Synthesis and Performance Evaluation of High-Temperature and High-Salinity Tolerance Polymer Microspheres

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(Received on 19th April 2016, accepted in revised form 29th December 2016)

Summary: Various technical problems are currently encountered in using regular plugging agents. The performance of this agent in terms of high temperature and salinity tolerance is poor. The cross-linking reaction time is difficult to control and the valid period of the operation measures is short. This study system of deep profile control and water shutoff was researched for high-temperature and high-salinity reservoirs. The microstructure of divinylbenzene-co-acrylamide microspheres were designed according to the principle of deep profile control and water shutoff. Scanning electron microscopy tests, showed that the interior of the microspheres was hollow and that the shell had a nanoporous structure. The basic performance of the microspheres was evaluated, including high temperature thermal stability, injection and plugging ability and plugging effect at 115 °C. Results showed that after 180 days, the microspheres did not appear to be carbonized. The residual resistance coefficient of the injection experiment was greater than 2. Only microsphere plugging slug was used. The amplitude of enhanced oil recovery reached 7 %. Domestic oil field tests showed that, by increasing the amount of oil by 5.11 t each day after profile control, the general water percentage decreased from 64.11 % to 32.08 %.

Keywords: High-temperature and high-salinity; Microspheres; Performance evaluation; Deep profile control.

Introduction

In the extant literature, on the field of stabilizing oil production and controlling the water in horizontal well water implementation trials, studies on high-temperature and high-salinity reservoirs abroad are seldom reported. Shizigou reservoirs of Qinghai Oilfield is low temperature and ultra-high salt reservoirs for domestic production [1-2]. The Zaoyuan Oilfield of Dagang and low-permeability reservoirs of Changqing Oilfield has low high-temperature and salinity reservoirs [3-4]. The Jin 45 block reservoirs of the North China Oilfield have medium high-temperature and salinity reservoirs [5]. The Qinghai Oilfield Gasikule E_3^1 reservoirs, Zhongyuan Oilfield, Tarim Oilfield, and Tahe Oilfield have the ultra-temperature and salt reservoirs [6-9]. Given that the above-mentioned oilfields entering the middle and late stages of development, the problems of stabilizing oil production and controlling water to enhance oil recovery urgently need to be solved. The profile and shutoff jobs of the above reservoirs were implemented, and technical applications had certain effects. However, no further reports were started on the continuous promotion and large-scale applications of these technologies. Thus, profile control and water shutoff are still considered technical problems for high-temperature and high-salinity reservoirs. Given that the conventional agents of profile control and water shutoff have many disadvantages, their performance in terms of high temperature and salinity tolerance is poor. Their cross-linking reaction time is difficult to control, and the validity period of the operation measures is short. A system with high temperature and salinity tolerance should be further studied. In recent years, deep profile control and water shutoff have been implemented in reservoirs using the new technology of the polymer microspheres.

Polymer microspheres are currently used in the deep profile control of oilfields mainly by inverse emulsion polymerization, inverse suspension polymerization and dispersion polymerization. Polymer microspheres are mainly copolymers of acrylamide (AM) and methylene-bis-acrylamide. According to the mechanism of their deep profile, microspheres can be divided into three categories.

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In the first category, the initial particle size of microspheres is in nanometers or micrometers. After swelling water of the microspheres, the water channel was plugged through bridging [10-12]. In the second category, the initial particle size of the microspheres was nanometers or micrometers. The molecular segments of the microspheres interact with calcium and magnesium ions to form a network structure after swelling water. The water channel was plugged using a network structure [13]. In the third category, oppositely charged leads to mutual adhesion and plugs the water channel after the expansion of the microspheres [14].

Profile control agent microspheres were successfully applied in the domestic part of medium-high permeability reservoirs and achieved good effect of profile control and water shutoff in the first category. The microspheres were of the water-swellable type. The microspheres could be easily broken during transport when the multiple series of their expansion was too large. After reaching the deep reservoirs, plugging efficiency was significantly reduced. If the multiple expansions were too small, the deformation capacity of the microspheres was poor. Transporting the pore and throat of reservoirs is and was easy to cause pollution and plugging of the reservoirs near the injection well. It was not able to achieve deep profile control of the reservoirs [15-16].

Microspheres profile control agent entails serious requirements for the reservoir environment. Water formation must contain high calcium and magnesium ions in the second category.

