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Water-Flooding Fluid Diversion Copolymeric Microsphere Prepared by Inverse Suspension Polymerization

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Abstract: In order to enhance oil recovery in high-temperature and high-salinity oil reservoirs, the copolymeric microspheres containing acrylamide (AM), acrylonitrile (AN) and AMPS was synthesized by inverse suspension polymerization. The copolymeric microsphere was very uniform and the size could be changed according to the condition of polymerization. The lab-scale studies showed that the copolymeric microsphere exhibit good salt-tolerance and thermal-stability when immersed in 20×10^5 mg/L NaCl(or KCl) solution, 7500 mg/L $CaCl_2$ (or $MgCl_2$) solution or 2000 mg/L $FeCl_3$ solution, respectively. The copolymeric microsphere showed satisfactory absorbency rates. The sand-pipes experiments confirmed that the average toughness index was 1.059. It could enhance the oil recovery by about 3% compared with the corresponding irregular copolymeric particle.

Introduction

During the middle or last period of oil exploration, many oil fields have taken measures of exploitation, such as water-flooding, polymer-flooding and so on[1]. In a serious heterogeneous reservoir, injected-water and polymer solution mainly flow into high-permeable layers [2]. This resulted in a lower sweeping efficiency, and a larger mount of residual oil remaining in the reservoir, which affected water injection and the implementation of polymer flooding. To solve this problem, the profile modification of water-ejected well was put in practice with many measures, especially by the uses of chemical agents.

In last decade, fluid diversion technology has been proved to be an effective way to increase oil production [3]. This not only included both profile-modification and water-shutoff to reduce water cut, but also included modification of differences between inner and outer layers, that is, in-depth performance control [4-7]. In this process, a cross-linked polymer solution was injected into the deep production zone that then blocked high-permeable water channel [2, 8]. As a result, water has to flow into the low-permeable zones, and oil recovery enhanced [9].

Nowadays, weak gel and colloidal dispersion gel [10, 11], represents major in-depth performance controllers. However, these polymeric materials showed drawbacks in terms of salt tolerance, temperature stability and their small size [7, 12, 13]. Because of these only low-permeable zones could be sealed, while little effect was found in high-permeable channels, especially in heavily water-flooded zones. At high temperatures, these polymeric materials could degrade and become smaller in size in concentrated salt solution, being less effective in blocking high-permeable channels. For this reason, a kind of copolymeric particle prepared by solution polymerization as fluid diversion was reported [14]. The copolymeric particle can exhibit special characters, such as salt tolerance, temperature stability and so on. However, the lab-scale direction visualization and physical model showed that the copolymeric particle can also exhibit bad changing-figure-ability and friability due to the irregularity and coarseness of the particle produced by mechanical shatter [14, 15]. Therefore, it's necessary to synthesize a kind of microsphere with ideal size and smooth surface. To this day, there are large number of methods to prepare copolymeric microsphere [16-19], such as Vanderhoff's multi-stepseeded polymerization [16], distillation-precipitation polymerization [17] and so on. Based on industry requirement, inverse suspension polymerization of water-soluble monomers is an ideal method to synthesize copolymeric microsphere [20-24]. The advantage of inverse suspension polymerization over other methods was that a powder sample of a copolymer can be obtained; the particle size can be easily controlled by controlling the reaction conditions and the regular figure can be relatively round [24-27].

In this article, the copolymeric microsphere was synthesized by inverse suspension polymerization and its salt tolerance, thermal stability, drivability and coreflood test is discussed.

Results and discussion

FT-IR analysis

Fig. 1 presents the FT-IR spectrometer of copolymeric microsphere. One could find the special peak value in Fig. 2: 3421cm^{-1} (NH_2), 3195cm^{-1}(-OH), 2930cm^{-1}(CH_2), 2240cm^{-1} (CN), 1663cm^{-1} (-CO-), 1449 and 1401cm^{-1} ($-CH_3$), 1206cm^{-1} (S=O) and 766cm^{-1} (S-O). No other impurity peak could be found on the FT-IR spectrometer. It indicated that the copolymeric microsphere was relatively pure.

