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Research progress of polymer microsphere conformance control technology

SUN Zhe[1], LAI Nanjun[2], WANG Dongdong[2]
(1. China National Offshore Oil Corporation (CNOOC) Research Institute Co., Ltd., Beijing 100028, China; 2. School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, China)
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[Abstract] As one of the popular conformance control technologies in recent years, polymer microspheres have shown excellent oil displacement effects in deep profile control and flooding. This article first elaborates the selection of polymer microspheres in detail,and summarizes the research status of polymer microspheres conformance control technology from two aspects. Finally, the problems and development directions of polymer microsphere conformance control technology are comprehensively analyzed.
[Keywords] polymer microspheres; composite flooding; conformance control; enhanced oil recovery

I. PREFACE

With the further exploitation of oil as a fossil fuel, reservoir exploitation has been developed to a deeper reservoir, and the geological conditions are becoming more and more complex.In high temperature and high salinity reservoirs, profile control and water plugging are still technical problems.The traditional profile control and water plugging agent has many disadvantages, such as poor high temperature and salt resistance, uncontrolled cross-linking reaction time, poor long-term effect and so on.Polymer microspheres, as a new technology in recent years, can be used for deep profile control and water plugging in reservoirs.It has great advantages in oil displacement, mainly including good temperature and salt resistance, absorption and expansion ability, and can be sealed in the deep part of the reservoir with long-term performance. At the same time,microspheres suitable for the pore characteristics of the target formation can be prepared by adjusting the polymerization reaction conditions. Microspheres block high permeability areas and preferential flow channels in porous media through the mechanism of migration, plugging, elastic deformation, deformation recovery, re migration and re plugging, so as to achieve the purpose of deep profile control and flooding [1-3].

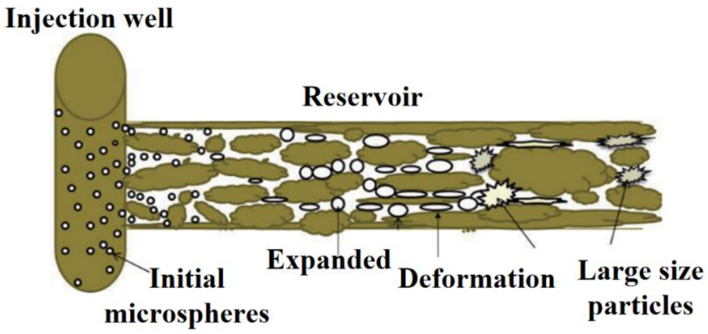


Fig.1 Schematic diagram of microsphere transfer process [4]

II. SELECTION OF POLYMER MICROSPHERES

The selection of polymer microspheres is mainly reflected by monomer, initiator and crosslinker. The details are as follows.

2.1 Selection of polymeric monomers

Polymer monomer is the primary factor affecting the stability of polymer microspheres.The introduction of monomers with specific groups can not only improve the temperature resistance and salt resistance of microspheres, but also make them have specific functions. It is also the main method for the modification of microspheres. Lou et al.[5] introduced amps monomer into yg370-1 microspheres. Compared with traditional microspheres,microspheresmodified by APMShave better thermal stability, salt resistance and swelling. It also have good water impact resistance and plugging strength. Zhao et al. [6] synthesized a terpolymer microsphere by inverse suspension polymerization withAM, AMPSand NVPas monomers. The experimental results showed that the maximum swelling rate of the microspheres was 21 at 25 ℃,and the microspheres were stable for 19 days at 120 ℃. Yu et al. [7] synthesized a heat-resistant amphoteric polyacrylamide microsphere by inverse microemulsion polymerization with dimethyldiallylammonium chloride (DMDAAC) AM, andAMPS as monomers. The results showed that the swelling ratio of the microspheres was 9.6 after aging at 90 ℃ in salt water for 7 days, and the average diameter decreased after 30 days. Wang et al. [8] used hydroxyethyl methacrylate (HEMA) andAMas monomers to synthesize highly crosslinked micron sized polymer microspheres by inverse suspension polymerization, and systematically studied the effects of polymerization parameters (including stirring rate, monomer loading, initiator concentration and crosslinker concentration) on the morphology and particle size distribution of the polymermicrospheres. Then, AM was grafted onto AM/HEMA microspheres to obtain grafted PAM－AM/HEMA microspheres. Bao et al. [9] introducedhydrophobic monomer α - Methylstyrene(α - MSt) copolymerized with AA and AMPS to synthesize AMPS series polymer microspheres. The experimental results showed that the swelling ratio of AMPS-8 was 8 to 9, and the salt resistance and plugging performance were good.

