Research Article

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Study on the variation of rock pore structure after polymer gel flooding

<https://doi.org/10.1515/epoly-2020-0004>

Received August 29, 2019; accepted October 30, 2019.

Abstract: Polymer gels have received an increasing attention as profile control agents in the heterogeneous reservoir water-flooded layers. The article focus on the profile control mechanism of polymer gels by plugging macro-pore. The micro-structures of polymer gel and pore were characterized by scanning electron microscopy (SEM). And the core displacement equipment was used to evaluate the properties of plugging properties. The variation of pore structure is measured by SEM, mercury intrusion meter and nuclear magnetic resonance instrument. Investigation results show that the molecules form a network structure with many dense layers after 15 days of cross-linking reaction, which results in the increase of the viscosity of the system from 15.3 to 6325 mPa·s. After the polymer gel forms a micelle at the middle end of the core and blocks the pores, the plugging rate of the core reaches 99.2%. The results obtained in this paper reveal the mechanism of plugging characteristics of polymer gels, and further prove the great potential of polymer gels to enhance oil recovery in oilfields.

Keywords: polymer gel; pore structure; dynamic migration; plugging capacity; EOR

1 Introduction

Many advanced technologies have shown good application prospects in profile control, which range from polymer gels, polymer particles, precipitates, emulsions

and so on. Injected water, which is preferentially seeping in the large pores, cannot displace oil in low permeability reservoirs during oilfield development (1,2). Because of the scouring water, the pore structure changes significantly and the permeability difference is further increased. The operating principle of polymer gel is to block the high permeability layer with gel so that the injected water can reach the low-permeability layer, and then to adjust the water absorption profile. However, the gel system generally only works as a plug in the oil layer near the water injection well, and water will quickly enter the high-permeability zone again, which results in limited deep-displacement. Therefore, the effective migration of the polymer gel system in the pore space and the effective sealing of the large pores after the gelation of polymer gel are the key parts of the deep profile control technology (3-5).

In recent years, the evaluation models of polymer gel profile control mechanism include core and etched glass (6-9). In these core displacement experiments, many scholars have found that polymer gel particles can be adsorbed and accumulated on the inner wall of the pore, which can reduce the effective flow area of the macro-pore (10). The experimental conclusion is usually indirectly obtained by a large increase in the injection pressure. Experiments used microscopy to observe the migration of polymer gels in glass channels, which simulated the pore structure of rocks, are impossible to simulate the adsorption and aggregation of polymer gels. Therefore, some advanced technologies, such as scanning electron microscopy, mercury intrusion and nuclear magnetic resonance, are necessary to evaluate the variation of pore structure after gel adsorption and accumulation (11-13).

In this article, SEM was used to measure the molecular structure of polymer gels, which can reveal the microscopic mechanism of profile control. After 15 days of cross-linking reaction, the polymer gel formed a stable spatial structure of layers and layers, resulting in a 400-fold increase in viscosity. Flooding pressure of core experiments indicate that the injection of the polymer gel can reduce the core permeability by 99.7%. SEM showed

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that a large number of micelles can also be found adsorbed on the inner surface of the pores and unable migrate to the rear end of the core with subsequent injection of water. Additionally, the changes of pore structure were systematically investigated.

2 Materials and methods

2.1 Materials

The polymer with a relative molecular mass of 1.9×10^6 was purchased from China Petroleum Refinery Company (Daqing, China). Chromium acetate and Thiourea were purchased from Huadong Reagent Company (Shenyang, China). Various inorganic salts were purchased from Beijing Chemical Company (Beijing, China). Experimental water is distilled by Northeast Petroleum University. The ion composition in water is shown in Table 1.

2.2 Preparation of the polymer gel

During the preparation of the polymer gel solution, 1.5 g of the polymer powder was dissolved in 1 L sewage stirred in 400 rpm for 3 h. 3 g chromium acetate and 0.3 g thiourea were sequentially added to the mixture until the solution becomes uniformity. Moreover, the polymer gel solution is ripened at 45°C for 12 h and then are separated into 10 sealed bottles.

2.3 Viscosity characterization of the polymer gel

The viscosity of polymer gel was observed by a RS150 rheometer (HAAKE, Berlin, Germany). The temperature range of the instrument is 0-500°C. The polymer solution was added to the cone plate system when the water temperature was constant at 45°C and the data of viscosity was automatically controlled by a computer.

2.4 Molecular structure of the polymer gel

The space structure of the polymer gels were measured by scanning electron microscopy (SEM, FEI Co., MA, USA). The first step was to freeze the polymer gels with liquid nitrogen and then rapidly raise the temperature to obtain a dried sample. Finally, a conductive metal film was sprayed on the surface of the sample to observe the microstructure of the polymer gels.