In the third category, the external part of the microspheres has a negative charge and can be dissolved in water to swell. The inner layer includes a cross-linked gel with a positive charge. The swelling speed of the inner layer in water is faster than at the outer layer component. Thus, when volume expansion reaches a certain extent, a positive charge is exposed. The microspheres have opposite charges, which occurred the adsorption each other to plug ability. However, such microspheres are easily plugged near well bore area.

At the same time, the temperature resistance of these three categories of microspheres is poor. The adaptation reservoir temperature ranges from 70 °C to 80 °C. In this study, divinylbenzene (DVB)-co-AM (DCA) microspheres of high temperature and salinity tolerance were copolymerized between DVB and AM. The performance of DCA microspheres was intensively investigated.

Experimental

Equipment

A DF-101S heat collector and thermostatic heating magnetic stirrer were purchased from HenanYuHua Instrument Co. Ltd. An SC-3610 low-speed centrifuge was purchased from Anhui USTC Zonkia Scientific Instrument Co. Ltd. An FEI Quanta 200 scanning electron microscope was purchased from FEI Co., the Netherlands. An MAGNA-IR 560 E.S.P Fourier transform infrared spectrometer was purchased from American Nicolet Co. Ltd, USA. Zetasizer Nano ZS was purchased from Malvern Instruments Co. Ltd, UK. An NETZSCH STA409PC thermogravimetric analyzer was purchased from NETZSCH Instruments Manufacturing Co. Ltd, Germany. A Zeiss optical microscope was obtained from Suzhou Matsushita Communication Industrial Co. Ltd. A KQ3200B Ultrasonic Cleaner was purchased from Kunshan Ultrasonic Instrument Co. Ltd.

Chemical Reagents

AM, purchased from Puyang Biological Chemical Co. Ltd, was used as a polymerized monomer. DVB, purchased from Beijing Chemicals Co. Ltd, was used as a crosslinked agent. 2,2-Azobisisobutyronitrile (AIBN), purchased from Puyang Biological Chemical Co. Ltd, was used as initiator. Sodium alcohol ether sulphate (AES) and polyoxyethylene sorbitan fatty acid ester (Span80), purchased from Beijing Chemicals Co. Ltd, were used as emulsifier. Ethanol was used as solvent. Oil and brine samples were collected from a domestic oilfield. The salinity of simulated water was 269000 mg/L. Major ionic composition of the analysis of the formation brine was shown in Table-1. The core, which was independently developed in a laboratory, was used in the physical simulation experiments.

Table 1 Analysis of formation brine from a domestic oilfield

Ion content (mg/L)						
Na^+、K^+	Ca^{2+}、Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	Fe^{3+}	Ba^{2+}、Sr^{2+}
91770	20240	157000	328	12.8	20	936.7

Synthesis of DCA Microspheres

A certain amount of AM and AES was dissolved in 100 mL deionized water to obtain an aqueous phase. A certain amount of Span80 and AIBN was dissolved in DVB to obtain an oil phase. The oil phase was poured into a 150 mL beaker. A water bath with constant temperature was made available. The magnetic stirring rate was set to 170 rpm. An appropriate amount of aqueous phase was added to the oil phase. After pre-emulsification for certain period of time, the remaining aqueous phase was added to the oil phase. The water temperature was set at a constant 70 °C. After about six hours, the reaction ended. The emulsion was centrifuged at 3500 rpm for 20 minutes to obtain a solid. The solid was washed with ethanol three times and dried for 24 h in vacuum at 50 °C. White powdery solid DCA microsphere was obtained. The reaction of AM and DVB is shown in Fig. 1.

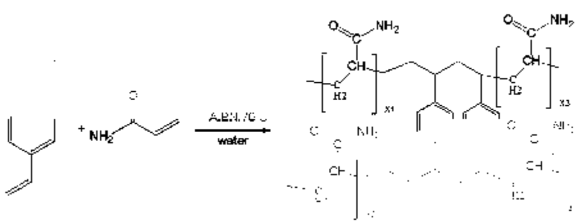

Fig. 1: Reaction of emulsion polymerization of AM and DVB.

High-Temperature Thermal Stability of DCA Microsphere

The DCA microsphere solution was placed in a high-temperature reaction tank. The experimental temperature simulated a target reservoir temperature of 115 °C. The thermal stability of the DCA microsphere was investigated. A sample of the DCA microsphere was taken at intervals. The microstructure of the DCA microspheres was observed using Zeiss optical microscope at 400 magnification.

Injection and Plugging Ability

The injection and plugging ability of the DCA microsphere were evaluated using an artificial homogeneous columnar core with a diameter of 2.5 cm and length of 30 cm at 115 °C. The gas permeability was 800×10^{-3}μm^2. Fig. 2 shows the experimental flow chart.