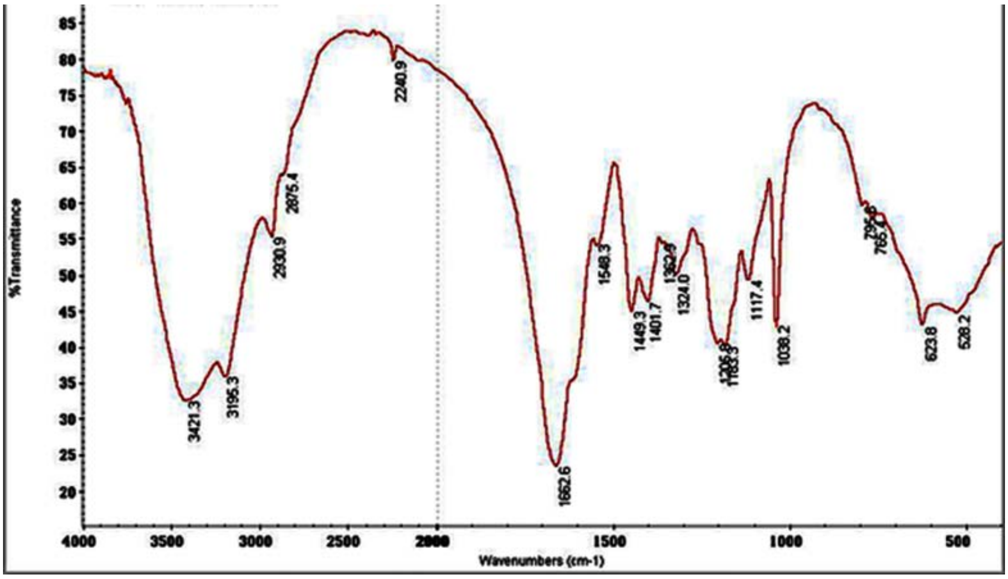

Fig. 1. FTIR spectra of PAM and HAPAM.

Effect of reactor factor on the size of microsphere

As shown in Fig. 2, uniform copolymeric microspheres were obtained with the size of 5 μm. The copolymeric microsphere was very round, which met the requirement. It also showed that inverse suspension polymerization could be an ideal method to prepare uniform microsphere.

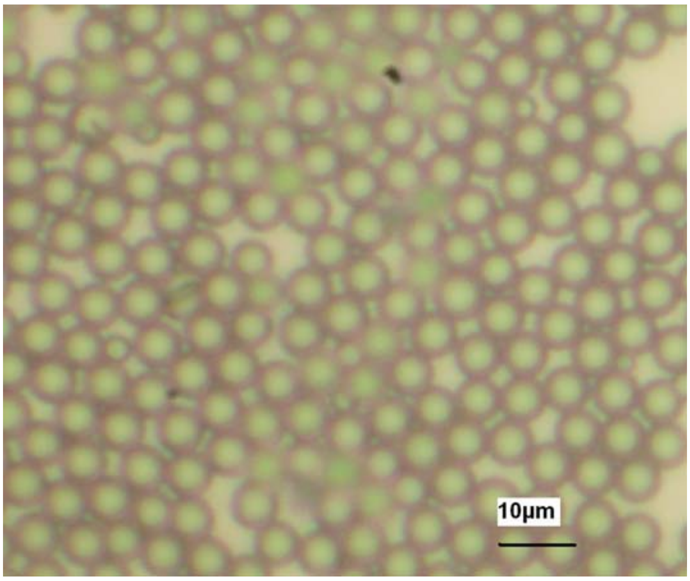

Fig. 2. The image of the copolymeric microsphere. The reaction conditions are: AM (15 g), AN (2 g), AMPS (3 g), NMBA (0.0018 g), water (30 g), cyclohexane and Span60 (120 g) and the hydroxyethel cellulose (1 g). The ratio of cyclohexane to Span60 is 10.

