in a 60 ºC water bath. The microsphere solution in the test bottle was observed at regular intervals for the appearance of agglomerates, and the time of agglomerate appearance was defined as the self-aggregation time. The composition of each ion in the simulated water is shown in Table I.

TABLE I
THE COMPOSITIONAL ANALYSIS OF THE SIMULATED WATER

Ion Type	K$^+$/Na$^+$	Ca^{2+}	Mg^{2+}	Cl$^-$	SO4^{2-}	HCO$_3^-$	Mineralization
Mass concentration / mg·L^{-1}	3743	421	45	5510	124	157	10000

F. Core Replacement Evaluation

We used artificial core replacement experiments to simulate the plugging properties of microspheres in the formation. The core was firstly pumped at a constant temperature of 60 ºC, and the water drive was 1.8 PV and then transferred to inject 1000 mg/L CSA microspheres 0.5 PV, and the pump was turned off, the outlet and inlet valves were turned off for a certain period of time, and the subsequent water drive was performed until the pressure was stable, and the pressure changes at each stage were recorded. The water drive rate was 1.0 mL/min and the injection rate of microspheres was 0.5 mL/min. The experimental water was simulated.

III. RESULTS AND DISCUSSION

A. Particle Size and Swelling Performance Analysis

The particle size and swelling properties of polymer microspheres have an important influence on the dissection effect of microspheres. Only the particle size of microspheres is small enough to enter the deep part of the reservoir smoothly, and then seal the high permeability of the water tampering layer to achieve the purpose of oil stabilization and water control. The particle size distribution of the prepared CSA microspheres is shown in Fig. 1. The particle size was distributed from 141.8 nm to 531.2 nm, and the average particle size was 250.7 nm. Table II shows the average particle size of CSA microspheres after different times of expansion. As shown in Table II, CSA

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microspheres can be swollen to 307.6 nm in a short time (6h) with a swelling multiple of 1.85. This is due to the small particle size and large specific surface area of microspheres, and therefore the rapid expansion rate relative to micron-sized microspheres. In addition, it can be seen from Table II that the expansion multiplier is still less than 2 when the microspheres reach expansion equilibrium. This indicates that the prepared CSA microspheres have limited low swelling characteristics, while conventional bulk-expanding polyacrylamide microspheres, which can swell tens or even hundreds of times, lead to a significant reduction in microsphere strength due to the excessive swelling multiples. Therefore, in the process of transporting traditional bulk microspheres to the deep part of the reservoir, they are easily sheared and broken, and lose the function of deep dissection. The prepared CSA microspheres with low swelling characteristics can effectively avoid the problem of shear fragmentation caused by excessive swelling multiples and ensure that the initial strength is maintained when transported to the deeper part of the reservoir.

TABLE II
AVERAGE PARTICLE SIZE OF CSA-SEAL MICROSPHERES AFTER DIFFERENT SWELLING TIMES

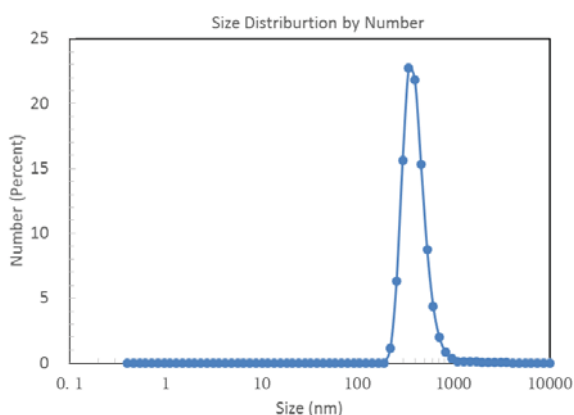| Swelling time	0	1h	6h	12h	24h	36h
size/nm	250.7	281.4	307.6	311.5	314	315
turgidity	1	1.41	1.85	1.91	1.96	1.98

