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Experimental Study on the Deep Profile Control and Oil Displacement Technology of Nanoscale Polymer Microspheres

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Abstract: In this paper, scanning electron microscopy (SEM), dynamic lighting scattering (DLS) and HAAKE rheometer experiments were adopted for investigating on the shape, size and rheological property of nanoscale polymer microspheres. Besides, nuclear-pore film filtration, sand packed tube displacement and core displacement experiments were also adopted to study the mechanism of deep profile control and oil displacement of nanoscale polymer microspheres. The results demonstrated that the original shape of the nanoscale polymer microspheres were typically spherical with a size range of 30-60nm. When the microspheres were dispersed in water, the grain diameter of them increased by 3-6 times due to swelling and the poly-dispersed system appeared but the conformation of microspheres still kept spherical. In a certain range of shear rate, the microsphere dispersed system with the concentration of 100-900 mg/L showed apparent shear thickening behavior and would be favorable for increasing the flow resistance of displacing fluid. These microspheres dispersed systems exhibited effective plugging on 0.4μm pore-size nuclear pore film and deep plugging in core and had a higher tendency to form effective plugging to the high permeability layer and drive crude oil of the low permeability layer in parallel sand packed tubes. Cross-linked polymer microspheres could reduce water permeability because microspheres were adsorbed, accumulated and bridged in the pore-throat and the adsorbed layers would be collapsed by pressure and entered into reservoir deeply owing to microspheres' good deformation property. Meanwhile these microspheres would drive crude oil on and in pores/throats while they transported in porous media and thereby achieved the coordinated and simultaneous effects of deep profile control and oil displacement and the ultimate purpose of improving oil recovery.

Keywords: nanoscale polymer microspheres, rheological property, plugging per-

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formance, oil recovery, profile control mechanism, oil displacement mechanism.

1 Introduction

The diagenetic and structural fractures with width of 1μm-20μm develop universally in low permeability reservoirs for their strong diagenesis and dense and fragile rocks [Hood, Nelson, Kamp (2003)]. The problem of low effective circulation channel has become one of the most important problems in the fractured reservoirs. Presently, based on the problems with near-well plug and profile controlling techniques [Ranganathan, Lewis, Mccool, Green and Willhite (1997); Lin, Li, Peng, Ji and Wu (1999)], various in-depth profiling techniques are practiced successfully to enhance oil recovery, among which the cross-linked polymer microspheres are given more concern because of their good resistance to water, high oil temperature and high salinity and their relatively low cost [Rousseau, Chauveteau, Renard, Tabary, Zaitoun, Mallo, Braun and Omari (2005); Frampton, Morgan, Cheung, Munson, Chang and Williams (2004); Zaitoun, Tabary, Rousseau, Pichery, Nouyoux, Mallo and Braun (2007)]. However, utilization of cross-linked polymer microspheres manufactured by the industry is limited to lab studies and small-scale circumstances. Chauveteau, Tabary, Blin, Renard, Rousseau and Faber (2004) from IFP has conducted some research on the primary physical and chemical properties of the linked polymer microspheres, and the results showed that the microspheres present good resistance to high temperature, salinity and sheer. In China, Lin, Guo, Xu, Zhang, Li and Peng (2011) performed a set of experiments to investigate the size and shape of experimental micron-size microspheres prior to and after swelling, followed by the plugging properties of those microspheres. Dong, Li, Lin and Li (2009) studied the swelling and rheological property of polymer micro-gel dispersions. The results demonstrated that the microspheres present good swelling property and unique rheological property. In terms of size, there are certain matching relationship between nanoscale polymer microspheres and diagenetic and structural fractures. However, the plugging properties of nanoscale polymer microspheres and how microspheres plugged the pores were barely studied in previous literature. In this paper, the shape, size, rheological property, plugging properties, profile control mechanism and oil displacement mechanism of the nanoscale polymer microspheres were investigated.