As shown in Fig. 3, the size of copolymeric microsphere decreased with the increase of the weight percentage of NMBA, indicating that the cross-linker (NMBA) played an important role in the control of the microsphere size. It could be understood by this way: the biggest the ratio of weight of cross-linker (NMBA) was, the better the cross-linking. It would make the microsphere compact, resulting in the smaller size of the copolymeric microsphere. Similar behaviour was reported by Zhong et al [28]. It was with this relationship that copolymeric microsphere with ideal size could be obtained according to the condition of oil reservoir.

As indicated in Fig. 4, the size of copolymeric microsphere dramatically increased with the increase of the ratio of water to oil. When the ratio of water to oil was larger than 0.3, this trend became more and more obvious. It indicated that the stability of polymerization will decrease with the increase of the ratio of water to oil. During the inverse suspension polymerization, one water drop could only form a resultant copolymeric microsphere. So, the increasing ratio of water to oil would increase the volume of the water drop, resulting in the increase of the microsphere size. It should also be noted that the explosive polymerization would occur when the ratio of water to oil was 0.5, suggesting that we cannot obtain a copolymeric microsphere which is larger than 15 μm. It may be ascribed to the fact that Span60 cannot stabilize the polymerization system when the ratio of water to oil is larger than 0.5 with the co-dispersant (hydroxyethel cellulose). If there was no co-dispersant, the ratio of water to oil would be small for the stable polymerization system.

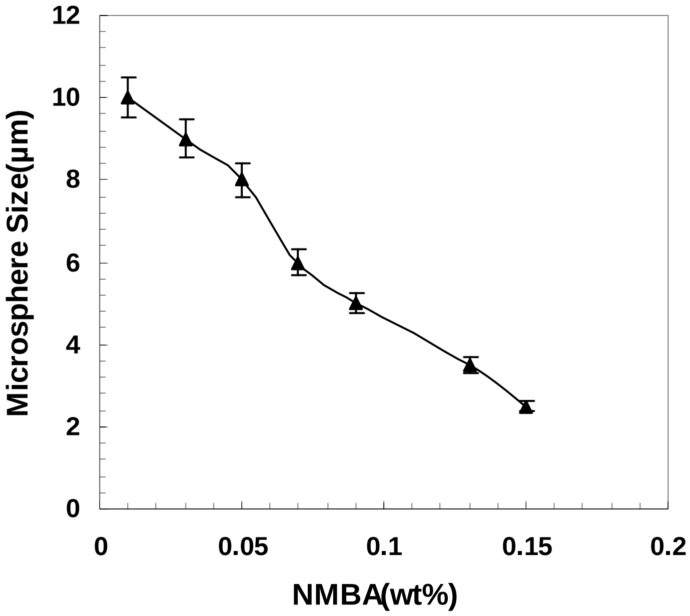

Fig. 3. Effect of NMBA on the microsphere size. The reaction conditions are: AM (15 g), AN (2 g), AMPS (3 g), water (30 g), cyclohexane and Span60 (120 g) and the hydroxyethel cellulose (1 g). The ratio of cyclohexane to Span60 is 10.