Fig. 1 Particle size distribution of CSA microspheres

B. Thermal Stability of Microspheres

High formation temperature and mineralization will seriously affect the stability of the microspheres. Excessive temperature will cause thermal decomposition of the molecular chains inside the microspheres and destroy the structure of the microspheres, thus affecting the effect of drive conditioning [19], [20]. Fig. 2 shows the JEM images of CSA microspheres aged at 110 ºC for different times. From Fig. 2, it can be seen that the particle size of microspheres increases after a period of aging, but still has a regular spherical shape, and the thermal stability of microspheres is stronger. Since CSA microspheres are polymerized with styrene and acrylamide as monomers, the microspheres contain rigid styrene chain segments inside the microspheres, and therefore, the microspheres have good temperature resistance. In addition, from the JEM images, it can be clearly observed that the CSA microspheres have a non-homogeneous core-shell structure with a denser polymer core at the center and a more loosely cross-linked polymer shell layer at the periphery. This is due to the fact that during the preparation of microspheres, styrene is the inner phase and the aqueous acrylamide solution is the outer phase, thus forming a polymerization medium in which the aqueous acrylamide solution wraps the styrene emulsion droplets. The primary radicals generated by the initiator enter the styrene emulsion droplets and initiate polymerization, and the resulting monomer radicals can trap the acrylamide monomer in the outer phase, thus forming microspheres with a core-shell structure.
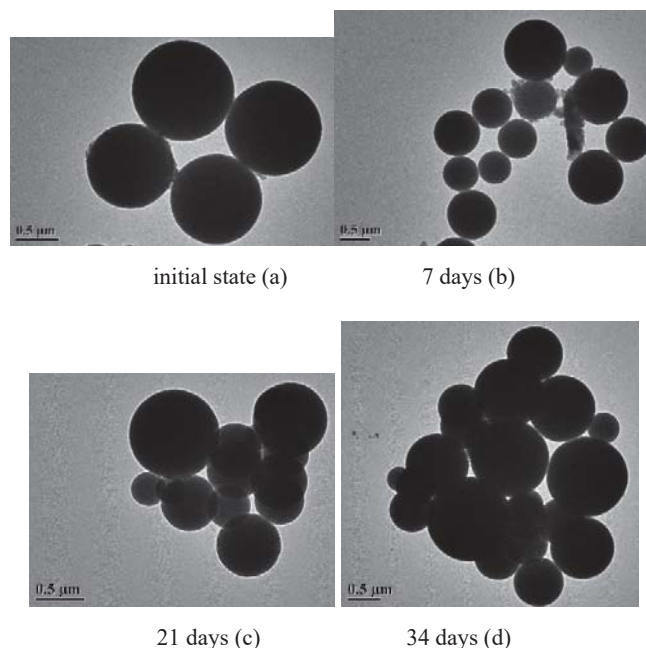

initial state (a)　　　7 days (b)

21 days (c)　　　34 days (d)

Fig 2 JEM images of CSA-seal microspheres in different periods

C. Self-Aggregation Performance

It is known from JEM images that the CSA microspheres have a non-homogeneous core-shell structure, and the shell of the microspheres is mainly dominated by the acrylamide chain segment, as the amide group will be partially hydrolyzed in water to form -COO-, making the microspheres negatively charged, and when the negatively charged microspheres meet with cations they will attract each other, thus destabilizing the solution of the microspheres and causing the microspheres to agglomerate and form clusters of microsphere particles. In addition, due to the small particle size of the microspheres, the large phase interface and the high Gibbs free energy on the surface, the microspheres tend to aggregate each other, which is the theoretical basis for the self-aggregation and blocking of the microspheres [21]-[23]. Since, the injection process of microspheres and the transport process to the deep requires a certain time, if the microsphere aggregation time is too fast, it will lead to the cluster of microsphere particles blocking the near-well zone and cannot achieve deep dissection, so the study of the microsphere aggregation time is of great significance.

