Formation damage due to asphaltene precipitation during CO₂ flooding processes with NMR technique

Kun Qian¹, Shenglai Yang¹*, Hong-en Dou², Jieqiong Pang¹, and Yu Huang¹

¹ State Key Lab of Oil and Gas Resources and Engineering, China University of Petroleum-Beijing, Beijing 102249, People’s Republic of China
² Research Institute of Petroleum Exploration and Development, CNPC, Beijing 100083, People’s Republic of China

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Abstract. In order to quantitatively evaluate the pore-scale formation damage of tight sandstones caused by asphaltene precipitation during CO₂ flooding, the coreflood tests and Nuclear Magnetic Resonance (NMR) relaxometry measurements have been designed and applied. Five CO₂ coreflood tests at immiscible, near-miscible and miscible conditions were conducted and the characteristics of the produced oil and gas were analyzed. For each coreflood test, the $T_2$ spectrum of the core sample was measured and compared before and after CO₂ flooding to determine the asphaltene precipitation distribution in pores. It is found that, the solubility and extraction effect of the CO₂ plays a more dominant role in the CO₂-EOR (Enhanced Oil Recovery) process with higher injection pressure. And, more light components are extracted and recovered by the CO₂ and more heavy components including asphaltene are left in the core sample. Thus, the severity of formation damage influenced by asphaltene precipitation increases as the injection pressure increases. In comparison to micro and small pores (0.1–10 ms), the asphaltene precipitation has a greater influence on the medium and large pores (10–1000 ms) due to the sufficient interaction between the CO₂ and crude oil in the medium and large pores. Furthermore, the asphaltene precipitation not only causes pore clogging, but also induces rock wettability to alter towards oil-wet direction.

1 Introduction

CO₂ flooding has been proven to be an effective technique to Enhanced Oil Recovery (EOR) through both laboratory experiments and field application for several decades [1–3]. The injected CO₂ could interact with crude oil in the reservoirs, leading to significant effects on EOR. The main mechanisms of CO₂-EOR technique include oil-swelling effect, viscosity reduction, light-hydrocarbon extraction and interfacial tension reduction [4]. However, it has been reported that the interaction between CO₂ and crude oil is the determine factor for asphaltene precipitation. For example, in Midale in Canada, no prior asphaltene problem was encountered until CO₂ injection. Asphaltene precipitation also occurred in other CO₂ floods, such as in Little Creek Field, Mississippi and West Texas [5].

Asphaltene precipitation could cause serious damages to formations [5–7]. This is because the precipitated asphaltene will deposit on to the reservoir rocks, which may cause reservoir plugging and wettability alteration [8, 9]. To investigate asphaltene precipitation during CO₂ flooding processes, extensive coreflood experimental studies have been conducted. Wang et al. [10] found that the degree of permeability reduction is positively correlated with the percentage of asphaltene precipitated through CO₂ coreflood tests. Cao and Gu [11] demonstrated that less amount of asphaltene remained in the cores in immiscible conditions while more asphaltene precipitation is observed under miscible conditions. Wang et al. [12] found that permeability reduction due to asphaltene precipitation mainly occurs in the middle and tail end of the reservoir in the miscible CO₂ Water-Alternating-Gas (WAG) injection after the continuous CO₂ injection through long coreflood experiments. Moreover, the wettability alteration also occurs due to asphaltene precipitation, which has negative influence on the formation. Amroun and Tiab [13] and Escrochi et al. [14] reported that the asphaltene precipitation was the main platform for wettability alteration and the porous media changed towards strongly oil-wet condition. Uetani [15] reported that the productivity dropped immediately and water cut increased from 2–3% to 10–15% in field ‘M’, which was caused by the rock wettability altered form water-wet to oil-wet because of asphaltene precipitation.

