Experimental study of asphaltene precipitation in the process of CO₂ flooding

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ABSTRACT

Because of the high displacement efficiency and greenhouse gas emissions reduction, CO₂ flooding technology is more and more attention from home and abroad, but in the process of CO₂ flooding, there is a phenomenon of asphaltene precipitation which can cause the reduction of permeability. With actual crude oil in certain oilfield as an example, the regular pattern of asphaltene precipitation in the process of CO₂ injection was studied, and the results showed that with the increase of injection pressure, amount of asphaltene precipitation increase gradually, and the core permeability decreases. For the influence of asphaltene precipitation, in the oil displacement process, the displacement efficiency decline.

Keywords: Asphaltene precipitation, CO₂ flooding, Displacement efficiency, Permeability

INTRODUCTION

In the process of CO₂ miscible flooding, CO₂ can extract the light component of crude oil or make its gasification, reducing interfacial tension to make CO₂ miscible in oil, this is the most important mechanism of CO₂ flooding to improve oil recovery. On the one hand, the technology of CO₂ flooding use greenhouse gas CO₂ as oil displacement agent to protect the ecological environment and improve economic efficiency, and on the other hand, this way of oil displacement can improve oil recovery significantly and economic performance, so CO₂ flooding technology is more and more attention from home and abroad[1-3].

Under the condition of normal oil reservoir, colloid-asphaltene-crude oil is in a state of dynamic balance. CO₂ flooding can reduce the asphaltene stability, causing asphaltene flocculation and sedimentation[4-5]. Asphaltene deposition would block reservoir and oil extraction equipment, reduce the oil well productivity, increase production and operation costs, processing costs faced by the current petroleum industry is one of the highest technical problem[6-7]. Therefore, the study of asphaltene precipitation of oilfield development has important guiding meaning and application value.

EXPERIMENTAL SECTION

Experimental principle

On the condition of formation pressure and temperature, CO₂ was injected into the core of saturated oil to simulate asphaltene precipitation behavior. First, oil known asphaltene content was injected into the core of saturated formation water to establish irreducible water saturation, and then using CO₂ to displace the fluid in core, measuring the content of oil swept from the core. Last, by comparing the asphaltene content in the crude oil before and after displacement, and the asphaltene content precipitated in the crude oil can be calculated, and the influence factors on asphaltene precipitation and the precipitation mechanism can be studied.
Experimental apparatus and materials
According to the experimental principle and purpose, considering the basic principle of core displacement experiment device and the discharged liquid flow metering and the need of sampling, a set of asphaltene precipitation measuring and displacement experimental device was designed and manufactured. The experimental device is mainly composed of the advection pump, hand pump, core gripper, back pressure regulating system, differential pressure gauge, pressure sensor, incubator, etc. The experimental device was a closed system to against the change of oil/gas component. The flow chart is as follows:

![Fig.1 The experiment flow diagram](image)

1. 2—container  3. 4. 8. 10. 12. 14. 16—valve
6. 11. 17—pressure gauge  7. 15. 21—manometer
13—hand pump  8—incubator
5—constant-flux pump  9—core holder
19—back-pressure valve  20—core

(1) Experimental apparatus
Experimental instruments used are shown in table 1.

<table>
<thead>
<tr>
<th>instrument</th>
<th>specification</th>
<th>quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>flask</td>
<td>250mL</td>
<td>2</td>
</tr>
<tr>
<td>extractor</td>
<td>250mL</td>
<td>1</td>
</tr>
<tr>
<td>beaker</td>
<td>80mL</td>
<td>5</td>
</tr>
<tr>
<td>measuring cylinder</td>
<td>250mL</td>
<td>2</td>
</tr>
<tr>
<td>measuring cylinder</td>
<td>25mL</td>
<td>10</td>
</tr>
<tr>
<td>hopper</td>
<td>φ90mm</td>
<td>1</td>
</tr>
<tr>
<td>electronic balance</td>
<td>accuracy rate 0.0001g</td>
<td>1</td>
</tr>
</tbody>
</table>

(2) Experimental materials
The purity of dioxide used in experiment is 99.99%. The oil used is compound of dehydrated crude from Yuan-284 area and aviation kerosene in accordance with the proportion of 1:2. The density of the oil is 0.75 g/cm$^3$ and the viscosity is 1.05 mPa.s at the temperature of 70℃. The cores used in the experiment are sand packed model with the size of Φ3.8cm×30cm. Core parameters are shown in table 2.

<table>
<thead>
<tr>
<th>No</th>
<th>Permeability /10$^{-3}$μm$^2$</th>
<th>Porosity /%</th>
<th>Length /cm</th>
<th>Sectional area /cm$^2$</th>
<th>Experimental program</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>152</td>
<td>15.6</td>
<td>30</td>
<td>6.25</td>
<td>pressure</td>
<td>5</td>
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<tr>
<td>2</td>
<td>148</td>
<td>15.6</td>
<td>30</td>
<td>6.25</td>
<td></td>
<td>Q=0.1ml/min T=70℃</td>
</tr>
<tr>
<td>3</td>
<td>156</td>
<td>15.6</td>
<td>30</td>
<td>6.25</td>
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<td>8</td>
</tr>
<tr>
<td>4</td>
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<td>15.6</td>
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<td>6.25</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>161</td>
<td>15.6</td>
<td>30</td>
<td>6.25</td>
<td></td>
<td>15</td>
</tr>
</tbody>
</table>

Experimental procedure
(1) The artificial core was vacuumized and saturated with formation water, and then measuring the permeability and porosity. (2) The core was put into core gripper, injecting kerosene into core to displace water, until the core outlet without the water out, calculating irreducible water saturation. (3) After gas pressure was adjusted to the displacement pressure, back pressure controller was connected with the outlet and the back pressure was adjusted to experiment
pressure. (4) The CO$_2$ was injected into the core to sweep oil until no oil flow out, and the oil and gas volume displaced by CO$_2$ were measured. (5) Measuring the content of asphaltene in sweepout oil. (6) Calculating residual asphalt in the core.

