A novel method for improving recovery of heavy oil reservoirs with high water cut based on polymer gel-assisted CO₂ huff and puff

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Received: 6 March 2021 / Accepted: 2 July 2021 / Published online: 17 July 2021
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Abstract
A novel enhanced oil recovery (EOR) method based on polymer gel-assisted carbon dioxide (CO₂) huff and puff was developed aiming to improve the development effect of heavy oil reservoirs with high water cut. The polymer gel prepared using partially hydrolyzed polyacrylamide (HPAM), hexamethylenetetramine, phenol, resorcinol, oxalic acid, and thiocarbamide as raw materials had a special network structure to overcome the challenge of significant heterogeneity in heavy oil reservoirs. The strength of polymer gel reached the maximum value 20,000 mPa·s within 22 h. The temperature resistance and salt resistance of polymer gel directly determined the plugging effect. The polymer gel was placed for 190 days at 85 °C, and its apparent viscosity retention rate was 66.4%. The salt resistance experiments showed that the apparent viscosity retention rate of this polymer gel at 1.8 wt % NaCl, 0.045 wt % CaCl₂, 0.045 wt % MgCl₂ was 71.3%, 78.5%, 71.4%, respectively. Huff and puff experiments confirmed that this method could be used to increase the sweep volume and improve the oil displacement efficiency of heavy oil reservoirs with high water cut. Furthermore, the EOR of this method was better than that of water huff and puff, polymer gel huff and puff or CO₂ huff and puff.

Keywords Heavy oil reservoirs · CO₂ huff and puff · Polymer gel · Enhanced oil recovery

Introduction
It is well known that the geological reserves of heavy oil are much higher than that of conventional crude oil (Huang et al. 2018; Guo et al. 2016). With the decreasing of conventional crude oil recoverable reserves, the position of heavy oil resources in energy structure is more and more important (Amirian et al. 2018; Cao and Gu 2013).

At present, thermal recovery technology (such as steam-assisted gravity drainage, steam huff and puff, steam flooding, burning oil layer, and hot water flooding) is used in the world to develop the heavy oil reservoir with a depth less than 1000 m and a thickness more than 10 m (Lyu et al. 2018; Butler et al. 2010; Sherratt et al. 2018; Ahmadi et al. 2014; Xu et al. 2013). Unfortunately, due to the reservoir heterogeneity, the displacing medium (steam, hot water, etc.) will flow along the high-capacity channel during the thermal recovery process, and the sweep efficiency of the displacing medium is relatively low (Ravalec et al. 2009; Kharrat et al. 2011; Ali et al. 2012). As a result, the water cut of heavy oil reservoir will reach 90% rapidly, and the recovery of thermal recovery technology is usually less than 20% OOIP (original oil in place) (Salmo et al. 2017; Taborda et al. 2016; Riazi and Golkari 2016; Mayorquin-Ruiz and Babadagli 2016). Moreover, thermal recovery technology generally requires high temperature (at least 95 °C), and it is very difficult to increase sweep efficiency using chemical methods under this conditions. Therefore, the effect of thermal recovery technology in high water cut heavy oil reservoir is generally not satisfactory (Salmo et al. 2017; Riazi and Golkari 2016).

In addition to the thermal recovery technology, the chemical cold recovery technology, such as polymer flooding, surfactant flooding, alkaline water flooding, carbon dioxide (CO₂) flooding, and chemical huff and puff, is mainly used for the exploitation of the heavy oil reservoir with a depth more than 1000 m or the marginal heavy oil reservoir...
with small reserves (Guo et al. 2013a; Sedaghat et al. 2013; Zhang et al. 2016; Jamaloei et al. 2016). Although chemical cold recovery technology can effectively reduce the viscosity of crude oil and interphase interface tension, the chemical agents are easy to form adsorption on the surface of the rock or dissolve in formation water, resulting in the waste of chemical agents and high cost (Guo et al. 2013b; Pei et al. 2014; Coskuner et al. 2015; Mohsenzadeh et al. 2015). At the same time, the primary and secondary high capacity channel will greatly reduce the application effect of chemical cold recovery technology (Ravalec et al. 2009; Kharrat et al. 2011; Ali et al. 2012). Similar to thermal recovery technology, the water cut of heavy oil reservoirs increases rapidly using cold recovery technology. However, there are very few methods to improve the recovery of heavy oil reservoirs with high water cut (Yang et al. 2018; Fang et al. 2018; Liu et al. 2017; Alemu et al. 2013; Wang and Gu 2011; Zhao et al. 2011). With the deepening of the world’s oil production, how to improve the recovery of heavy oil with high water cut economically and effectively is a challenge for petroleum workers.