Although, the asphaltene precipitation during CO₂ flooding could be determined through the measurement of...
permeability reduction combined with the asphaltene content of the produced oil [16, 17]. The pore-scale distribution of asphaltene deposition has been rarely investigated. Srivastava et al. [18] used X-ray CAT (Computer Aided Tomography)-scanning technique to visualize the asphaltene deposition along the length of the core. Song et al. [19] made a microscopic model to observe the distribution of asphaltene precipitation, and the influence of asphaltene precipitation on the pores cannot be quantitatively evaluated. In order to quantitatively analyze the distribution of asphaltene precipitation in pores, Wang et al. [10] applied Nuclear Magnetic Resonance (NMR) to scan tight artificial cores before and after CO2 flooding. Besides determining the distribution of asphaltene precipitation, NMR technique is a powerful tool for non-invasively analyzing the wetting state of rock [20, 21]. Shikhov et al. [22] studied the wettability change of sandstone cores over aging time with low-field NMR measurements.

In this study, an analysis method reference to Amott method [23] was proposed to quantitatively evaluate the wettability alteration before and after CO2 flooding combined with determining the distribution of asphaltene precipitation. First, in order to determine the influence of CO2-brine-rock interaction on the core samples, two core samples saturated with kerosene which does not contain asphaltene were applied to conduct CO2 coreflood experiments. Then, five CO2 coreflood tests were conducted at different injection pressures. The oil recovery factors, the viscosity and the asphaltene contents of the produced oil were measured during these tests. Then, through comparing the difference in the NMR transverse relaxation time \( (T_2) \) spectrum for the water-saturated cores before and after CO2 flooding, the distribution of asphaltene precipitation in the pores and throats of core samples was quantitatively evaluated. At the same time, the wettability alteration condition was evaluated by calculating the condition of oil saturation in pores before and after CO2 flooding. On these bases, this study can help to improve the system of quantitatively evaluating the distribution of the asphaltene precipitation and wettability alteration in pores and throats.

### 2 Experimental section

#### 2.1 Materials

In this study, the Stock Tank Oil (STO) sample was collected from Changqing Oilfield, China. The density and viscosity of the cleaned STO were measured to be 833.4 kg/m\(^3\) and 4.76 mPa s at the atmospheric pressure and 61 °C and the MW\(_{\text{oil}}\) = 229.7 g/mol. The asphaltene content of the cleaned crude oil was measured to be 0.94 wt\% \((n\)-pentane insoluble) with the standard ASTM D2007-03 method [24]. The wax content was measured by the Thin-Layer Chromatography/Flame Ionization Detection (TLC-FID) method and the Saturate, Aromatic, Resin and Asphaltene (SARA) analysis of the crude oil was measured with the standard SATM D4124, as shown in Table 1. The density and viscosity of the kerosene were measured to be 792.0 kg/m\(^3\) and 1.01 mPa s at the atmospheric pressure and 61 °C. The Gas Chromatography (GC) compositional analysis of the cleaned crude oil sample and kerosene is given in Table 2.

The reservoir brine sample was collected from the same formation and cleaned. The reservoir brine has the Total Dissolved Solids (TDS) of 30 917.8 mg/L, which was considered to be the water type of calcium chloride. The brine viscosity was measured to be 0.4 mPa s at the atmospheric pressure and 61 °C. The purity of the CO2 used in this study was equal to 99.99% supplied by Beijing Huayuan Gas Chemical Co. Ltd.

### Table 1. Wax content and SARA analysis of the crude oil.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight percent (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wax</td>
<td>0.10</td>
</tr>
<tr>
<td>Saturates</td>
<td>66.63</td>
</tr>
<tr>
<td>Aromatics</td>
<td>27.54</td>
</tr>
<tr>
<td>Resins</td>
<td>4.89</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>0.94</td>
</tr>
</tbody>
</table>

### Table 2. Compositional analysis of the crude oil with the asphaltene content of \( w_{\text{asp}} = 0.94 \text{ wt\%} \) \((n\)-pentane insoluble) and the kerosene without asphaltene.