2.5 Plugging capacity and gel retention of the core pores

The experimental equipment, which was shown in Figure 1, mainly includes the displacement pump, the pressure collection system and the middle container. A core with a length of 9.5 cm, a diameter of 2.5 cm and a permeability of $2015 \times 10^{-3} \mu\text{m}^2$ was used to determine the plugging capacity of the nanoparticles. Firstly, the core is vacuumed for 4 h and then saturated with sewage. Secondly, injecting water into the core until the pressure is steady to a constant value P1. Thirdly, 0.3 times the pore volume (PV) polymer gel was injected into the core. After 15 days gelling reaction is completed, water is injected again until the pressure at both ends of the core reaches a steady level. Calculate the permeability of the core before and after injection of the gel using the Darcy formula. In this method, core plugging rate is an important index to measure plugging capacity of profile control agent. The calculation formula is conducted as follows:

$$D_p = \frac{K_1 - K_2}{K_1} \cdot 100\% \quad (1)$$

The core after the polymer gel flooding is divided into three equal parts, which are used to determine the gel adsorption at different positions of the core. Sampling the front face of three cores after cutting, and then the retention morphology of the polymer gel in the core pore was observed by a scanning electron microscope after freezing, drying and gold spraying.

Table 1: Ions in brine.

Ion	Cation			Anion				Total mineralization
	Na ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ²⁻	Cl ⁻	SO ₄ ²⁻	CO ₃ ²⁻	
Concentration (mg/L)	1265.0	32.1	7.3	1708.5	780.1	9.6	210.0	4012.7

Figure 1: Diagram of oil displacement experiment.

2.6 Mercury intrusion test of pore-size distribution

The pore size and distribution frequency of the cores before and after the polymer gel flooding were optically analyzed using a mercury porosimeter (Micromeritics, New York, USA). The mercury is injected into the core until the pressure stabilized, recording the pressure value and the volume of the incoming mercury, increasing the injection pressure and repeating the above experiment steps. By continuously increasing the injection pressure, the capillary pressure curve can be obtained and it which is combined with the mercury volume can be used to calculate the distribution probability corresponding to different pore radius intervals.

2.7 NMR test of the pore

The pore size of the core sample is analyzed by testing the transverse relaxation curve (T_2 spectrum) by NMR (Quantum Design, New York, USA). The longer the relaxation time, the larger the pore diameter; and the peak area enclosed by the signal amplitude and relaxation time can characterize the liquid volume in the pore. The large peak area indicates the large volume of liquid in the pore.

3 Results

3.1 Characterization of the polymer gels

The viscosity of the polymer gels were analyzed by rheometer, which were illustrated in Table 2. In the

initial stage of cross-linking reaction, the viscosity of the polymer gel solution rise rapidly, and reached equilibrium at 15 days, then began to decline which indicates that the gel has broken. According to Table 2, the viscosity increased 400 times from 15.3 mPa·s. This is mainly due to the hydrolysis of carboxylic acid radicals on the polymer branched chain in water and the cross-linking reaction with Cr^{3+} in the solution, resulting in the rapid increase of the viscosity of the system. At the end of the experiment, the viscosity of the gel solution was flat due to the fact that Cr^{3+} in the solution reached a dynamic equilibrium with the polymer during crosslinking.

The morphology of the polymer gel was analyzed by scanning electron microscopy (SEM) after the cross-linking reaction. The structure of polymer and gel were analyzed by SEM, which were illustrated in Figures 2a and 2b, respectively.

As shown in Figure 2a, the polymer forms a colloidal structure with the lowest energy hexagons while a large number of fine branches were not crosslinked to form a dense spatial structure. The network structure was sparse with more space. It can be clearly seen from Figure 2b that after the polymer reacts with the chromium ion crosslinker to form a colloid, the molecules form a network structure with many dense layers. The layers are almost superimposed between the layers, so that the second layer network structure can be observed below the first layer network structure. In the spatial structure, the branches become thick trunks from the small branche, which made the whole network structure compact and compact. In the association process of polymers and crosslinkers, the single-layer network structure is closely connected to form a dense multi-layer three-dimensional network structure.

Table 2: Viscosity of polymer gel solution.

Time (Day)	0	1	3	5	7	15	30	60	90
Viscosity (mPa·s)	80.3	98.6	225.6	752.1	4253	6325	5930	4423	3762

(a) 0 day

(b) 15 day

Figure 2: SEM images of polymer gel microstructure.

3.2 Characterization of the plugging capacity (permeability decreases)

In this section, the plugging capacity of polymer gel is measured at different crosslink times. The pressure variation the injection of water and the polymer gel are plotted against the injection volume (PV) which can be used to calculate permeability through Darcy's formula, the results are shown in Figure 3. According to Figure 3, the core permeability is calculated as $2015 \times 10^{-3} \mu\text{m}^2$ through the small differential pressure in the water flooding stage. In the subsequent water flooding stage after the injection of 0.3 PV polymer gels, the pressure rise rapidly to 0.585 MPa and then slightly drops to 0.47 MPa. The plugging rate of the colloid formed by the injection of polymer gel into the pore space of the core reached 99.7%, which proved that the plugging agent selected in this paper has a good effect of blocking large pores.