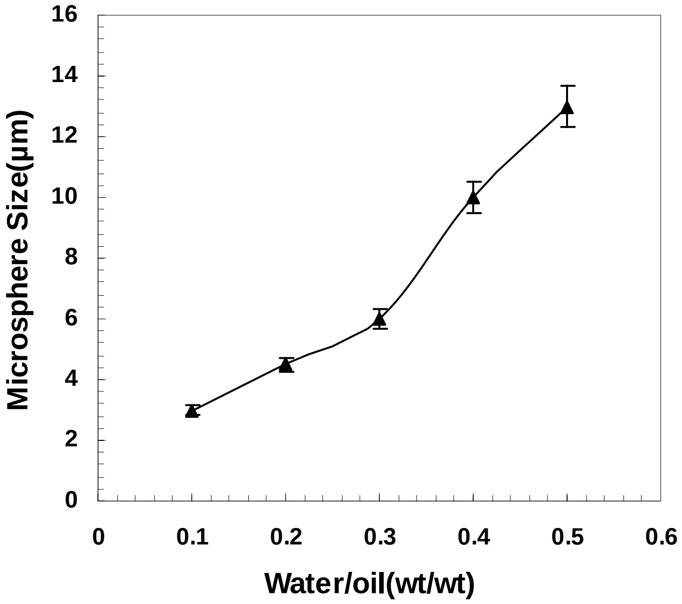

Fig. 4. Effect of the ratio of oil to water on the microsphere size. The reaction conditions are: AM (15 g), AN (2 g), AMPS (3 g), NMBA (0.0018 g) and the hydroxyethel cellulose (1 g). The ratio of cyclohexane to Span60 is 10.

Salt tolerance and thermal stability

-Effect of KCl and NaCl on dilatation

Fig. 5 showed the effect of salinity on the dilatation of copolymeric microsphere. The curves could be divided three areas: the first part where the dilatation drops drastically from 115 g/g to 55 g/g as salinity increases; the second part where dilatation keep line as salinity increases; and the third part (salinity: 25×10^4 mg/l to 35×10^4 mg/l) where further increasing the salinity results in a drastic drop in dilatation. It's important to note that the dilatation of copolymeric microsphere in NaCl solution was a little better than in KCl solution, this might be explained by that potassium ion was larger than sodium ion which formed the difference of hydration-ability. It also showed that the copolymeric microsphere exhibited good salt tolerance with the salinity below 25×10^4mg/L. This indicated that this kind of copolymeric microsphere could be used in all oil field in China.

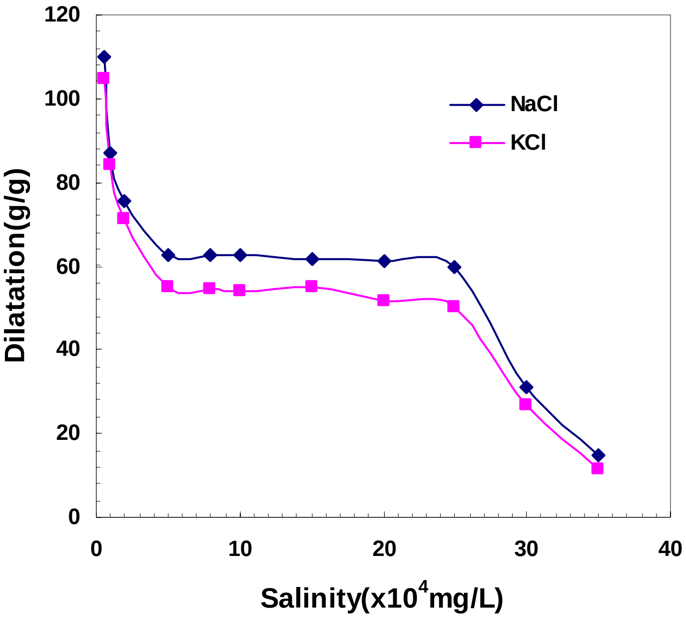

Fig. 5. Solution concentration of NaCl(KCl) versus dilatation.

Effect of $MgCl_2$, $CaCl_2$ and $FeCl_3$ on dilatation

Fig. 6 showed that the dilatation of microsphere dropped drastically from 100 g/g to 55 g/g when the salinity increased blow 3000 mg/L. Then, the dilatation line almost kept level in $MgCl_2$ solution, and it decreased slowly in $CaCl_2$ solution. It showed the dilatation of copolymeric microsphere seemed to be independent from the salinity when the salinity varied from 3000 to 7500 mg/L, indicating a lager usage region. Based on engineering standard, there was no good application foreground while the dilatation of microsphere lowered to 40 g/g. So the dilatation of copolymeric microsphere was not measured when the salinity was above 7500 mg/L. Fig. 6 also showed that the effect of $CaCl_2$ on absorbency was larger than that of $MgCl_2$. This could account for the difference of ion-complexation which led to high-crosslink degree resulting in the decrease of dilatation.