Polymer gel plays a good role in preventing gas channeling in CO₂ flooding (Secaeddin et al. 2012). Keep in mind the requirement of enhanced oil recovery (EOR) technology, herein, a novel EOR method based on polymer gel-assisted CO₂ huff and puff was proposed aiming to develop heavy oil reservoirs with high water cut economically and effectively. The main ideas of this method are as follows: (1) polymer gel is used to block the high capacity channel, prevent CO₂ from channeling along the high capacity channel and increase sweep efficiency of CO₂. (2) CO₂ is injected to improve the flow performance of heavy oil. After dissolved in crude oil, CO₂ can reduce the viscosity of heavy oil and interfacial tension of heavy oil/water. (3) Shut the well to make CO₂ and heavy oil fully function. (4) Open-well production.

In this paper, a new method to enhance oil recovery for high water cut heavy oil reservoirs after thermal recovery or cold recovery was provided, especially for the heavy oil reservoirs with a depth more than 1000 m and the marginal heavy oil reservoir with small reserves.

### Experimental section

#### Materials

Partially hydrolyzed polyacrylamide (HPAM, degree of hydrolysis: 20%, viscosity molecular weight: 20 × 10⁶) was purchased from Sichuan Guangya Polymer Chemical Co., Ltd. Hexamethylenetetramine (C₆H₁₂N₄, AR), phenol (C₆H₆O, AR), resorcinol (C₆H₆O₂, AR), oxalic acid (C₂H₂O₄, AR), thiocarbamide (CH₄N₂S, AR), sodium chloride (NaCl, AR), potassium chloride (KCl, AR), calcium chloride anhydrous (CaCl₂, AR), magnesium chloride hexahydrate (MgCl₂, AR), sodium bicarbonate (NaHCO₃, AR), sodium sulfate (Na₂SO₄, AR), and kerosene were obtained from Chengdu Kelong Chemical Reagent Plant. All chemicals and reagents were used as received without any further purification. CO₂ with purity of 99.9% was purchased from Tangshan Sihai Gas Company. The injected water and formation water were taken from Jidong Oilfield. Their ionic composition is shown in Table 1.

Crude oil was obtained from Jidong Oilfield. The density and apparent viscosity of the crude oil on the ground were 0.956 g/cm³ and 1089.9 mPa·s at 25 °C, respectively. Oil sand was taken from Jidong Oilfield. The crude oil on the oil sand surface was cleaned by kerosene and hot water in turn and then dried for 24 h at 100 °C. The length and

| Table 1 The ionic composition of the injected water and formation water |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Items | Na⁺ + K⁺ | Ca²⁺ | Mg²⁺ | SO₄²⁻ | Cl⁻ | HCO₃⁻ |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Content of injected water (wt %) | 0.2093 | 0.0074 | 0.0041 | 0.0095 | 0.3225 | 0.0418 |
| Content of formation water (wt %) | 0.3072 | 0.0131 | 0.0054 | 0.0125 | 0.4581 | 0.0573 |
diameter of sand packed model (Fig. 1) were 30 cm and 2.5 cm, respectively.

**Preparation of polymer gel**

In a 1000-ml beaker, 400 g injected water and 1.8 g HPAM were added, and the polymer solution was prepared after 2 h of agitation at room temperature. A total of 200 g injected water, 0.48 g hexamethylenetetramine, 0.48 g phenol, 0.09 g resorcinol, 0.3 g oxalic acid, and 0.06 g thiocarbamide were added to a 500-ml beaker, respectively. The mixed solution was stirred for 20 min at room temperature, and the cross-linker solution was obtained. Then the cross-linker solution was added to the polymer solution and stirred for 5 min to prepare the mixture of polymer solution and cross-linker solution (MPSC).