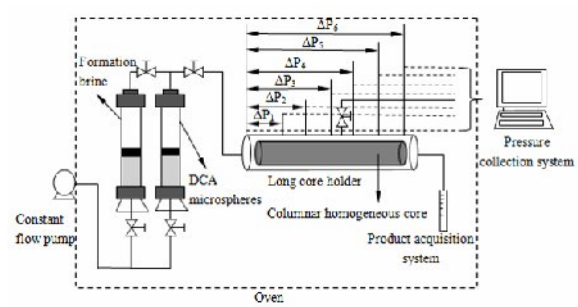

Fig. 2: Experimental flow chart of injection and plugging ability.

1. The phase of the water permeability test. The flooding speed of ISCO advection pump was 8.8 m/d. The distribution location of the measurement pressure points of the core was 5, 10, 15, 20, and 25 cm. 2. The phase of the injection microspheres. The flooding speed was 8.8 m/d. The pressure distribution along the cylindrical core was monitored in real time. The microsphere injected the amount of 1.7 pore volume (PV). 3. The phase of subsequent water flooding. The flooding speed was 8.8 m/d. Subsequent water flooding injected the amount of 1.96 PV.

Evaluation of Plugging Effect of DCA Microspheres

The plugging effect of the DCA microsphere was evaluated using three layers of the heterogeneous artificial core. The length, width and height of the core were 30, 4.5, and 4.5 cm respectively. The thickness of each layer was 1.5 cm. The distribution of the longitudinal gas measured permeability of each layer was 200×10^{-3} μm^2, 500×10^{-3} μm^2 and 800×10^{-3} μm^2. Fig. 3 shows the model.

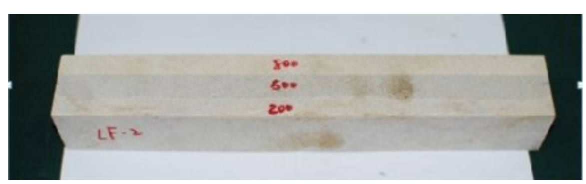

Fig. 3: The size of three layers of heterogeneous artificial core: 30 cm×4.5 cm×4.5cm.

Three layers of the heterogeneous artificial core were placed in the holder according to positive rhythm. A similar experimental flowchart is shown in Fig. 4. The phase of water displacing oil. The flooding speed of the ISCO advection pump was 3 m/d. The pressure distribution along the core was monitored in real time. Flooding continued until the produced fluid was saturated with oil. The phase of injection microspheres. The flooding speed was 12 m/d. The microspheres injected the amount of 1.7 PV. The phase of subsequent water flooding. Flooding speed was 3 m/d, and subsequent water flooding injected the amount of 2 PV.

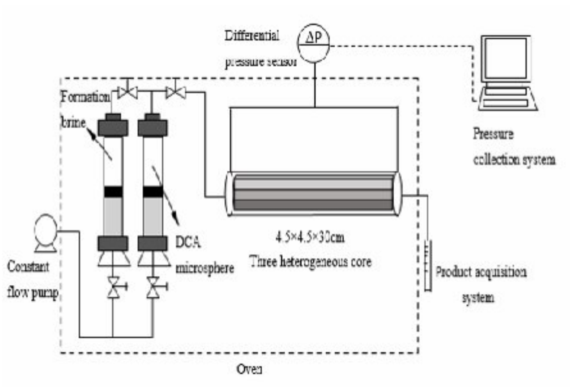

Fig. 4: Experimental flow chart of evaluation of plugging effect of DCA microsphere.

Results and discussion

Design Ideas and Microstructure of the DCA Microsphere

To achieve a better plugging effect, the following special performance requirements are proposed for the material of deep profile control and water shutoff: “injection in reservoirs,” “better plugging effect,” “better migration,” and “long life,” In “injection in reservoirs,” the materials are required to have good stability in water. In “better plugging effect,” the microspheres implement bridging and plugging through covalent bonds between the surface molecular chain of the microspheres in the pore and throat to generate flow resistance. In “better migration,” polymer microspheres can break, migrate and enter the deep reservoirs under certain conditions of pressure. In “long life,” the material degradation of the microspheres does not occur under the conditions of high temperature and high salinity. Based on the above performance requirements, a nanometer and micrometer DCA microsphere was synthesized by emulsion polymerization.