3.3 Gel retention in core pores

The morphology of pore structure before gel flooding and the polymer gel retention in the pores at different positions after gel flooding were analyzed by scanning electron microscopy (SEM), the results are presented as Figures 4 and 5, respectively. The microscopy images of Figure 4 show that the debris particle, which are round and

Figure 3: Injection pressure of polymer gel.

prismatic, have good sorting ability before the polymer gel enters the core. The contact relationship between the particles was point contact. The pore development type was mainly composed of intergranular pores, followed by granular dissolved pores. There were fewer debris materials in the throat which mainly included the reduced portion of the pores in the throat and the contracted portion of the variable section.

According to Figure 5, the gel solution is largely retained in the form of micelles on the front end face of the core which blocked the pore space. In the middle of the core, some micelles are also found adsorbing on the

Figure 4: Morphology of core pore structure before gel flooding.

Figure 5: Morphology of core pore structure after gel flooding.

inner surface of the pore, which reduces the effective pore volume and permeability of the core. But at the back end of the core, pore morphology is still clearly visible with a small amount of micelles, which indicates that the polymer gel did not migrate to the rear end of the core with subsequent injection of water. The polymer gel has a good plugging effect so that the diffusion area of the injected water can be enlarged in the heterogeneous reservoir, thereby improving the oil recovery.

3.4 Core pressure mercury test

The pore radius distribution frequency of the core before and after polymer gel flooding is shown in Figure 6. The capillary pressure curve in the process of mercury intrusion can reflect the distribution law of the pore structure. The longer the flat section is, the more uniform the distribution of the microscopic pore structure and the larger the throat size. In this paper, the main oil channel radius and the effective seepage channel radius are used to describe the contribution of the pore throat radius to

the permeability. The oil channel radius refers to the pore throat radius distribution interval corresponding to the peak of the permeability contribution distribution curve. The peak frequency of the core pore throat distribution before gel flooding appeared at $25\ \mu\text{m}$ while value is reduced to $16\ \mu\text{m}$ after the injection gel was profiled.

The pore structure parameters in the mercury intrusion test are extracted in Table 3, which can directly reflect the change of the pore structure of the polymer gel retention. Meanwhile, the plugging ability of the polymer gel to the core can also be reflected. After the polymer gel is detained in the core, the average pore radius decreased from $19.82\ \mu\text{m}$ to $12.99\ \mu\text{m}$, which is reduced by 34.5%.

3.5 Core NMR test

Nuclear magnetic resonance relaxation is divided into transverse relaxation and longitudinal relaxation according to the direction of the mass subsystem, which is closely related to the structure and dynamic processes

(a) Before gel flooding

(b) After gel flooding

Figure 6: Distribution frequency of pore radius.

Table 3: Pore structure parameters of cores.

Parameters	Before displacement	After displacement
Permeability ($10^{-3} \mu\text{m}^2$)	1918.6	866
Porosity (%)	29	26.8
Discharge pressure (MPa)	0.013	0.014
Average pore radius (μm)	19.82	12.987
Maximum mercury saturation (%)	91.845	86.485
Permeability distribution peak (%)	46.215	58.642
Pore distribution peak (%)	37.462	28.562

of the material molecules and the environment. Since the longitudinal relaxation is measured in the actual test for a long time and the number of measuring points is small, the physical properties of the samples before and after the core profile are analyzed by the transverse relaxation curve (T2 spectrum), the results are shown in Figure 7. It can be seen from Figure 8 that the peak area gradually decreases with the injection of the polymer, which proves that the pore space in the core is gradually reduced.

Figure 7: Changes of T2 spectrum during displacement process.

Figure 8: Porosity component distributions before and after gel flooding.

In the water flooding stage, the T2 value corresponds to the peak of the water content of the porosity component is 27.9%. After the gel plugging, the water content of the porosity component decreases by 19.5%, and the drop rate reaches 30%.

4 Conclusions

In this paper, the polymer gel can form a stable spatial network structure after 15 days of crosslinking reaction, which resulted in a 400-fold increase in solution viscosity. The SEM results showed that the gelled micelles are mainly retained at the front end of the core without propelling with the subsequent injection of water. In addition, polymer gel can effectively plug the pores, which the plugging rate can reach 99.32% and the average pore radius decreased by 34.5%. Because of excellent plugging ability, the polymer gel has great potential in improving oil recovery in oilfields.

Acknowledgment: The project was supported by Youth Science Fund Project of Northeast Petroleum University (228QNC-37).

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