**Gelation time and strength**

The glass bottle equipped with MPSC was placed in the thermostat at a temperature of 65 °C, and the apparent viscosity of polymer gel was regularly measured with a Brookfield DV3T viscometer at 65 °C.

**Temperature resistance**

MPSC prepared using the injected water was packed in three glass bottles, and these glass bottles were put into the thermostats with different temperatures (65 °C, 75 °C, 85 °C). The apparent viscosity of polymer gel small sample was regularly measured with a Brookfield DV3T viscometer at 65 °C.

**Salt resistance**

The salt resistance of MPSC was investigated by NaCl, CaCl$_2$, and MgCl$_2$ with different concentrations, respectively. The apparent viscosity of MPSC after gelling was measured with a Brookfield DV3T viscometer at 65 °C.

**Evaluation experiment of profile improvement performance**

Double-tube experiments were carried out to study the profile improvement ability of polymer gel at 65 °C. After being cleaned and dried, the oil sand was used to fill the sand packed model, and the filling pressure was 10 MPa. The high-permeability sand packed model and the low-permeability sand packed model were prepared using 40–80 mesh oil sand and 100–140 mesh oil sand, respectively. The experimental instruments were installed as shown in Fig. 2. In the process of experiments, the back pressure was 12 MPa.

The sand packed models were saturated with the formation water at 1.0 ml/min until injection pressure was stable. 0.3 PV (pore volume) MPSC was injected into the sand packed models at 0.2 ml/min. At 48 h later, the injected water was injected into the sand packed models at 1 ml/min until pressure was stable. The water production of the sand packed models was measured.

The profile improvement rate of polymer gel was calculated with the following equation:

$$f = \frac{Q_{hb}/Q_{lb} - Q_{ha}/Q_{la}}{Q_{hb}/Q_{lb}}$$

(1)

where $f$ is the profile improvement rate of polymer gel, %; $Q_{hb}$ is liquid flow velocity of the high-permeability sand packed model before polymer gel plugging, ml/min; $Q_{ha}$ is liquid flow velocity of the high-permeability sand packed model after polymer gel plugging, ml/min; $Q_{lb}$ is liquid flow velocity of the low-permeability sand packed model before polymer gel plugging, ml/min; $Q_{la}$ is liquid flow velocity of...
the low-permeability sand packed model after polymer gel plugging, ml/min.

**Polymer gel-assisted CO₂ huff and puff experiment**

The huff and puff experiments were used to study the EOR effect of polymer-assisted CO₂ huff and puff at 65 °C. According to Fig. 2, the experimental devices were connected. All experiments were carried out under the 12 MPa back pressure. The formation water was injected into the sand packed models at 1 ml/min until pressure was stable. The sand-packed models were saturated with the crude oil at 0.2 ml/min to obtain bound water saturation, and then the injected water was used to displace the crude oil at 1 ml/min until the water cut reached 99%.

According to Fig. 2, the experimental devices were connected. All experiments were carried out under the 12 MPa back pressure. The formation water was injected into the sand packed models at 1 ml/min until pressure was stable. The sand-packed models were saturated with the crude oil at 0.2 ml/min to obtain bound water saturation, and then the injected water was used to displace the crude oil at 1 ml/min until the water cut reached 99%.

According to Fig. 3, the experimental devices were prepared. 0.1 PV MPSC was injected into the sand packed models at 0.2 ml/min. 48 h later, 0.2 PV CO₂ (temperature 65 °C, pressure 12 MPa) was injected into the sand packed models at 0.2 ml/min. Ten days later, the outlet valves were opened, and the oil production of the sand packed models was measured.

The EOR of the polymer gel-assisted CO₂ huff and puff was calculated with the following equation:

\[
\text{EOR} = \frac{E_1 - E_2}{E_0} \times 100
\]

(2)

where EOR is enhanced oil recovery of the polymer gel-assisted CO₂ huff and puff, %; \(E_1\) is the oil production of the whole experiment process, ml; \(E_2\) is the oil production of water flooding stage, ml; \(E_0\) is the amount of crude oil in the sand packed models, ml.