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1. Effect of Cations on the Self-Aggregation Time of Microspheres

From Figs. 3 (a) and (b), it can be seen that the self-aggregation time of microspheres gradually shortens with the increase of ionic strength, and the effect of divalent ions on the self-aggregation time of microspheres is more obvious than that of monovalent ions. When NaCl and KCl are added at 25000 mg/L, the self-aggregation time of microspheres is already less than 20 h, while when $CaCl_2$ and $MgCl_2$ are added at only 1000 mg/L, the self-aggregation time is already less than 15 h. This is because divalent cations carry more charge relative to monovalent cations. In addition to electrostatic attraction, Ca^{2+} and Mg^{2+} can also combine with -COO- through covalent bonding, which has a bridging effect between microspheres (Fig. 4), resulting in faster agglomeration and sinking of microspheres. Therefore, it has a greater effect on the self-agglomeration time of microspheres. For ions with the same valence, the smaller hydration diameters of K^+ (3 Å) and Ca^{2+} (6 Å) cations are more likely to come into contact with negatively charged microspheres than Na^+ (4.5 Å) and Mg^{2+} (8 Å) [24], therefore, it has a more pronounced effect on the self-aggregation time of microspheres.
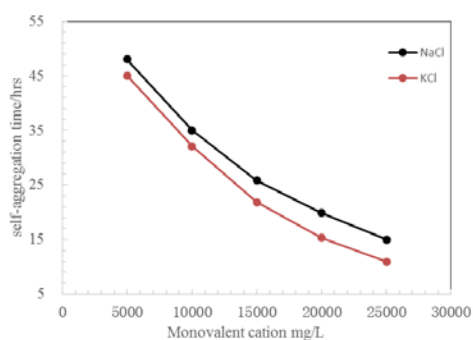
(a) monovalent cation
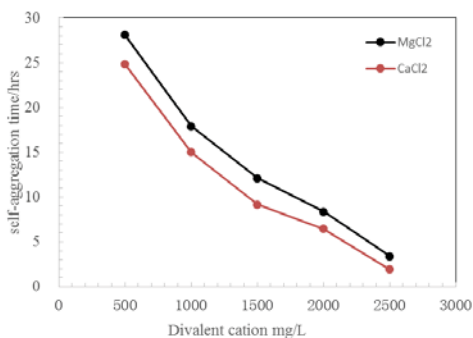
(b) divalent cation

Fig. 3 Effect of ion types and concentration on self-aggregation time

2. Effect of Temperature on Self-Aggregation Time of Microspheres

Fig. 5 shows the variation of self-aggregation time of microspheres in simulated water with temperature. As shown in Fig. 5, with the increase of temperature, the trend of self-aggregation time decreases gradually, and when the temperature increases from 50 ºC to 75 ºC, the self-aggregation time decreases from 39 h to 17 h. An increase in temperature will cause more frequent inter-particle contact, thus reducing the stability of the microsphere solution and resulting in a decrease in self-aggregation time. Fig. 6 shows the state of the microsphere solution before and after aggregation at 60 ºC. It can be clearly observed from Fig. 6 (a) that the microspheres can be uniformly dispersed in the simulated water, while after self-aggregation, large clusters of particles were formed and settled at the bottom of the beaker (Fig. 6 (b)). AFM observation of the particle clusters in the beaker clearly shows that the microspheres in the particle clusters are squeezed together with each other (Fig. 6 (c)), which fully demonstrates that the CSA has some elastic deformation ability.
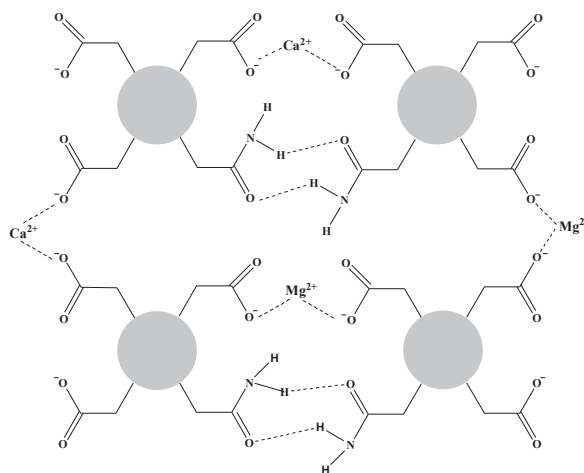