2 Experimental

2.1 Materials

Acrylamide, acrylic acid and NaOH, (AR), provided by Beijing Yili Fine Chemicals Co., Ltd.; Span-60 and Span 80, (CP). Deionized water is filtrated by cellulose microporous membranes with the diameter of 0.22μm. Nuclear-pore membrane with pore size of 0.4μm and thickness of 10μm is provided by China institute of atomic energy. Nanoscale polymer microspheres are synthesized by our laboratory.

2.2 Observation with SEM

The solid powder of nanoscale polymer microspheres settled by adding ethanol to microemulsion was directly put onto the electric conduction film, compacted using a clean glass sheet, and then dried at room temperature in a dust-free working cabinet. Powder sample was sprayed with metal for 3minutes, observed with the SEM Quanta 200F produced by the United States FEI company.

2.3 Laser diffraction analysis

Based on the technique of laser diffraction, the size distribution of the swelling microspheres was investigated by the analyzer Mastersizer 2000 produced by British MaErWen company. This analysis was made under constant temperature 25°, and the analyzer used the He-Ne lasers and the wavelength was set to 630.0nm.

2.4 Measurement of rheological parameters

The rheological parameters of the polymer microsphere dispersion were measured by using HAAKE RS 600 rheometer made by HAAKE company (German) at 30°C after the samples being placed in the rheometer for 20 minutes.

2.5 Nuclear-pore membrane filtration

The installation of the nuclear-pore membrane is referred to reference [Lin, Han, Li and Wu (2003)]. The time and the filtrate volume were recorded when 20mL microsphere dispersion passed though the membrane under the pressure of 0.1Mpa provided by nitrogen gas cylinder as the driving force of filtration process. In this experiment, the membranes with pore size of 0.4 μm and thickness of 10μm were used.

2.6 Core displacement experiment

The installation of the core tube displacement experiment is referred to reference [Izgec, Zhu and Hill(2009)]. The experiment was carried out at 25°of room temperature and the flow was 0.40mL/min when water-flooding and microspheres-flooding occurred, respectively. A level fracture filled with 250-300 mesh quartz sand was pressed in the core with length of 25cm, and the confining pressure was set to 6Mpa in this experiment.

2.7 Sand packed tube displacement experiment

The installation of the sand packed tube displacement experiments is referred to reference [Lin, Zhao, Li, Dong and Peng (2009)]. The experiments were carried out at formation temperature about 60°and the flow was 0.40mL/min when water flooding and microspheres flooding occurred, respectively. The tubes which were 30cm long, Gudao crude oil with viscosity of 86mPa·s at 60° and Gudao sewage water with a pH of 7.5 were used in the experiment.

3 Results and perspectives

3.1 Conformation and size of nanoscale polymer microspheres

Fig.1shows the initial conformation and size of polymer microspheres observed with SEM. It could be seen that a great quantity of microspheres were gathered together, with a broad and heterogeneous range of size distribution between 30 nanometers and 60 nanometers or so, and the conformation of the polymer microspheres is typically spherical.

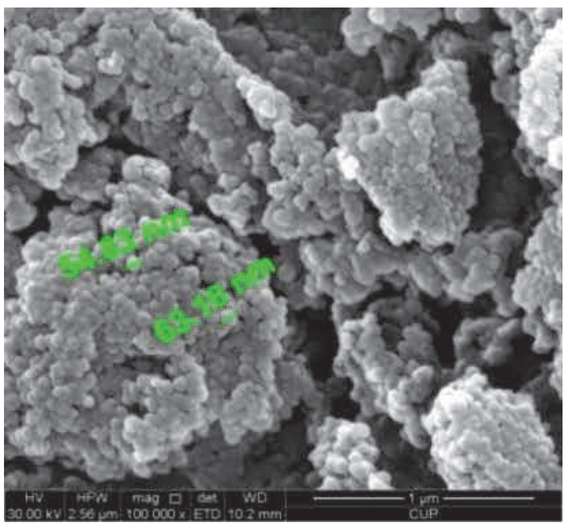

Figure 1: Scanning electron micrograph of crosslink polyacrylamide microspheres.