2.2 Selection of initiator

During the synthesis of polymer microspheres, initiators mainly include water-soluble initiators (potassium persulfate, ammonium persulfate, etc.), oil-soluble initiators (azodiisobutyronitrile, azodiisopentylnitrile, etc.) and redox initiators (ammonium persulfate/sodium bisulfite, potassium persulfate/sodium bisulfite, etc.). The water-soluble initiator is evenly dispersed in the aqueous solution,and the free radicals decomposed by heating can act directly on the micro droplets, so its initiation efficiency is high. However, the particle size of oil soluble initiator is larger. In addition to the above initiators, there are some special initiators. Yildiz et al. [10] reported a polymerization system using allyl terminated polyoxyethylene (PEO) macromonomer as initiator and styrene (st) and methyl methacrylate (MMA) as monomers. This kind of initiator has azo group, which has the functions of initiation and stabilization.

2.3 Selection of crosslinking agent

Crosslinking agents are usually divided into organic crosslinking agents (organic phenolic) and inorganic crosslinking agents (high valence metals). Wang et al. [11] prepared phenolic resin/am microspheres with strong thermal stability by reverse suspension method with phenolic resin as crosslinking agent and potassium persulfate as initiator. The results showed that the microspheres could maintain their thermal stability at 140 ℃, and the swelling ratio was 2.72. Xu et al. [12] prepared a highly crosslinked high temperature resistant polymer microsphere with MMA and AMPS as polymerization monomers and ethylene glycol dimethacrylate (EGDMA) as crosslinking agent. The results showed that the microspheres maintained good thermal stability at 190 ℃. Jia et al. [13] proposed that conventional crosslinking agents (such as formaldehyde, phenol salt or chromium salt) could be added to the micro gel solution during the synthesis process, and predicted that this crosslinking agent would react with the expanded micro gel to form a blockgel. Yu et al. [7] used n, N-methylene bisacrylamide (NMBA) as crosslinking agent to prepare microspheres.

Table 1 Flooding control effect of different particle size microspheres in Chi 46 block

No.	Particle size /nm	Number of profile control and flooding wells	Effective time /d	Effective days /d	Daily oil increase of single well group/t
1	800	4	30	270	2.8
2	300	4	45	365	4.2
3	300+100	12	60	335 Continuously effective	1.9

III. RESEARCH PROGRESS

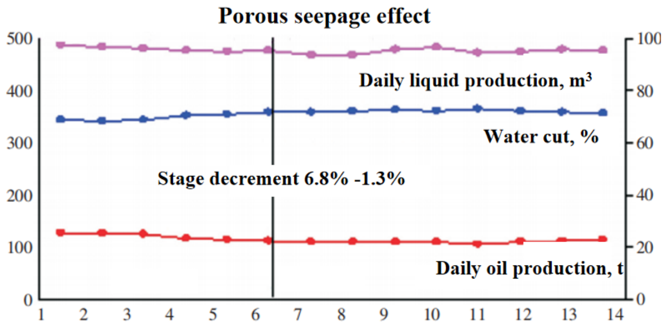
3.1Single polymer microsphere conformance control technology

In recent years, polymer microsphere conformance control has become a research hotspot technology. Since 2004, PetroChina, Sinopec, CNOOC and other petrochemical engineering companies have carried out research on polymer microspheres conformance control technology, and conducted field experiments in Shengli, Changqing, Bohai and other oilfields. The effect of oil increase and water reduction is very obvious.

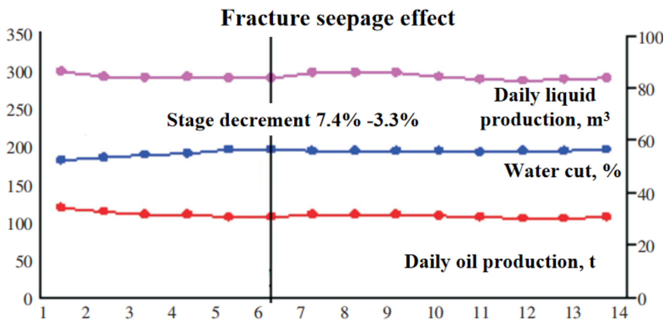
Early research mainly focused on medium and high permeability reservoirs. In 2005, Wang et al. [14] reported the field test of polymer microspheres in well group 114 in the east of Gudao Oilfield. The results show that the microspheres have good profile control effect, excellent oil increase effect, and good temperature and pressure resistance in reservoir. In 2006,Lei et al. [15] reported the pilot test of polymer microsphereprofile control and flooding in Zhongernan NG3-4 test block of Gudao Oilfield. It is predicted that the recovery rate increase in the pilot area can be increased by 1.05%, and the increase effect can be maintained for four years.