Fig. 4 Schematic diagram of complexation between bivalent cations and microspheres
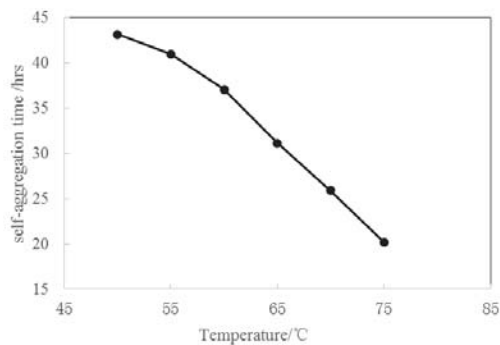

Fig. 5 Effect of temperature on self-aggregation time

The above analysis showed that the prepared CSA microspheres can form microsphere clusters with larger particle size under the action of cations in the groundwater, and the self-aggregation time of CSA microspheres can be changed by changing the cation content. Therefore, the self-aggregation property of CSA microspheres can be fully utilized to inject the dispersion solution of microspheres with particle size much smaller than the pore throat size into the formation, and under the action of cations, the microspheres will self-aggregate into particle clusters, so as to seal the larger pore throat of the high permeability layer and achieve the purpose of deep dissection.
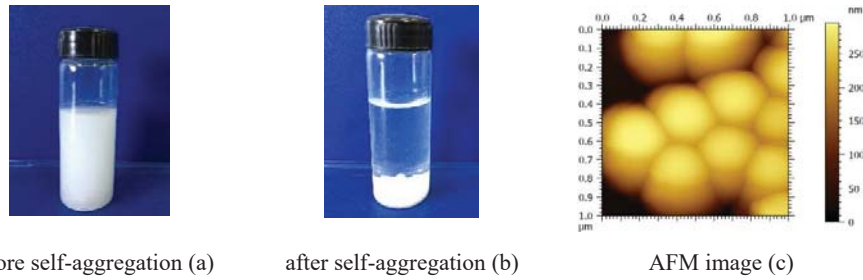
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before self-aggregation (a)   after self-aggregation (b)   AFM image (c)

Fig. 6 States of microsphere solution (before self-aggregation (a), after self-aggregation (b)) and AFM image (c) (60ºC)

D. Core Evaluation

In order to verify that the microspheres can seal the large pore throat of the high permeability layer by self-aggregation, a core with the size of 30×2.5 cm, its water phase permeability of 16.98×10^{-3} μm^2 and average porosity of 13.3% was selected for sealing evaluation experiments. According to the Kozeny model equation, the equivalent pore radius of the core is 1.01 μm about 4.04 times the average diameter of the microspheres. The scanning electron microscopy shows that the aggregated CSA particles accumulate in clusters and dispersion at the core pore throat, as shown in Fig. 7. According to the 1/3 bridging theory of Abrams, microspheres of this size are not able to form an effective seal, and if a seal is produced, it can be proved that it is feasible to seal the high permeability water tampering layer by self-aggregation of microspheres.
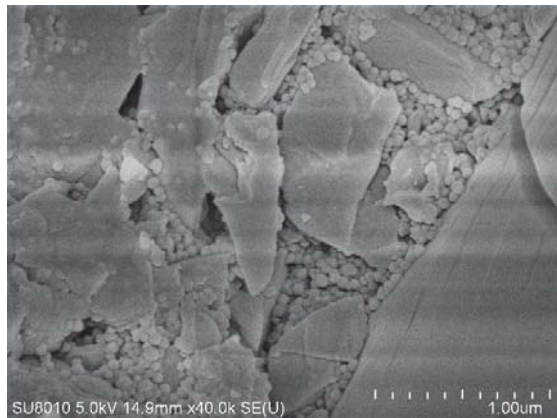