The size distribution of the microspheres dispersed in Semonga oil field injection water with a concentration of 700mg/L, after swelled at 82° for 5 days, was measured by Laser diffraction analysis, as shown in Fig.2. The laser diffracting measurement manifested that the crosslink polyacrylamide microspheres had a good property of swelling and could be about 3 to 6 times larger than original size without swelling.

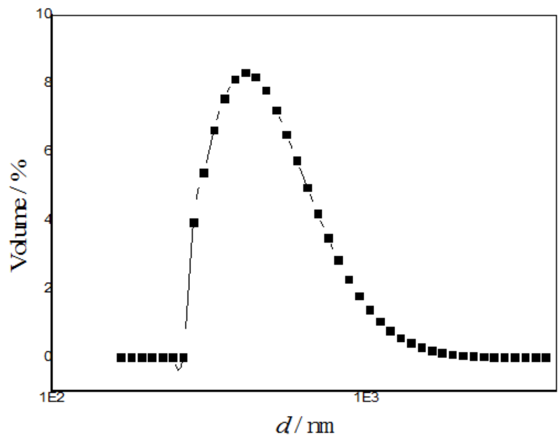

Figure 2: The size distribution of microspheres system.

3.2 Rheological property of nanoscale polymer microspheres

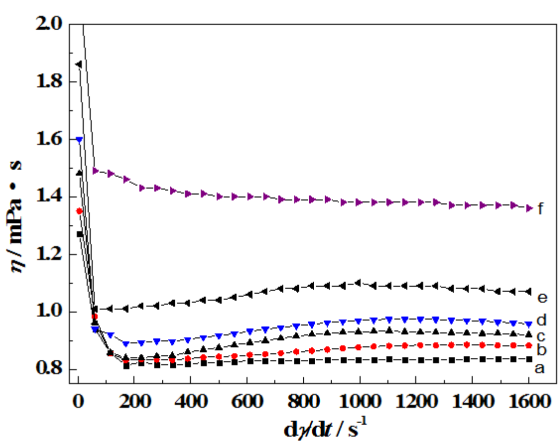

Figure 3: Viscosities of crosslink polyacrylamide microspheres dispersed system with different concentration ρ(microsphere)/(mg·L^{-1}): a. 50; b. 100; c. 300; d. 600; e. 900; f. 1500.

Fig.3 shows the viscosity vs. the shear rate of polymer microspheres dispersed system after swelled at 40° for 10 days, with 2,000 mg·kg^{-1} NaCl, at different concentrations. The results showed that the viscosity of dispersed system was obviously affected by concentration and the apparent viscosity of dispersed system increased with the concentration being increased. At the mid shear-rate range, the viscosities of the polymer microspheres dispersed system increased with the raising of shearing rate if the concentration of microspheres was limited in 100-900mg/L, i.e., the dispersed system presented the phenomenon of shear thickening which was the character of dilatant fluid, and the dilatant property of polymer microspheres dispersed system was strengthened with the increase of microspheres concentration when the concentration was limited in100-600mg/L.

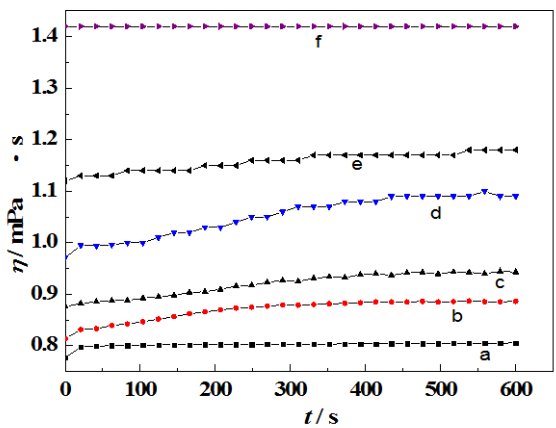

Figure 4: Flow behaviors of crosslink polyacrylamide microspheres dispersed system with different concentration ρ(microsphere)/(mg·L^{-1}): a. 50; b. 100; c. 300; d. 600; e. 900; f. 1500.