As noted in Fig. 6, there was a turning point on the cure of the relationship between dilatation and concentration in $FeCl_3$ solutions. And the absorbency dropped drastically from 125 g/g to 40 g/g as salinity increases blow 2000 mg/L. It indicated that the copolymeric microsphere exhibited salt tolerance when the concentration of Fe^{3+} lowered below 2000 g/L.

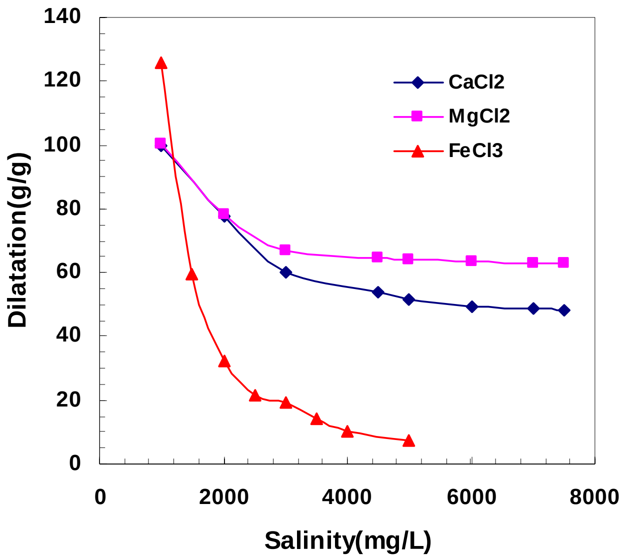

Fig. 6. Solution concentration of $CaCl_2$ ($MgCl_2$, $FeCl_3$) versus dilatation.

Thermal stability

Fig. 7 indicated that the copolymeric microsphere still kept good absorbency in salt solution with increasing the temperature, indicating their thermal ability within the measured temperature range (40-80 °C). There was no obvious difference of dilatation at 70 °C and 80 °C, indicating that copolymeric microsphere could keep stable in high temperature. It would fit water shutoff and performance control in high temperature oil reservoir.

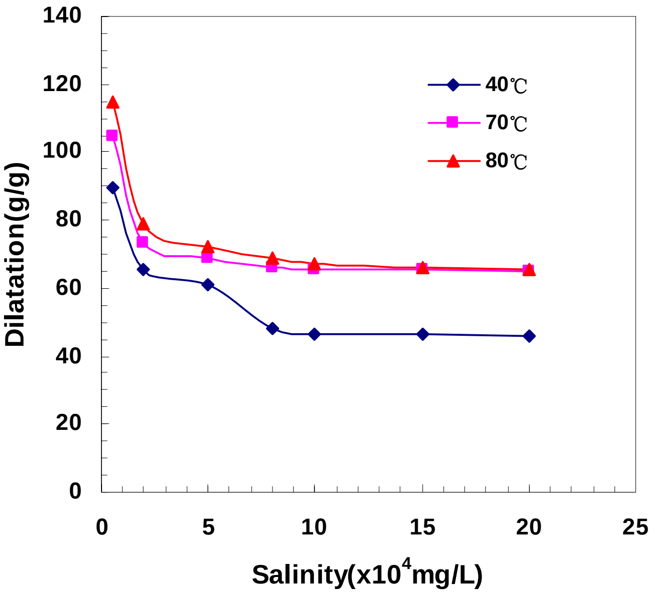

Fig. 7. Dilatation versus salinity at different temperature.

Rate of water absorbency

Fig. 8 indicated that the dilatation reached the half of the biggest dilatation at 3.5 h. After that, it swelled gradually. There was a small turning point on the curve at 10 h.

After 12 h, the dilatation kept steady. The whole curve showed that this kind of copolymeric microsphere exhibited good delaying-dilatation, which was what engineering application needed.