According to the above experimental method, EOR of water huff and puff, CO₂ huff and puff, and polymer gel huff and puff was determined under the same conditions. The amount of water, CO₂, and MPSC was 0.3 PV.

**Results and discussion**

**Gelation time and strength**

The apparent viscosity–time curve of polymer gel is presented in Fig. 4. When MPSC was put into the thermostat at a temperature of 65 °C, its apparent viscosity increased rapidly. After 22 h, the apparent viscosity of polymer gel reached 20,000 mPa-s. Subsequently, the apparent viscosity of polymer gel fluctuated at around 20,000 mPa-s. It could be found that the gelation time and strength of polymer gel were 22 h and 20,000 mPa-s, respectively.

**Temperature resistance**

The influence of temperature on the apparent viscosity of polymer gel was studied. The results are shown in Fig. 5.

![Fig. 4 The apparent viscosity-time curve of polymer gel](image-url)

*Fig. 3 Flow chart of the huff and puff stage*
The apparent viscosity of polymer gel decreased slowly with the increase in storage time at different temperatures. After 190 days, the apparent viscosity of polymer gel at 65 °C, 75 °C, and 85 °C was 17,450 mPa·s, 16,060 mPa·s, and 13,280 mPa·s, and the apparent viscosity retention rate of polymer gel was 87.3%, 80.3%, and 66.4%, respectively. The colloidal morphology of polymer gel is shown in Fig. 6. We could easily find that the colloid was less affected by temperature, and the gel breaking phenomenon is not observed in Fig. 6. The above experiments proved that the temperature resistance of polymer gel basically met most heavy oil reservoir requirements, because the temperature of these heavy oil reservoirs was usually below 75 °C (Sun et al. 2017; Xie et al. 2017; Zuloaga et al. 2017).

**Salt resistance**

The influence of NaCl on apparent viscosity of polymer gel is shown in Fig. 7. The influence of CaCl$_2$ or MgCl$_2$ on apparent viscosity of polymer gel is shown in Fig. 8. It could be found that the decrease in apparent viscosity of polymer gel was smaller when the concentration of NaCl exceeded 1.0 wt % or the concentration of two valence salt (CaCl$_2$ or MgCl$_2$) exceeded 0.03 wt %. This phenomenon could be well explained by the polyelectrolyte behavior of the polymer in brine-free water (Liu et al. 2013). Because the concentration of cations was increased in the solution, the stretched polyelectrolyte chain started shrinking due to a reduction in intra-anionic electrostatic repulsion. When the cations concentration reached the required amount of complete shrinking, the apparent viscosity would no longer decreased with the increase of salt concentration (Liu et al. 2012; Ye et al. 2013). The apparent viscosity retention rate of this polymer gel at 1.8 wt % NaCl, 0.045 wt % CaCl$_2$, and 0.045 wt % MgCl$_2$ was 71.3%, 78.5%, 71.4%, respectively. The buried depth of conventional heavy oil reservoirs was less than 1000 m. The contents of NaCl, CaCl$_2$, and MgCl$_2$ in formation water were usually lower than 1.8 wt %, 0.045 wt %, and 0.045 wt %, respectively. Therefore, the salt resistance of MPSC could meet the requirement of plugging the high capacity channel in heavy oil reservoirs.
Profile improvement ability of polymer gel

The parameters and results of the double tube experiments are shown in Table 2. Before the polymer gel plugging, the liquid flow velocity of the high-permeability sand packed model and the low-permeability sand packed model were 0.83 ml/min and 0.17 ml/min, respectively. During water injection process after polymer gel plugging, the liquid flow velocity of the high-permeability sand packed model was reduced to 0.32 ml/min. The liquid flow velocity of the low-permeability sand packed model was increased to 0.68 ml/min correspondingly. Profile improvement rate of the polymer gel was 89.6% under the above experimental conditions. The experimental results confirmed that the water injection profile was improved after polymer gel plugging.