<table>
<thead>
<tr>
<th>Carbon no.</th>
<th>Crude oil</th>
<th>Kerosene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol%</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>1.90</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>0.33</td>
<td>1.13</td>
</tr>
<tr>
<td>C4</td>
<td>3.82</td>
<td>0.99</td>
</tr>
<tr>
<td>C5</td>
<td>6.46</td>
<td>0.54</td>
</tr>
<tr>
<td>C6</td>
<td>7.05</td>
<td>0.69</td>
</tr>
<tr>
<td>C7</td>
<td>10.62</td>
<td>2.32</td>
</tr>
<tr>
<td>C8</td>
<td>9.90</td>
<td>8.84</td>
</tr>
<tr>
<td>C9</td>
<td>8.49</td>
<td>28.36</td>
</tr>
<tr>
<td>C10</td>
<td>6.82</td>
<td>38.78</td>
</tr>
<tr>
<td>C11</td>
<td>5.73</td>
<td>14.23</td>
</tr>
<tr>
<td>C12</td>
<td>4.34</td>
<td>2.52</td>
</tr>
<tr>
<td>C13</td>
<td>3.49</td>
<td>0.96</td>
</tr>
<tr>
<td>C14</td>
<td>3.64</td>
<td>0.71</td>
</tr>
<tr>
<td>C15</td>
<td>3.26</td>
<td>0.60</td>
</tr>
<tr>
<td>C16</td>
<td>2.60</td>
<td>0.52</td>
</tr>
<tr>
<td>C17</td>
<td>2.33</td>
<td>0.51</td>
</tr>
<tr>
<td>C18</td>
<td>2.17</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Total 100.00 100.00
2.2 MMP tests

Figure 2 shows the schematic diagram of the slim-tube apparatus (CFS-100, Core Lab, Tulsa, OK, USA) for conducting a series of displacement experiments to determine the Minimum Miscibility Pressure (MMP) of the crude oil – CO₂ system in this study. The apparatus was consisted of a displacement pump (260D, ISCO, Lincoln, NE, USA), a stainless steel slim tube packed with silica sands (Shenfu Mining Industry Co. Ltd., China), a back-pressure regulator (Huada, Haian, China) and two pressure transducers to monitor injection pressure and back pressure constantly. A burette was used to collect and measure the produced oil and a gas flow meter to measure the volume of the produced gas.

In this study, the MMP of the CO₂-crude oil system was determined by six slim-tube tests with different injection pressure at the formation temperature of 61 °C. The displacement system was cleaned by petroleum ether and dried by nitrogen several times in preparation of each slim-tube tests. Then, the apparatus was saturated with the crude oil at the reservoir temperature of Tres = 61 °C with a constant flow rate of 0.2 cm³/min and the back pressure should be maintained the desired production pressure in order to prevent the crude oil from degassing. The CO₂ was injected into the slim tube to displace the crude oil with a constant flow rate of 0.1 cm³/min at the set injection pressure. The injection and production pressure was continuously monitored and recorded during the entire experiment. The volume of the produced oil and gas was measured at every 0.1 PV of pure CO₂ until 1.2 PV CO₂ was injected.

2.3 Coreflood tests

Figure 2 depicts the schematic diagram of the high-pressure coreflood apparatus used for CO₂ coreflood tests. A constant flow pump (260D, ISCO, Lincoln, NE, USA) was applied to displace dead crude oil, brine and CO₂ through the core plug inside a high-pressure stainless steel coreholder (Huada, Haian, China) with the inner diameter and outer diameter of 25 mm and 40 mm. Three high pressure cylinders were applied to store and deliver crude oil, brine and CO₂, respectively. Another ISCO syringe pump was used to exert the confining pressure which was always kept 2–3 MPa higher than the injection pressure on the core plug. All above mentioned components were placed inside an air bath which was heated by two electronic heat guns. A temperature controller was used to keep the air bath at the reservoir temperature of 61 °C. A back-pressure regulator (Huada, Haian, China) was used to target the desired production pressure during the coreflood test. A burette was used to collect and measure the produced oil and a gas flow meter to measure the volume of the produced gas.