Fig.4 shows flow behaviors of dispersed systems with different concentrations at constant shear rate of 600s^{-1}. The experiment results showed that the time effect of polymer microspheres dispersed system differed with concentration. The apparent viscosities increased visibly with shearing time being increased when the concentration of microspheres reached 100-900mg/L, so the dispersed system showed apparent negative thixotropy and time dependent. The different rheological properties in the various concentrations of dispersed system resulted from aggregation state of microspheres.

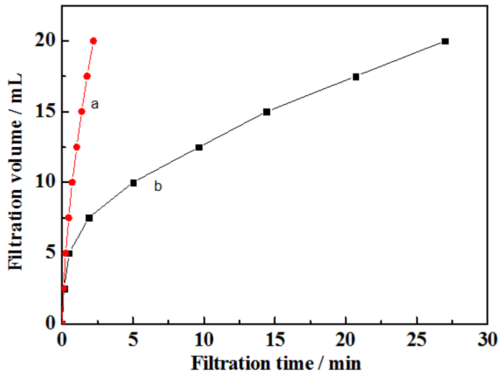

Figure 5: Relationship of filtration volume and filtration time of microspheres dispersed system and HPAM solution (a. HPAM; b. microspheres)

3.3 Plugging performance of nanoscale polymer microspheres

As seen in Fig.5, the HPAM solution filtrated rapidly and finally the filtration time was less than 5 min as the twenty milliliter of HPAM solution went through the film. Therefore the microspheres could not plug the nuclear-pore film effectively. However the filtration rate decreased dramatically when microspheres dispersed system with the same concentration was used and the relationship of filtration volume and filtration time exhibited a parabola going downwards, which demonstrated the microspheres could plug the film with the diameter of 0.4 μm effectively.

As can be seen from Fig.6, for the fractured core with the permeability of 0.02 μm^2, polymer microspheres dispersed system with the concentration of 3000mg/L was injected into the core holder after water flooding reaching to equilibrium. After being injected with about 1.0Vp polymer microspheres dispersed system, all of the pressures at four pressure measurement points of core holder increased with the increase of the injection volume of dispersed system, which illustrated that polymer microspheres not only had certain sealing properties to the fractured core with permeability of 0.02 μm^2 but also could enter into the core deeply, bring about effective plugging, and play the role of deep profile control.

3.4 Profile control and oil displacement effect of nanoscale polymer microspheres

Table 1 gives some key parameters of heterogeneous double-tube sand pack model. The oil recovery was 68.5% for high permeability model while 58.4% for low per-

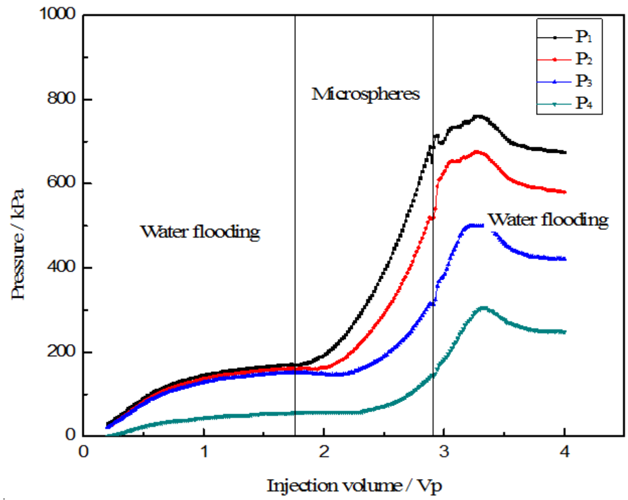

Figure 6: Relationship of pressure and injection volume ofcrosslink polyacrylamide microspheres dispersed system.