Zhongyuan Oilfield has successively conducted pilot tests of polymer microspheres in Wen 10 and Wen 25 reservoirs [16]. The results show that the initial particle size of microspheres can meet the needs of deep profile control and flooding, and the effect of enhanced oil recovery is obvious. It is proved that polymer microsphere flooding can be used to enhance oil recovery after water flooding in medium and low permeability reservoirs.

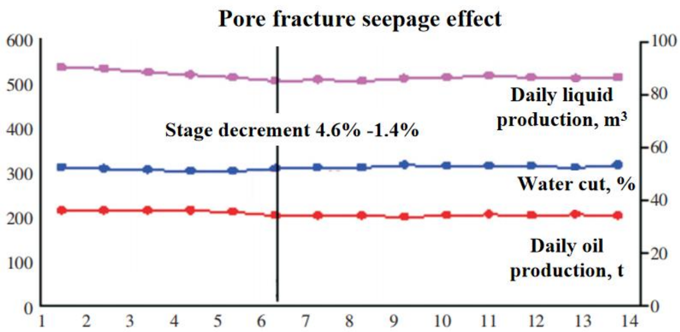
In2010, Changqing Oilfield successively conducted research on polymer microsphere profile control and flooding technology in low permeability reservoir in 16 wells. The results show that the polymer microspheres synthesized according to the geological characteristics of low permeability reservoirs can disperse rapidly under the condition of formation simulated water, and the solution viscosity is particularly low, which is enough to meet the needs of field application. Later, Changqing Oilfield conducted field tests of polymer microspheres in Jing'an, Ansai, Xifeng, Jiyuan and other oilfields [17-26]. The oil well type, pore fracture, injection well profile, water content of injection well and microsphere size are analyzed. The results show that the microspheres have excellent adaptability in low permeability reservoirs.The effect of polymer microspheres on oil increment and water reduction in porous water flooded wells is better than that in poreand fracture types, and its effective ratio can reach 39.8% [27], see Fig. 2.The water content of injection wells and the particle size of microspheres are the main factors affecting the effect of oil increment. The smaller the particle size, the smaller the pressure increase, and the better the migration performance, see Table 1.In the process of microspheres profile control and flooding,the injection pressure shows a step-by-step rise,which is basically consistent with the flooding mechanism of polymer microsphere “migration, expansion, plugging, breakthrough, migration and re plugging”, that is, it is a step-by-step deep profile control and flooding process.



(a) Porous seepage effect



(b) Fracture type seepage effect



(c) Pore fracture seepage effect

Fig 2. Oil-increasing effect of different flooding types

Since2008, CNOOC has carried out a series of research on the application of polymer microsphere conformance control technology in offshore heavy oil fields in Bohai Oilfield [28-32]. According to the numerical simulation calculation and experimental results, it is found that when the particle size of the microsphere is 1.2 to 1.5 times of the core pore throat, its migration and plugging effect is the best[32], see Table 2. It is proved that in the middle and late development of heavy oil field, polymer microspheres can effectively block the large pore channel, so as to change the fluid flow direction, improve the injection water swept volume, and improve the oil recovery rate. At the same time, the polymer microspheres showed a slow swelling phenomenon in mineralized water.

Table 2 The plugging of polymer microspheres with different particle sizes in the core

multiple	Plugging rate /%	End face
0.08	0	No residue
0.14	15.26	No residue
0.33	36.40	No residue
0.45	32.40	No residue
0.60	28.00	No residue
0.80	30.80	No residue
1.00	32.63	No residue
1.20	40.30	No residue
1.50	50.80	Little residue
3.00	69.16	Particle residue
4.50	85.84	Large area accumulation
6.00	96.63	Large area and large amount of residue
10.00	99.26	Large area and large amount of residue

3.2Polymer microsphere composite conformance control technology

Polymer microsphere conformance control technology has been proved to be effective in improving oil recovery through a series of field experiments. However, for high permeability and large pore reservoirs, the effect of polymer microsphere on increasing oil and reducing water is more and more unsatisfactory. Therefore, composite conformance control technology, combined with the advantages of various profile control and displacement agents, is one of the research hotspots of microsphere conformance control technology at present.