Fig. 5 shows the SEM photograph of the microstructure of the microspheres and crushed microspheres. As shown in Fig. 5a, b and c, the particle size of DCA microspheres is 25 µm, and they have a hollow structure. The thickness of the cross-linked polymer layer is 12.79 µm. The initial judgment of the DCA microspheres shows that they have better suspension in line with the performance requirements of “injection in reservoirs". The shell of the microspheres consists of nanoporous materials. The droplets of the emulsion are in the form of oil-in-water presence during the pre-emulsification phase. As the reaction continues, water does not result in the solvation or only extremely small solvation of the oligomers of the excluded AM and those containing AM structural unit. Compared with no water, the length of the critical precipitation chain was basically unchanged. Thus, the oligomers of the excluded AM and those containing an AM structural unit firstly precipitate from the solution and participate in a nucleating during the reaction process. Two kinds of oligomers contain more structural units of DVB. Thus, the formation of putamen is more closely. However, with the reaction progress, the oligomer, which does not precipitate and later precipitates AM structural units or more pure AM and monomer free radicals is constantly trapped by the microsphere core from the solvent to achieve the particle size growth of the microspheres. These trapped oligomers have not only longer molecular chains, but also less structural units of DVB. The oligomers can not be closely integrated with the putamen. Thus, the formation of microspheres ultimately has a close putamen and loose shell. As shown in Fig. 5d, the surface of shell has the structure of the hydration layer of an AM segment.

IR Characterization of DCA Microspheres

The synthesis conditions of the double reaction are identical. Fig. 6 shows the Fourier transform infrared spectroscopy of the product of the DCA microspheres. The figure shows that the characteristic absorption peak of the DCA microspheres in the two experiments by synthesis substantially have the same tendency. The vibration absorption peak of the benzene ring is υ (C=C) at 1601 cm^{-1} and υ (=C-H) at 3190 cm^{-1}, which indicates that DVB is crosslinked into the copolymer. The vibration absorption peak of the amide group is υ (C=O) at 1660 cm^{-1} and υ (-N-H) at 3450 cm^{-1}. The vibration absorption peak is at 2920 cm^{-1} because of the υ (C-H) of ($-CH_2-$) or (-CH-) bond. The above findings show that the polymerization of AM and DVB successfully prepares the crosslinked polymer microspheres of the poly (DVB -co- AM).

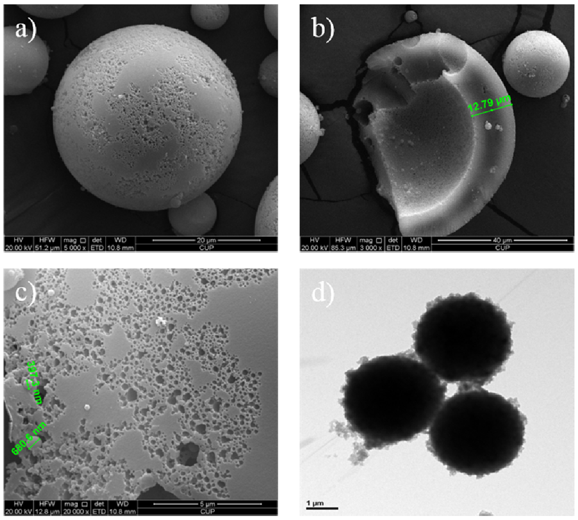

Fig. 5: External structure (a), internal structure (b) and external microstructure (c) of DCA microspheres. Microstructure of DCA microspheres in water (d).

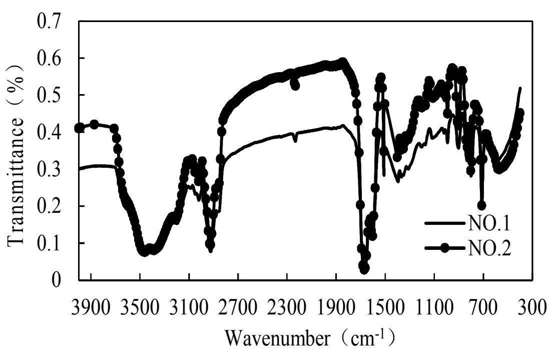

Fig. 6: Fourier transform infrared spectroscopy of the DCA microspheres

High Temperature Thermal Stability

The decomposition temperature of the DCA microspheres is 300 °C. Further qualitative studies are needed on the high temperature thermal stability of the DCA microspheres. The concentration of the DCA microspheres is 1000 mg/L. Fig. 7 shows that the microscopic state of the DCA microspheres is not damaged and is not degraded after 180 days at the experimental temperature of 115 °C. Only a small amount of microspheres exhibit structural deformation, and even then, these microspheres remain spherical to some extent, which meets the design idea of “a long life”. A large amount of microspheres that are not carbonized by high temperature are still suspended in the solution. Thus, the DCA microspheres show good thermal stability for a long period of time.