RESULTS AND DISCUSSION

Effect of pressure on the content of deposited asphaltene

Table 3 Experimental data of the content of deposited asphaltene

<table>
<thead>
<tr>
<th>No.</th>
<th>Pressure /MPa</th>
<th>Saturated oil /g</th>
<th>Initial asphaltene quality of oil/%</th>
<th>Quality of oil swept /g</th>
<th>Asphaltene content in oil swept/%</th>
<th>Asphaltene content deposited in core /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>76.19</td>
<td>0.6</td>
<td>25.33</td>
<td>0.58</td>
<td>0.02</td>
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<tr>
<td>2</td>
<td>8</td>
<td>75.24</td>
<td>0.6</td>
<td>26.57</td>
<td>0.56</td>
<td>0.04</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>75.24</td>
<td>0.6</td>
<td>27.24</td>
<td>0.52</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>74.29</td>
<td>0.6</td>
<td>27.64</td>
<td>0.45</td>
<td>0.15</td>
</tr>
<tr>
<td>5</td>
<td>17</td>
<td>72.80</td>
<td>0.6</td>
<td>28.10</td>
<td>0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

At the experiment temperature of 70°C, with the increase of injecting pressure, the content of asphaltene precipitation increase gradually.

Based on the colloid theory, because CO$_2$ or other small molecule hydrocarbon and asphaltene are highly asymmetric component on the thermodynamics, the main show of the asymmetric is: (1) There is a huge difference in the molecular size. (2) There are large difference between polar molecules. As the injected CO$_2$ dissolved in the oil, its concentration in the solvation layer increases, and a large number of CO$_2$ molecules occupy the surface space of asphaltene molecules, which make the gum concentration decreased relatively and the surface energy of system greatly increased, and the micelle can not form or the thickness of micellar solvation layer is not enough, which cause asphaltene molecules associating each other to form bigger molecules in order to reduce the surface energy. When the colloidal particles continue to increase to critical point (that is, the asphaltene precipitation point), asphaltene began to deposit. The higher the injection pressure, the dissolution ability of CO$_2$ in the oil stronger, more of the small molecular components of crude oil increase, and the more the asphaltene colloid concentrations of stabilizer is smaller, the more conducive to the asphalt mutual association formed precipitation.

When the system temperature and pressure is greater than the critical temperature and pressure of CO$_2$, CO$_2$ is supercritical fluid, and the extraction ability for the light component in crude oil is stronger. In the CO$_2$-crude oil system, the extraction efficiency of CO$_2$ on crude oil increased with the increase of the pressure. And its function is to reduce oil solvation layer in the concentration of the small molecule hydrocarbon deposits, and reduce the amount of asphaltene deposition.

The sedimentary asphalt quality will be the result of comprehensive effect of the above two. When CO$_2$ injection pressure is low, the deposition effect obviously, and asphaltene deposition quantity increased with the increase of gas injection pressure increase; When the CO$_2$ pressure reaches a certain extent and make the effect is greater than the deposition effect after the dissolution of supercritical fluid, asphaltene precipitation amount will decrease with the increase of gas injection pressure.

Based on the above theory, the curve of Fig.2 should be the trend of first increasing then decreasing, but the curve in
Fig. 2 is that the amount of asphaltene precipitation increase with the injecting pressure increase. Analyzing the reason, because the original formation pressure of study block HuaQing Chang 6 reservoir is 16.7 MPa, so the highest pressure in this study is only 17 MPa, and it is mainly sedimentary effect in the experimental pressure range.

Effect of asphaltene precipitation on permeability
As shown in Fig. 3, with the increase of injection pressure, amount of asphaltene deposition increases gradually and the permeability of core decreases. At the highest test pressure of 17 MPa, the permeability decreased 12% from the original permeability 161 mD dropped to 142 mD.

![Fig. 3. The curve of permeability reduction value vs. injection pressure](image)

Effect of asphaltene precipitation on displacement efficiency
As shown in Fig. 3, with the increase of injection pressure, the displacement efficiency of kerosene and simulated oil increases also, and at the same pressure, the displacement efficiency of kerosene is higher than that of simulated oil, and the displacement efficiency difference of kerosene and simulated oil increases with the increase of injection pressure, which show that part of the asphaltene deposited in core in the process of oil displacement and precipitation amount increases with the increase of injection pressure. But on the whole, because the asphaltene content of crude oil in HuaQing Chang6 reservoir is low (0.6%), and precipitation amount is small, so the influence of asphaltene precipitation on oil displacement efficiency is not big.

![Fig. 4. The curve of oil displacement efficiency value vs. injection pressure](image)

CONCLUSION

With the increase of injection pressure, amount of asphaltene precipitation increase gradually. With the increase of injection pressure, the core permeability decreases. At the highest test pressure of 17 MPa, the permeability decreased 12%. For the influence of asphaltene precipitation, in the oil displacement process, the displacement efficiency decline.

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REFERENCES