The core samples used in this experiment are tight cores collected from Changqing Oil Field, China. It is noted that the core samples with nearly the same gas permeability pore size distribution are selected, which are from the same formation. The properties of cores are listed in Table 3.

The general procedure for the CO₂ coreflood tests is briefly described as follows:

1. Prior to each test, the core plugs were thoroughly cleaned by using a Dean–Stark extractor (SXT-02, Shanghai Ping Xuan Scientific Instrument Co., Ltd., China) for 20–30 days. After the core plugs were cleaned and dried at 100 °C. The gas permeability and porosity were measured with nitrogen (High-Pressure Gas Permeameter/Porosimeter, Temco, Tulsa, OK, USA).
2. The core plug was placed in the high-pressure coreholder and vacuumed for 24 hours. Then the formation brine was injected at the flow rate of 0.2 cm³/min to saturate the core plug. Then, the NMR apparatus was used to measure T₂ transverse relaxation time of the core sample under initial water-saturated condition.
3. The core was displaced with the MnCl₂ solution (15 000 mg/L) of 5 PV. And then the saturated core was scanned again by NMR apparatus to make sure the hydrogen signal of the brine eliminated.
4. After that, 3.0 PV of the crude oil was pumped through the core plugs at a constant rate of 0.1 cm³/min until no water was produced to achieve the connate water saturation (Swc) the initial oil saturation (S₀) at the reservoir temperature of 61 °C. The physical properties of core plugs were listed in Table 3. The T₂ spectrum was measured again after the core had been saturated with crude oil.
5. In each test, 2.0 PV CO₂ was pumped into the coreholder to displace the crude oil at the desired injection pressure and reservoir temperature of 61 °C. The injection and production pressure was continuously monitored and recorded during the entire test. The cumulative produced oil volume was recorded by a video camera and the cumulative volume of the produced gas was measured and recorded by using the gas flow meter. The produced oil and gas were collected during each coreflood test and the components of the produced oil and gas were analyzed by GC technique.
6. After the CO₂ coreflood test, the core samples, were cleaned by a Soxhlet Extractor with the solvent of petroleum ether which cannot dissolve asphaltene [25] and dried for 12 h at 100 °C. The gas permeability core samples were measured by permeameter with nitrogen.
7. The cleaned core sample was conducted the same treatments from step 1 to step 4.

2.4 NMR tests

NMR refers to the response of atomic nuclei to magnetic fields. The NMR apparatus (Mini-MR, Niumag, Suzhou, China) used in this study detects the transverse relaxation motion of ¹H of fluids in the pores, which produces a relatively strong signal compared to other elements in earth formations [26]. The magnetic intensity, gradient value control precision and frequency range of the NMR apparatus are...
0.5 T, 0.025 T/m, 0.01 MHz and 1–30 MHz, respectively. As for the NMR transverse relaxation time of fluid in the pore is given as [27, 28]:

\[
\frac{1}{T_2} = \frac{1}{T_{2S}} + \frac{1}{T_{2D}} + \frac{1}{T_{2B}}.
\]  

(1)

\(T_{2S}\): the surface relaxation time (ms);

\(T_{2D}\): the relaxation time as induce by diffusion in magnetic gradients (ms);

\(T_{2B}\): the bulk relaxation time of the pore-filling fluid (ms).

Because \(T_{2B}\) is much larger than \(T_2\) for fluid in porous media, \(T_{2B}\) is usually neglected. \(T_{2D}\) is reasonably neglected, when the magnetic field is thought to be uniform with a quite small field gradient and echo time is small enough. Furthermore, \(T_{2S}\) is associated with specific surface of a pore. Then,

\[
\frac{1}{T_2} \approx \frac{1}{T_{2S}} = \rho_2 \left( \frac{S}{V} \right),
\]  

(2)

\(\rho_2\): the surface relaxation rate (um/ms);

\(S\): the interstitial surface area (um\(^2\));

\(V\): the pore volume (um\(^3\)).