Fig. 7 SEM images of microsphere aggregation

During the core replacement experiment (Fig. 8), the pressure at each measurement point started to rise significantly after the injection of 0.3 PV of CSA polymer microspheres. When 0.5 PV was injected, the pressure at all three measurement points in the 0~15 cm core section increased by 100 kPa compared to the water drive stage, and the pressure at the three measurement points in the 15-30 cm core section increased by 50 kPa compared to the pressure at the water drive stage. It indicated that after reaching a certain injection volume, the CSA microspheres start to increase the pore throat resistance to achieve seepage reduction and sealing due to the self-aggregation effect, and the injectability of CSA microspheres was better. The pressure at each measurement point in the core increased by about 500 kPa compared with the

water drive stage, and the resistance coefficient reached 1.83, which reduced the permeability of the scouring channel, the purpose of deep dissection was achieved.
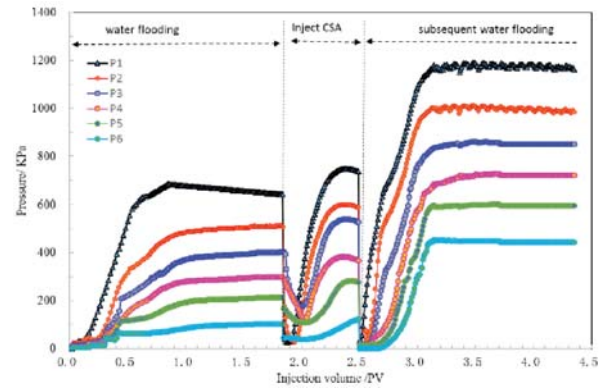
Injection pressure (a)
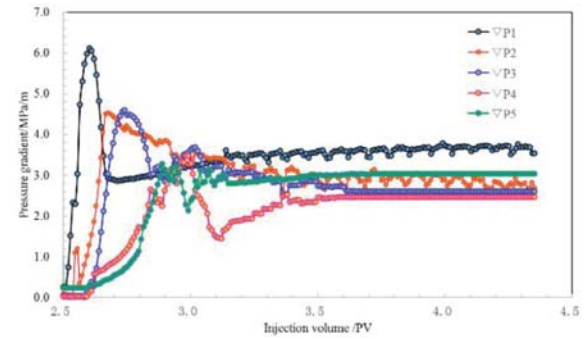
Subsequent water drive pressure gradient (b)

Fig. 8 Characteristic curve of the injection pressure (a) and pressure gradient (b)

The variation of pressure gradient in each section of the core during the subsequent water drive phase of microsphere static aggregation is shown in Fig. 8 (b). Due to the end effect, the pressure gradient at the injection end and outlet end is larger than the pressure gradient in the middle section of the core during the repulsion process. After injecting CSA polymer microspheres 0.5PV and standing to make the microspheres fully aggregated, the pressure gradient of $\triangledown P\,1$ and $\triangledown P\,2$ in the subsequent water drive stage showed sawtooth-shaped fluctuations. The process of pressure rise and release caused by CSA polymer particle clusters at the pore throat indicates that the microspheres break through and move forward from the

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already assembled and blocked throat under a certain pressure gradient, and then continue to accumulate and block the later throat, indicating that CSA polymer microspheres can still extend the high permeability flow channel to the deeper part of the reservoir in the subsequent water flooding stage to achieve deep dissection.

IV. CONCLUSION

1. In this paper, a submicron-sized CSA microsphere with good temperature resistance and low expansion factor was prepared by emulsion polymerization because the expansion factor of conventional bulk polyacrylamide microspheres is too high and it is easy to shear and break during the transportation to the deeper part of the reservoir.

2. In response to the contradiction between the injectability of microsphere regulator and deep regulating, the self-aggregating seal of microsphere is proposed. CSA microsphere dispersion solution, whose particle size is much smaller than the pore throat diameter, is injected into the reservoir, and after transported to the deep part of the reservoir, the microspheres can self-agglomerate into large-sized particle clusters under the effect of physicochemical effects, thus realizing the sealing of fluid channels.

3. With the increase of cation concentration, the aggregation time of CSA microspheres gradually shortens, and the effect of divalent cations is greater than that of monovalent ions. By adjusting the cation concentration, the self-aggregation time of CSA microspheres can be controlled.

4. The core simulation plugging experiments show that when the average pore diameter is about 4.04 times of the average diameter of microspheres, it can effectively plug the core, increase the pressure of microsphere injection process by 100 kPa, increase the subsequent water drive injection pressure by 500 kPa, and the resistance coefficient can reach 1.83, and it can transport in the reservoir high permeability channel and achieve the effect of deep dissection.

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