Table 2 The parameters and results of the double tube experiments

| Sand packed models | Porosity | Permeability before plugging | Liquid flow velocity before plugging | Injected gel | Permeability after plugging | Liquid flow velocity after plugging | Profile improvement rate |
|--------------------|----------|------------------------------|-------------------------------------|--------------|-----------------------------|-------------------------------------|--------------------------|
| 1#                 | 30.1     | 1531                         | 0.83                                | 20.1         | 106                         | 0.32                                | 89.6                     |
| 2#                 | 23.2     | 319                          | 0.17                                | 3.4          | 225                         | 0.68                                |                          |

The sand in the sand packed model was cooled by liquid nitrogen and then vacuumed. Scanning electron microscopy (SEM) was used to observe the plugging of polymer gel at room temperature. As shown in Fig. 9c, we could clearly found that there existed space network structures of the polymer gel after being cooled and dried in the pore throat of the sand. The results indicated that the high-permeability sand packed model was blocked by polymer gel. Therefore, its permeability was greatly reduced after the polymer gel was injected (Lai et al. 2013). In addition, due to the presence of electrostatic and hydrogen bonds, the polymer gel would be adsorbed on the surface of the sand, which helped to improve the blocking strength and anti-erosion property of polymer gel (Xu et al. 2015; Alcázar-Vara et al. 2015; Cheraghian et al. 2017; Pang et al. 2015). As shown in Fig. 9b, d, on the
contrary, polymer gel had little effect on the pore throat of the sand in low-permeability sand packed model, because MPSC mainly entered high-permeability sand packed model during injection process.

**EOR of the polymer gel-assisted CO₂ huff and puff**

Huff and puff experiments were carried out to evaluate the EOR effect of several different huff and puff methods under the same experimental conditions. The parameters of the sand packed models and experimental results are shown in Table 3. In the four huff and puff methods, the polymer gel-assisted CO₂ huff and puff had the largest EOR, the second was the CO₂ huff and puff, and the water huff and puff was the least.

As shown in Table 3, most of the oil production came from the high-permeability sand packed models (3#, 5#, 7#, 9#) due to smaller flow resistance to crude oil in the water flooding stage. For water huff and puff and CO₂ huff and puff, as the high-capacity channel being not blocked, the injected huff and puff media mainly entered the high-permeability sand packed models in the huff stage, and most of these media could be taken out during the puff stage. Because the remaining oil of the high-permeability sand packed models was less, the EOR of these two methods was relatively low. Compared with water huff and puff, the EOR of CO₂ huff and puff was higher, because CO₂ could dissolve in crude oil and reduce oil/water interfacial tension. At the same time, CO₂ could reduce the viscosity of crude oil (Mao et al. 2018; Li et al. 2018; Ren et al. 2017; Fang et al. 2017).

For polymer gel-assisted CO₂ huff and puff, the high-permeability sand packed model would be blocked by polymer gel, and CO₂ would enter the low-permeability sand packed model with higher oil saturation. Then the crude oil would be produced from the low-permeability sand packed model. Compared with polymer gel huff and puff, polymer gel-assisted CO₂ huff and puff could not only expand the sweep volume, but also improve the oil displacement efficiency, so it had a higher EOR (11.30% vs. 4.88%).

**Conclusions**

A novel EOR method base on polymer gel-assisted CO₂ huff and puff was put forward aiming to improve the development effect of heavy oil reservoirs with high water cut. A polymer gel was prepared using HPAM, hexamethylenetetramine, phenol, resorcinol, oxalic acid, and thiocarbamide as raw materials, and its heat resistance and salt tolerance could meet the requirement of plugging high capacity channel for heavy oil reservoirs. The experimental results confirmed that this method could be used to increase the sweep volume and improve the oil displacement efficiency of heavy oil reservoirs. The EOR of this method was better than that of water huff and puff, polymer gel huff and puff or CO₂ huff and puff.

**Funding** This work was funded by the Science and Technology Project of Sichuan University of Science and Engineering (2020RC05).

**Declarations**

**Conflict of interest** The authors declare that they have no conflict of interest.

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