\(S/V\) can be written as a function of the dimensionless shape factor of a pore, \(F_S\), and pore radius, \(r\) (um), as follows,

\[
\frac{S}{V} = \frac{F_S}{r},
\]  

(3)

Combining equations (2) and (3),

\[
T_2 = \frac{1}{\rho_{2F_S}} r,
\]  

(4)

then,

\[
T_2 = Cr,
\]  

(5)

\(C\) is considered to be a constant for equations (5) and (6) so the \(T_2\) response is proportional to the pore radius. In our work, 0.1–1 ms of \(T_2\) is defined as micro pores, 1–10 ms defined as small pores, 10–100 ms defined as medium pores and 100–1000 ms as large pores.

3 Results and discussion

3.1 Experimental identification of CO\(_2\)/brine/rock interactions with NMR technique

In the CO\(_2\) flooding process, the solid precipitation was partly generated due to CO\(_2\)/brine/rock reactions. The solid
precipitation and clay particles would migrate in the pore and possibly cause a blockage in the pore throat [29]. So that, the CO₂/bine/rock reactions would induced permeability reduction of the cores [30]. Nevertheless the studies on the permeability reduction due to CO₂/bine/rock reactions are basically about aquifers. It is necessary to investigate the influence of the CO₂/bine/rock reactions on permeability reduction of oil reservoir formation before the experimental study on the impact of asphaltene precipitation on permeability. Therefore, instead the crude oil, the kerosene without asphaltene was used to conduct the core-flood experiments first.

As shown in Figure 3, the \( T_2 \) spectrum for the initial water-saturated cores 1–1 and 1–2, and the \( T_2 \) spectrum for the water-saturated cores after CO₂ flooding, were measured. It can been seen from Figures 3a and 3b that the \( T_2 \) spectrum for the water-saturated core after CO₂ flooding did not deviate from the \( T_2 \) spectrum for the initial water-saturated cores. Thus, in the case of experimental error, the distribution of pores was considered unchanged.

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**Table 3. Basic properties of tight core plug samples.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Length (cm)</th>
<th>Diameter (cm)</th>
<th>( k ) (mD)</th>
<th>( \varphi ) (%)</th>
<th>Saturated oil</th>
<th>( S_{oi} ) (%)</th>
<th>( S_{wc} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–1</td>
<td>5.872</td>
<td>2.504</td>
<td>2.67</td>
<td>16.74</td>
<td>Kerosene</td>
<td>67.58</td>
<td>32.42</td>
</tr>
<tr>
<td>1–2</td>
<td>6.370</td>
<td>2.504</td>
<td>3.23</td>
<td>17.35</td>
<td>Crude oil</td>
<td>66.71</td>
<td>33.29</td>
</tr>
<tr>
<td>2–1</td>
<td>5.126</td>
<td>2.504</td>
<td>2.61</td>
<td>16.23</td>
<td></td>
<td>68.30</td>
<td>31.70</td>
</tr>
<tr>
<td>2–2</td>
<td>6.722</td>
<td>2.504</td>
<td>2.91</td>
<td>17.27</td>
<td></td>
<td>65.24</td>
<td>34.76</td>
</tr>
<tr>
<td>2–3</td>
<td>5.874</td>
<td>2.504</td>
<td>2.98</td>
<td>16.18</td>
<td></td>
<td>62.75</td>
<td>37.25</td>
</tr>
<tr>
<td>2–4</td>
<td>5.660</td>
<td>2.504</td>
<td>3.14</td>
<td>17.94</td>
<td></td>
<td>65.24</td>
<td>34.76</td>
</tr>
<tr>
<td>2–5</td>
<td>5.938</td>
<td>2.504</td>
<td>3.31</td>
<td>17.07</td>
<td></td>
<td>70.93</td>
<td>29.07</td>
</tr>
</tbody>
</table>