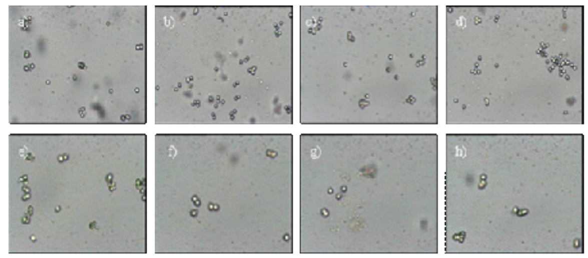

Fig. 7: Microstructure of DCA microspheres in different periods at initial state (a), 24 hours (b), 9 days (c), 30 days (d), 60days (e), 90 days (f), 120 days (g) and 180 days (h).

Injection and Plugging Ability

To determine the plugging ability of the DCA microspheres for large pores and cracks, their injection and plugging ability were evaluated. Fig. 8 shows the diameter distribution of the DCA microspheres in this test. The diameters are mainly 0.41 μm (94.3 %) and 5.47 μm (5.7 %), which satisfy the design requirements of the DCA microsphere size.

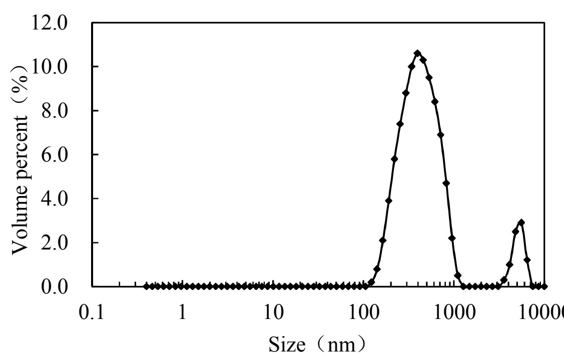

Fig. 8: Diameter distribution of the DCA microsphere.

The concentration of the microspheres at 115 °C is 1000 mg/L. The plugging ability of DCA microspheres is characterized by the resistance coefficient and residual resistance coefficient, which are calculated using of the Eqs. (1) and (2), where R_F is the resistance coefficient, R_K is the residual resistance coefficient, K_1 is water permeability of the core before the injecting of the microspheres, K_2 is the reduced permeability of the core during the injecting of the microspheres, and K_3 is water permeability of the core after the injection of the microspheres.

$$R_F = \frac{K_1}{K_2} \quad (1)$$

$$R_k = \frac{K_3}{K_1} \quad (2)$$

The result of evaluating the injection and plugging ability of the DCA microspheres is shown in Fig. 9. The microspheres have a stable plugging ability to migrate into all the measure points of the core to achieve the deep plugging. As shown in Fig. 10, the residual resistance coefficient along the cylindrical core is greater than 2. Hence, the DCA microspheres show high-strength deep plugging in reservoirs.

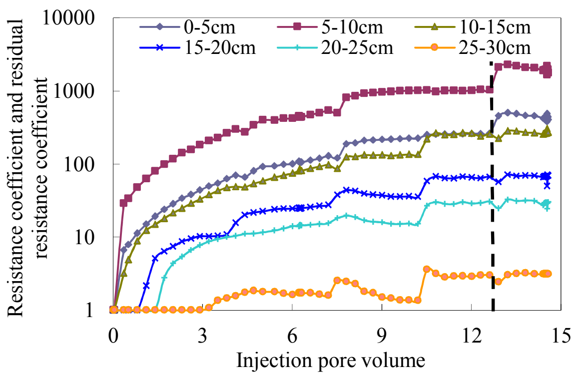

Fig. 9: Resistance coefficient and residual resistance coefficient change with PV each measurement point.

Evaluation of Plugging Ability in Heterogeneous Reservoirs

Based on the control technique of the microsphere diameter and the matching relationship between the diameter and pore constriction, the plugging ability of microspheres in heterogeneous reservoirs was evaluated. The distribution of the main diameter of the DCA microspheres is 0.41 µm (94.3 %) and 5.47 µm (5.7 %). The experiment is investigated at 115 °C, with a microsphere concentration of 1000 mg/L. The experiment consists of three phases: water flooding, injection of microspheres, and subsequent water flooding.