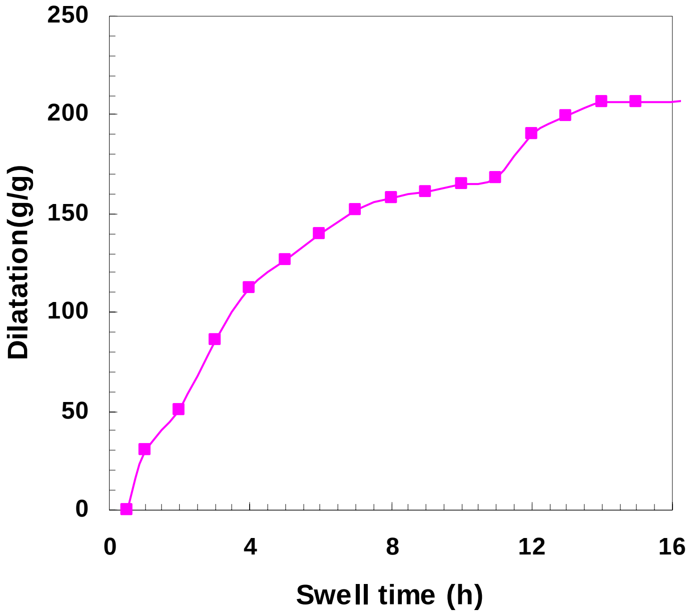

Fig. 8. Dilatation versus swell time.

Gel toughness

According to J.E.Smith Method [29], the toughness index was the ratio of the pressure difference and the flux when the water-absorbed grains (content 0.5%, 200 mesh, 20 ml) are screened twice. Namely

$$f_{tay}=(\Delta P_1/\Delta Q_1)/(\Delta P_2/\Delta Q_2) \qquad (1)$$

Let $\Delta Q_1=\Delta Q_2$, then $f_{tay}=\Delta P_1/\Delta P_2$ was a dimensionless constant and surpasses 1, the larger the f_{tay} was, the more crisp the gel. If its value approaches to 1, in the extreme, the gel would show the optimal toughness. Then, the gel would have better tensile strength and compression strength properties, and would not be suitable to disintegrate.

Tab. 1. Toughness of copolymeric microsphere.

Content of copolymeric microsphere（mg/l）	ΔP_1	ΔP_2	f_{tay}	average value
100	0.031	0.029	1.068	1.059
150	0.049	0.046	1.065	
200	0.062	0.059	1.051	
300	0.081	0.077	1.052	

As shown in Table 1, the toughness index showed that copolymeric microsphere exhibited better flexibility and could flow into pores in deep reservoir without being brittle. The toughness of copolymeric microsphere was smaller than that of irregular copolymeric particle (1.12), as described in literature [30]. It suggested that copolymeric microsphere exhibit better toughness than irregular copolymeric particle because of the sphericity and smooth surface.

Gel-ejection properties

As shown in Fig. 9, the copolymeric particle could not flow into the pore and the flux exhibited the maximum value at the low pressure (0.1MPa). With increasing pressure, grains began to flow into the pore, and the flux declined sharply. As pressure continued to rise, the flux began to increase, which revealed that the grain was beginning to deform and flow into deep zones. When the pressure reached a certain value, the flux tends to be steady. When the pressure was above 0.2 MPa, the flux of copolymeric microsphere system was larger than that of irregular particle. The data of irregular copolymeric particle could be found in Lu's research [30]. It's important to note that copolymeric microsphere exhibit better deformability than that of irregular copolymeric particle. For irregular particle, it would crack and move into the pore [14]. For copolymeric microsphere, it might move into the pore without cracking. This could be observed with larger flux; the microsphere might not be cracked during the movement due to the sphericity.