\( k \): gas porosity of the core plugs;  
\( \varphi \): absolutely gas permeability of the core plugs;  
\( S_{oi} \): initial oil saturation;  
\( S_{wc} \): initial connate water saturation.
experimental result is different from similar experimental results in other literature that the CO2/bine/rock reactions occur and change the pore structure in the cores during CO2 coreflood tests [31, 32]. That is because that the reaction time of these coreflood tests is too short in comparison with experiments in other literature. Therefore, the CO2/bine/rock reactions are considered to have no influence on the pore distribution of the sandstone cores saturated with oil during the CO2 flooding process.

3.2 CO2-oil MMP

In this study, the slim-tube tests at six different injection pressures under a constant reservoir temperature of 61 °C were conducted to determine the MMP of the crude oil sample. The measured Oil Recovery Factors (ORF) versus Pore Volume (PV) of injected were illustrated in Figure 4. As expected, the ORF increased with the injection of CO2 at each injection pressure, and the growth rate of the ORFs decreased rapidly after 0.6 PV of injected CO2 because of the CO2 breakthrough. There was no more oil obtained in each test at 1.2 PV of injected CO2 which was the terminal point. Because the rate of CO2 extraction and dissolution accelerated with the growth of injection pressure [16], leading to stronger swelling effect and lower capillary resistance. The ultimate ORF of each slim-tube test increased as the injection pressure increased. In addition, the ultimate ORFs at \( P_{\text{inj}} = 20 \) MPa, 23 MPa and 26 MPa have no obvious growth, which indicates that the MMP measured by slim-tube test is between 16 MPa \( \leq P_{\text{inj}} \leq 20 \) MPa. After that, the ultimate ORFs of each slim-tube test versus injection pressure were depicted in Figure 5 to determine the MMP. Figure 5 shows that the first three points and the last three points are linear respectively. The intersection point of two fitting curves is regarded as the MMP of the CO2-crude oil system measured by slim-tube test, which is 17.02 MPa.

3.3 Physicochemical characterization of produced fluids

Figure 6 shows the measured ORF versus PV of injected CO2 at different injection pressures of five coreflood tests.
under the reservoir temperature of 61 °C. As expected, the ORF increased with the injection of the CO2 until no more oil was produced at 2.0 PV of injected CO2. And, the ORFs increased faster before the injected CO2 of 0.30 PV, 0.55 PV, 0.85 PV, 1.00 PV and 1.10 PV corresponding to the injection pressure of $P_{\text{inj}} = 9.1 \text{ MPa}, 13.5 \text{ MPa}, 16.2 \text{ MPa}, 19.5 \text{ MPa}$ and $22.1 \text{ MPa}$, respectively. More specifically, the ORF of lower injection pressure was greater than that of higher injection pressure in the initial period of process. Because a less portion of injected CO2 was dissolved into the light crude oil at a lower injection pressure due to the lower solubility and a larger portion of the injected CO2 played a major role in displacement at the same injection rate. With the growth of the injection pressure, the ultimate ORF at the terminal 2.0 PV increased due to the stronger interaction ability between the CO2 and the crude oil.

Figure 7 shows the oil recovery, asphaltene content and viscosity of the produced oil for five coreflood tests at different injection pressures. The oil recovery factor increased significantly with the increasing injection pressure until reaching the MMP = 17.02 MPa. This is because the viscosity of the crude oil and the InterFacial Tension (IFT) between the crude oil and CO2 decreased at higher injection pressure [11]. In addition, it can be seen from Figure 7 that the viscosity of the produced oil decreased from 10.18 mPa s to 3.72 mPa s when the injection pressure increased from 9.1 MPa to 22.1 MPa. And, the asphaltene content of the produced oil decreased from 0.78 wt% to 0.58 wt% as the injection pressure increased from 9.1 MPa to 16.2 MPa, while the asphaltene content barely changed when the injection was higher than the MMP (Fig. 7).