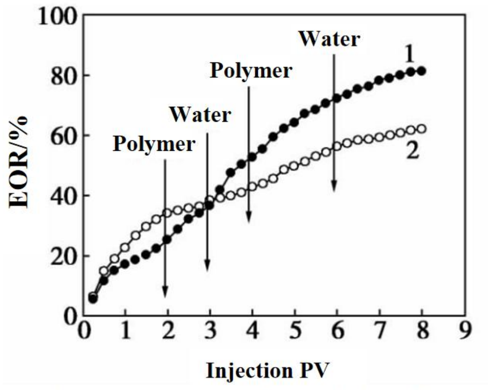
As a highly efficient oil displacement agent, surfactant has been widely used in some domestic reservoirs. Polymer microspheres and surfactants form a composite flooding system, which will give full play to their advantages and improve their oil displacement effect. Guo [33] reported the oil displacement performance evaluation of the composite flooding system composed of polymer microsphere SQ-5 and new surfactant FA-2. The results show that in the reservoirs with high temperature, high salinity and low permeability, compared with water flooding, the EOR increment of the composite system is 27.28%, and 14.85% higher than that of surfactant alone. Qu et al. [34] reported the research on the composite flooding technology of polymer microsphere WQ-2 and alkanolamide surfactant FPS,and the results showed that the system has excellent compatibility. On this basis, the influence of polymer microspheres and surfactant solution concentration on oil displacement effect is investigated. The results show that 0.4 PV microspheres solution (2000 mg/L) and 0.3 PV surfactant solution (2000 mg/L) have the best oil displacement effect. On the basis of water flooding, the recovery efficiency of the composite system can increase by more than 15%, see Table 3. Wang et al. [35] reported a composite flooding system composed of polymer microspheres and non-ionic surfactants. The experimental results show that the initial appearance of polymer microspheres is regular spherical, and the expansion ratio is about five times. Water flooding and microbial flooding have been applied in some reservoirs because of its green environmental protection, simple process, wide application range and other advantages. However, it is difficult to reduce the water channeling phenomenon in the high permeability channel, and it still has the disadvantage of low efficiency after injection. Polymer microsphere and microbial composite flooding can effectively block the main seepage channels and solve the shortcomings of single microbial flooding. Since 2017, Changqing Oilfield has carried out research on “microbial + polymer microsphere” composite flooding technology [36, 37]. The results show that the compatibility of microspheres and microorganisms is good, and the recovery increase of composite flooding technology is more obvious than that of single microorganism flooding, and the water injection profile is effectively adjusted. Polymer flooding has become one of the most widely used oil displacement agents in oil fields because of its simple synthesis and high oil recovery. However, limited by some reservoir heterogeneity and platform operation conditions, single polymer flooding can not meet the current oil displacement demand. The composite application of polymer microspheres and polymers can increase the fluid diversion ability and sweep efficiency of polymer flooding, so as to further improve the oil displacement effect. Li et al. [38] reported the research on oil displacement effect of polymer microsphere Q41 and associated polymer composite system. The results show that the oil displacement effect of the composite system is more significant than that of a single polymer flooding, see Fig. 3. Yang et al. [39] reported the research on oil displacement effect of polymer microsphere ESS and polymer PA composite system. The results show that when the total concentration of the system is 1750mg/l, the greater the solution concentration of polymer microspheres in the system, the greater the recovery increase. Compared with the single polymer flooding, the recovery increase of the composite flooding system is 8% ~ 11%.

Table 3 Experimental results of enhanced oil recovery with polymer microsphere and surfactant composite profile control and flooding system

Core No.	Permeability K_w /$10^{-3}\mu m^2$	Porosity /%	Recovery rate /%		
			Water flooding	Final	Increment
FLF-1	25.75	17.77	27.46	44.19	16.73
FLF-2	26.29	17.92	23.77	39.20	15.43
FLF-3	28.54	18.35	26.90	42.11	15.21

Gel has been widely used in oil fields because of its strong plugging strength. However, deep profile control and flooding often need to transfer the oil displacement agent to the deep formation,and effectively block the large pores and high permeability channels, which is impossible for a single gel flooding. The composite application of gel and polymer microspheres can effectively improve the above situation [40-42]. Cao et al. [40] reported the composite flooding effect of Cr^{3+} polymer weak gel, strong gel and polymer microspheres. The results show that polymer microspheres have strong transport and migration ability and slow swelling phenomenon in deep pores during oil displacement, while polymer gel has strong plugging effect. On the basis of water flooding, the composite flooding system of weak gel, strong gel and polymer microspheres showed the largest increase in oil recovery 22.5%,see Fig. 4.Li et al. [41] reported that the composite system of gel and polymer microspheres showed an efficient effect of increasing oil and reducing water for high and ultra-high permeability reservoirs. Compared with single polymer microsphere flooding, the composite system can maintain a long-term stable oil increase effect.