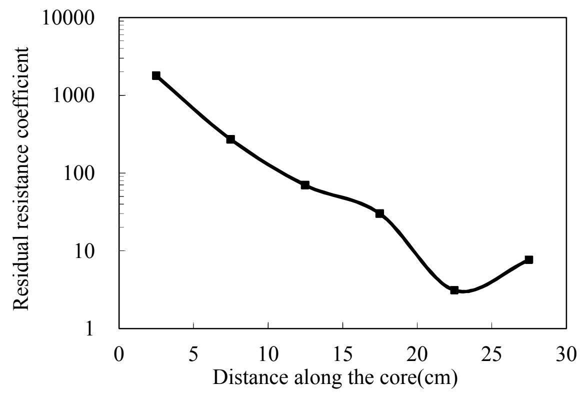

Fig. 10: Residual resistance coefficient change with the distance along the core.

Fig. 11 shows that the water cut drops by 5 % after injecting only the slug of the microspheres. The rate of enhanced oil recovery reaches 7 % in the end. The microspheres flow into the high-permeability layer, preferentially at $800 \times 10^{-3} \mu m^2$. The chain of the acrylamide molecule of the microsphere surface is bridged and blocked in the pore constriction through a covalent bond. The shell of the microspheres has pores in the size of nanometers. These shells slightly swell upon contact with water and also produce flow resistance. The injected water subsequently flows into the low-permeability layers, which are not involved in starting the residual oil. Thus, the subsequent injection of fluid forces the occurrence of flow steering. The remaining oil of the unswept regional, whose relative permeability is lower, is started. Thus, the DCA microspheres adapte well to deep profile control and water shutoff in the high-temperature and high-salinity reservoirs.

Pilot Testing Effect

To optimize the process parameters of the DCA microspheres, a large number of small and pilot scale experiments were performed in a laboratory. The process parameters included types of monomer and emulsifier, usage, reaction temperature, rotation rate, reaction time, and stirring speed. Based on the determination of the process parameters, each step of the industrial production of the DCA microspheres was verified. Each reactor produced two tons of microspheres, which completed the preparation for the pilot testing.

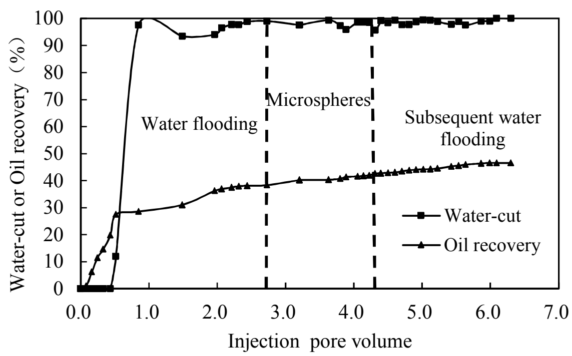

Fig. 11: Plugging effect of the DCA microspheres.

The well group of the domestic oilfield was used for the pilot testing application. The oilfield belongs to reservoirs of low high temperature and salinity. Using DCA microspheres as the main slug, the average diameter was 2.74 μm, which was reasonably combined with different functions of the micro-swap slug.

The profile control of the A well groups started in August 2014 and ended in October 2014. After the construction was completed, the oil production of every production well increased and has remained in high production to date. Before the construction of the profile control was completed, eight production wells in the A well groups had a total production of 25.08 m^3/d, oil production of 7.56 ton/d, and total water cut of 64.11 %. After injecting the profile control agents in the A well groups, oil production increased to 5.11 ton/d, and the total water cut was decreased by 32.08 %. By November 2014, the total oil production in the A well groups increased to 257.4 ton. The profile control test achieved remarkable effects.

Conclusions

The DCA microspheres had a good long-term thermal stability. The particle size of the DCA microspheres could migrate and reach deep reservoirs. The residual resistance coefficient of injection experiment along the cylindrical core was greater than 2.

The rate of enhanced oil recovery reached 7 % in the end after injecting only the slug of microspheres. The DCA microspheres were superior and adapted well to deep profile control and water shutoff in high-temperature and high-salinity reservoirs.

Domestic oilfield tests showed that, in combination with other different functional slugs, the main slug of the DCA microspheres could flow remotely into the reservoirs. After plugging, oil production evidently increased, and the total water cut apparently decreased.

Acknowledgment

This research was financially supported by National Key Scientific and Technological Project (Grant No.2011ZX05009-004) and National Basic Research Program of China (973 Program) (Grant No.2011CB707305).

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