3.4 Effect of asphaltene precipitation during CO2 flooding

3.4.1 The effect of asphaltene precipitation on permeability

In this study, the percentage of permeability reduction was obtained by comparing the gas permeability of the core before and after CO2 flooding, as in the following equation:

$$Pr = \frac{K_{gb} - K_{ga}}{K_{gb}},$$

$Pr$: the permeability reduction percentage of the core sample, %;
$K_{gb}$: the gas permeability of the core sample before CO2 flooding, mD;
$K_{ga}$: the gas permeability of the core sample after CO2 flooding, mD.

Figure 8 plots the percentage of permeability reduction of the core samples and asphaltene content of the produced oil at different injection pressures. The asphaltene left in the pores could be inferred from the content of the produced oil. If the asphaltene content of the produced oil was higher, it indicated that there was less asphaltene precipitation in the pores of core sample. It can be seen from Figure 8 that the asphaltene content of the produced oil decreased with the increased injection pressure. But, when the injection pressure approached the MMP, the asphaltene content was almost unchanged.

Similarly, the percentage of permeability reduction significantly increased from 2.4% to 7.41% as the injection pressure increased in the immiscible stage from 9.1 MPa to 16.2 MPa. When the injection pressure reached the MMP, the percentage of permeability reduction still increased with the injection pressure increasing, but changed slowly compared with that in the immiscible stage.
The results were consistent with the asphaltene content of the produced oil at different injection pressures. As a result, more asphaltene would precipitate and block the pores with increasing pressure until the injection pressure reached the MMP.

3.4.2 The effect of asphaltene precipitation on pore structure

As mentioned in the coreflood experimental procedure, the $T_2$ spectrum for the initial water-saturated cores and the $T_2$ spectrum for the water-saturated cores after CO2 flooding were measured and compared. Figure 9 illustrates the $T_2$ spectrum distributions for cores 2–1, 2–3 and 2–5. The NMR spectrum of the core samples was typical bimodal distribution as shown in Figures 3 and 9. It could be seen from Figure 9 that the $T_2$ spectrum measured for the water-saturated core after CO2 flooding moved a slightly lower position compared to that measured for the initial watersaturated core. Because the petroleum ether was used to clean the cores after CO2 flooding and asphaltene cannot dissolve in the petroleum ether[12]. The reduced amplitude of the $T_2$ spectrum indicated the pores were clogged due to the asphaltene precipitation and deposition, which could not be saturated with water. The initial water saturated in the pores and the water saturated in the pores after CO2 flooding is defined as $S_{wb}$ and $S_{wa}$ respectively, the severity of formation damage due to asphaltene precipitation could be calculated as follows:

$$D_w = \frac{S_{wb} - S_{wa}}{S_{wb}} \times 100\%,$$  \quad (8)

$D_w$: the severity of formation damage due to asphaltene precipitation;

$S_{wb}$: the summation of the water saturated in the pores of the core before CO2 flooding;

$S_{wa}$: the summation of the water saturated in the pores of the core after CO2 flooding.

The severity of formation damage due to asphaltene precipitation of the cores 2–1, 2–3 and 2–5 was 3.67%, 8.20% and 13.75%, respectively. And the permeability reduction corresponding to the three cores was 2.4%, 7.41%, 8.32%. The severity of formation damage due to asphaltene precipitation increased as the injection pressure
increased. Moreover, the pore distribution influenced by asphaltene precipitation expanded in the miscible stage (Fig. 9). Because CO₂ could expand sweep area and enter smaller pores to interact with the crude oil at higher injection pressure.

The amplitude variation of the micro (0.1–1 ms) and small pores (1–10 ms) was smaller than the amplitude variation of the medium (10–100 ms) and large pores (100–1000 ms). That indicated that the asphaltene precipitation had a greater influence on the medium and large pores. The interaction between the CO₂ and crude oil in the medium and large pores was sufficient, so that the asphaltene precipitation in the medium and large pores was more serious than micro and small pores (Fig. 9). When the asphaltene precipitated in the tight sandstone reservoirs, the larger particles could block up the pore throat directly [33], while the smaller ones could cause an obstacle or blockage in the pore or pore throat [8]. On the other hand, although part of the micro and small cores were blocked by precipitated asphaltene particles, the medium and large pore radius decreased due to asphaltene precipitation. The medium and large pores transformed into the micro and small pores. Thus, the amplitude of micro and small cores changed little.