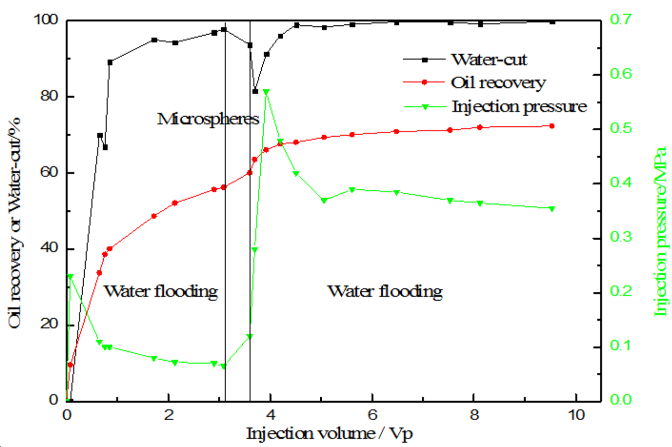

Figure 7: The displacement test curve of heterogeneous double-tube sand pack model.

meability mode during water flooding. After being injected about 0.5Vp polymer microspheres dispersed system with the concentration of 1800mg/L, the oil recovery of the high- and low-permeability tubes was enhanced by 5.7% and 12.0%, respectively. So the enhanced oil recovery mainly came from the low-permeability tube. In Fig.7, by injecting polymer microspheres dispersed system, the water content dropped obviously, the oil recovery was enhanced greatly, and the displacement pressure continued to rise until it reached 0.57Mpa. Therefore, in this experiment, the effects of the polymer microspheres on profile control and oil displacement behavior was remarkable.

Table 1: Key parameters and EOR of polymer microspheres of heterogeneous double-tube sand pack model.

Sank pack type	Ψ (%)	K (μm^2)	Soi (%)	R_w (%)	EOR (%)
High-permeability tube	41.9	0.97	70.8	68.5	5.7
Low-permeability tube	39.5	0.32	70.3	58.4	12.0

3.5 Profile control and oil displacement mechanism

[Lin, Guo, Xu, Zhang, Li and Peng (2011)] give SEM photographs of plugged membranes by linked polymer microspheres. The experimental result demonstrated that there were certain relationships between the size of the nuclear pores and the experimental microspheres. When the microsphere size was larger than the nuclear pore size, microspheres remained on the surface and could not go into the nuclear pore. When the microsphere size was basically equal to the nuclear pore size, microspheres could deform under pressure and go deep into the nuclear pore to plug it effectively. When the microsphere size was 2∼3 times smaller than the nuclear pore size, microspheres could be adsorbed, accumulated and bridged in the nuclear pore where plugging occurred effectively. When the microsphere size was much smaller than the nuclear pore size, microspheres would easily pass through the nuclear pore and could not plug the nuclear pore.

The microspheres could be adsorbed, accumulated and bridged in the pore-throat channel in reservoir so reduce water permeability. And it could be observed that the bridged layers would be collapsed under displacement pressure and entered into reservoir deeply owing to the good deformation property of microspheres, which illustrated that polymer microspheres not only had certain sealing properties to pore-throat but also could enter into the model deeply, bring about effective plugging, and play the role of deep profile control. In the fracture, large amounts of solid particles provided contact points for microspheres to be bridged. When displacement pressure was large enough, the bridged layers of microspheres in pore-throat channel or fracture with diameter could migrate and entered into reservoir deeply.

4 Conclusions

The nanoscale polymer microspheres in microemulsion were spherical with original diameter between 30nm to 60nm or so, and microspheres after swelled in water were about 3 to 6 times larger than the original ones but remain spherical; Within a certain range of shear rate, the microsphere dispersed system with the concentration of 100-900 mg/L showed the character of dilatant fluid and time dependent shown as negative thixotropy; Polymer microspheres were soft, flexible, deformable micro-gel particles and they could entered into reservoirs deeply. In the process of migrating, microspheres not only displaced crude oil in the pore-throat channels forward but also formed new adsorbed and bridged layers, and thereby achieved the coordinated and simultaneous effects of deep profile control and oil displacement and the ultimate purpose of improving oil recovery.

Acknowledgement: This work was supported by National Key Scientific and Technological Project (Grant No. 2011ZX05009), National Natural Science Foundation of China No.51274211 and Basic Subject Fund of China University of Petroleum, Beijing.

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