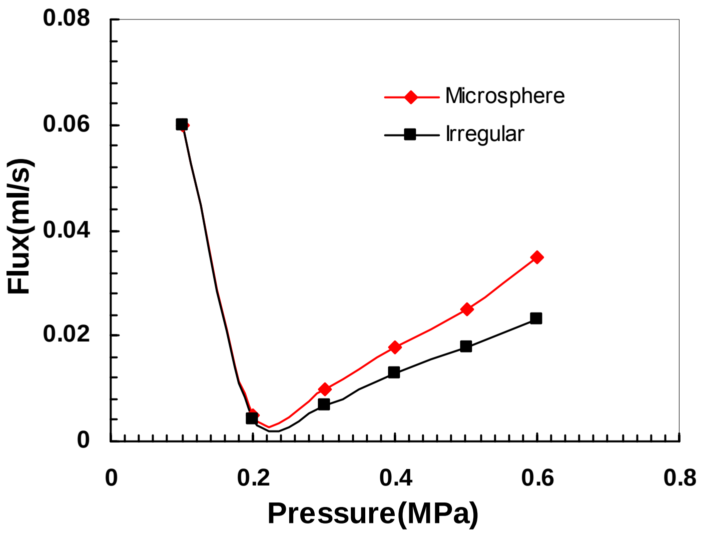

Fig. 9. Flux versus pressure.

Properties for enhance oil recovery

After injection of 0.5PV copolymeric particle (or copolymeric microsphere) solution, the water was used to replace copolymeric particle (or copolymeric microsphere) solution. As indicated in Fig. 10, the recovery ratio increased with the increase of water volume. However, when the volume of injected-water was larger than 4.0 PV, the recovery ratio for copolymeric microsphere system was obviously higher than that of copolymeric particle system. When the volume of injected-water was larger than 10 PV, the recovery ratio kept constant for copolymeric system. For copolymeric microsphere system, the recovery ratio kept slowly increasing. It showed that copolymeric microsphere as an in-depth performance controller was better than copolymeric particle. The average recovery ratio was 11.14% for microsphere system but 9.02 for irregular copolymeric particle system after the injection of 15.0PV water.

It suggested that copolymeric microsphere can exhibit better in-depth performance control than that of irregular copolymeric particle.

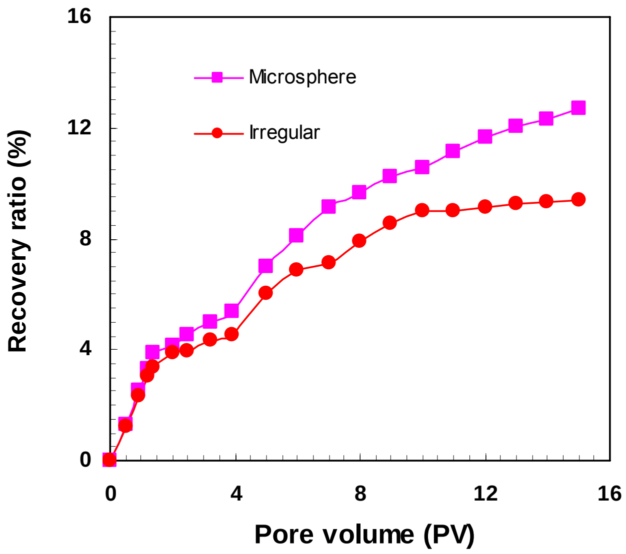

Fig. 10. Flux versus pressure.

Conclusions

In this paper, copolymeric microsphere with size-control was synthesized by inverse suspension polymerization. The microsphere was very uniform. It also showed good salt-tolerance with the salinity up to 250,000 mg/l in solution of NaCl and KCl, in 7500 mg/l $CaCl_2$ and $MgCl_2$ solution and 2000 mg/l $FeCl_3$ solution. The dilatation of copolymeric microsphere increased with increasing temperature of salt solutions. It also exhibited better injection capability and delaying-dilatation rate which makes it easier to enter the depth-reservoir. The important fact was that the toughness of the copolymeric microsphere was lower than that of irregular copolymeric particle, suggesting that the copolymeric microsphere could exhibit good anti-friability. It is worthy to note that the copolymeric microsphere could enhance the oil recovery compared with the corresponding irregular copolymeric particle. Further research is in progress.

Experimental part

Materials

N,N'--methylene-bis-acrylamide(NMBA, Aldrich), acrylamide (AM, Aldrich), acrylonitrile (AN, Fluka) and 2-acrylamido-2-methylpropane sulfonic Acid (AMPS, Aldrich). Other materials were purchased from Beibei Reagent Ltd. (Chongqing, China), including cyclohexane, Span60, hydroxyethyl cellulose, sodium chloride (NaCl), potassium chloride (KCl), ferri chloride ($FeCl_3$), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), potassium persulphate (KPS), ethanol and methanol.