In addition to the above composite systems,some polymer microspheres and other profile control and displacement technologies have been reported recently. Zouj et al. [43] reported the study on the composite displacement effect of polymer microspheres and CO_2. The results show that under high temperature and high salt environment, polymer microspheres show strong injection capacity and plugging capacity, and compared with single CO_2 flooding or microsphere flooding, the composite flooding system of polymer microspheres and CO_2 shows a larger CO_2 sweep volume, thus the maximum range of enhanced oil recovery 22.65%. Liang et al. [44] reported the composite flooding effect of polymer microspheres and nitrogen foam. The results show that the plugging efficiency of polymer microspheres can reach 96%, and the enhanced oil recovery of composite system is greater (24.65%) than that of single polymer flooding (12.35%) and nitrogen foam flooding (18.3%). The pilot test results of W1 well group in Bohai AOilfield show that the combined flooding technology can increase oil production by 64461 barrels.



1-Composite system; 2-Associative polymer

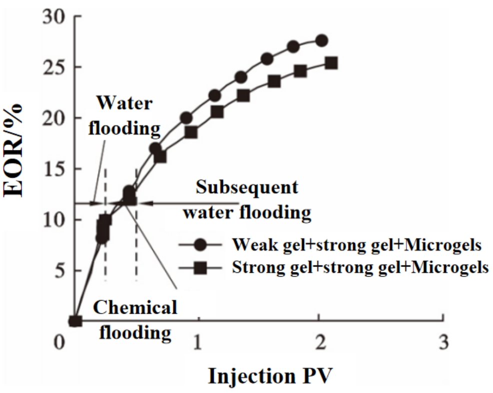


Fig.3 Recovery curveFig.4 The relationship between the recovery factor of the two combination methods and the PV number

IV. EXISTING PROBLEMS AND DEVELOPMENT DIRECTION

(1) Polymer microsphere composite conformance control technology should be further developed. Polymer microspheres have small particle size and poor formation selectivity, which are not suitable for plugging large pore channels. In the process of profile control and flooding, low permeability layers are easy to be polluted. At the same time, the higher the temperature, the faster the hydration expansion. In order to solve

the above problems, other oil displacement agents and polymer microspheres can be used for composite flooding. However, the composite flooding technology is not universal. Therefore, for specific reservoir conditions, selecting the appropriate flooding system is one of the issues that should be paid attention to in the future research.

(2) Develop low-cost and environmentally friendly polymer microspheres with higher effective components. When the injection concentration and initial particle size of polymer microspheres are fixed, the more effective components, the better plugging performance. Therefore, the development of low-cost and environmentally friendly microsphere materials with higher effective components is one of the research directions.

(3) Study on the dynamics and mechanism of polymer microsphere flooding technology. The main advantage of the composite system lies in the synergy between oil displacement agents. Therefore, combining the experimental results, establishing a reasonable numerical model to study the dynamics and synergistic mechanism of polymer microspheres, especially its composite flooding system is the key point of future research.

V. CONCLUSION

To sum up, compared with traditional polymers, polymer microspheres have the following advantages: (1) controllable size and expansion ratio, making it easier to enter the deep formation; (2) High mechanical strength and strong shear resistance; (3) The process is simple and the oil displacement cost is low. At present, polymer microsphere flooding technology has been applied in many oilfields, and has achieved good oil displacement effect and economic benefits. However, for poor formation conditions and high temperature and high salt operating environment, on the basis of reducing costs,it is still necessary to develop temperature and salt resistant polymer microspheres or conduct composite flooding with other technologies to improve oil recovery. In addition, the mechanism of polymer microsphere flooding still need further exploration. In general, polymer microsphere flooding technology has made great progress. In the subsequent research, how to combine the numerical simulation and experimental results to explore the flooding mechanism and develop a cheaper and more efficient flooding system will be the focus of the research.

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