Synthesis of copolymeric microsphere

A 250-mL thermostatic flask equipped with a reflux condenser and a stirrer was charged with required amount of cyclohexane, hydroxyethyl cellulose and Span60.

The mixture was stirred until the Span60 was solved and kept at 40 ^{0}C. Certain amount of distilled water, NMBA, AM, AN, AMPS was introduced into a 100 mL beaker. Then the obtained solution in beaker was added dropwise into the flask in 30 minutes. The stirrer speed was maintained at 400 rpm. Air was flushed from the reactor by introducing nitrogen until the entire process was completed. There was a marked increase in the viscosity of the medium and the colour changed from milky white to pink. The inversion of phases occurred. And 10 ml 0.02% KPS solution was dropped into 250 mL flask in 15 minutes. After 1.5 h, a little of water soluble cellulose in water was charged into mixture system. Then the temperature was kept 70 ^{0}C for 8 h. After the reaction, the suspension system was cooled and then precipitated by 1000 mL cool ethanol under stirring. The production was filtered and washed by the mixture of water and methanol (1:9 volumes) three times; the copolymeric microsphere was dried under vacuum at 50 ^{0}C for 24 h. A white powder was obtained.

The microscopic image of the resultant copolymeric microspheres was observed by XSS-2 optical microscope. The microspheres' average particle size and size distribution were determined by laser diffraction particle size analyzer (Mastersizer 2000, Malvern, UK). It is necessary to point out that the particle size distribution was evaluated by uniformity. Uniformity is statistically a measure of the absolute deviation from the median of microsphere size; the wider the particle size distribution, the larger the uniformity.

FT-IR

The samples were crushed with KBr to get pellets by applying a pressure of 600 kg/cm^2. Spectral scans were taken in the range between 4000 and 500 cm^{-1} on a Nicolet (Model Impact 410, Milwaukee, WI, USA) instrument. The samples were run 2 (HAPAM) and run 12(PAM)

Salt tolerance and thermal stability

0.1 g of dry copolymeric microsphere was swelled completely in NaCl, KCl, $FeCl_3$, $CaCl_2$, $MgCl_2$ solutions at 25 ^{0}C. The weight of the swelled gel was measured using tea bag method [21-26]. Dilatation of the copolymeric microsphere can be calculated by the following equation:

$$Q = (W_{sp} - W_p)/W_p \tag{2}$$

where $W_{sp,}$ W_p represent the weight of swelled and dry microsphere respectively.

The abovementioned experiment was repeated at 40 ^{0}C, 70 ^{0}C and 80 ^{0}C.

Rate of water dilatation

0.1 g of dry copolymeric microsphere which was put into stocks was immersed in NaCl solutions at 25 ^{0}C. The weight of the swelled gel was measured at intervals.

Gel toughness

The copolymeric microsphere were suspended in a polymer solution and dispersed in the middle container of coreflood device designed based on Smith's procedure [29]. Pressure difference (ΔP_1) was recorded until no fluid flowed out. Then the used fluid was put back into the middle container, the pressure difference (ΔP_2) was recorded when the above were repeated. Similar experimental process has been described in literature [15].

Gel-ejection properties

The sand pipe was made with water permeability of 2-20 μm^2, length of 40.0 cm, and a cross-sectional area of 0.95 cm^2. Then the copolymeric microsphere containing HPAM (partially hydrolyzed polyacrylamide) solution (100 mg/l) was poured into the middle container and allowed it to flood through the pipe. The corresponding flux and the fluid pressure difference of the particle containing HPAM solution were recorded [15, 31, 32].

Enhance oil recovery experiment

To examine the property of copolymeric microsphere for EOR, the coreflood was performed. The detail can be found in the literature [15, 30]. The difference was that irregular copolymeric particle was replaced by the copolymeric microsphere. It is necessary to point out that this study was based on the comparison between the behaviours of copolymeric microsphere and irregular copolymeric particle.

Acknowledgements

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