Table 4 shows the $T_2$ spectrum distribution which corresponds to pore distribution for the three core samples. The proportion of medium and large pores of the cores after CO₂ flooding decreased while the proportion of micro and small pores increased, compared to the initial water-saturated cores. The pore distribution of tight cores after CO₂ flooding overall changed to the direction of pore radius reduction after CO₂ flooding. Moreover, the proportion changed more greatly at higher injection pressure.

### 3.4.3 The effect of asphaltene precipitation on wettability

In consistent with the variation of $T_2$ spectrum in Figure 9 due to the asphaltene precipitation, the $T_2$ spectrum measured for oil saturated core after CO₂ flooding also deviated slightly lower from that for initial oil-saturated core, as shown in Figure 10. The amount of saturated oil decreased more in medium and large pores (10–1000 ms) than in micro and small pores (0.1–10 ms), as well. However, compared with the difference between the initial water-saturated cores and the water-saturated cores after CO₂ flooding (Fig. 9), the difference between the initial oil saturated in pores and the oil saturated in the pores after CO₂ flooding is smaller (Fig. 10).

$S_{ob}$ and $S_{oa}$ respectively stands for the initial oil saturated in the pores and the oil saturated in the pores after CO₂ flooding. The relative variation of the $T_2$ spectrum in Figure 10 due to asphaltene precipitation could be calculated, as follows:

$$D_o = \frac{S_{ob} - S_{oa}}{S_{ob}} \times 100\%$$

$$I_{WA} = D_w - D_o,$$

where $D_o$: the relative variation of the $T_2$ spectrum due to asphaltene precipitation;

$S_{ob}$: the summation of the oil saturated in the pores before CO₂ flooding;

$S_{oa}$: the summation of the oil saturated in the pores after CO₂ flooding;

$I_{WA}$: the wettability alteration index of the core before and after CO₂ flooding.

The pores occupied by asphaltene deposition are constant, so that the $D_o$ should have been same as the $D_w$, theoretically. However, the $D_o$ is less than the $D_w$, which means that some pores could be saturated more oil than water after the CO₂ flooding compared with that before CO₂ flooding, relatively. The wettability alteration was assumed to occur due to asphaltene precipitation. The wettability of the rock after CO₂ flooding altered to the oil-wet direction. The index of the wettability alteration can be represented by $I_{WA}$. When the $I_{WA}$ is zero, there is no wettability

<table>
<thead>
<tr>
<th>Core no.</th>
<th>Injection condition</th>
<th>$T_2$ distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1–1 ms</td>
</tr>
<tr>
<td>2–1</td>
<td>Before CO₂ flooding</td>
<td>14.07</td>
</tr>
<tr>
<td></td>
<td>After CO₂ flooding</td>
<td>15.19</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
<td>+1.12</td>
</tr>
<tr>
<td>2–3</td>
<td>Before CO₂ flooding</td>
<td>11.84</td>
</tr>
<tr>
<td></td>
<td>After CO₂ flooding</td>
<td>12.22</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
<td>+0.38</td>
</tr>
<tr>
<td>2–5</td>
<td>Before CO₂ flooding</td>
<td>13.12</td>
</tr>
<tr>
<td></td>
<td>After CO₂ flooding</td>
<td>16.13</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
<td>+3.01</td>
</tr>
</tbody>
</table>
alteration. When the $I_{WA}$ is higher than zero, the wettability changes to oil-wet direction and the larger $I_{WA}$ means stronger oil-wet alteration. The $I_{WA}$ of the core samples after CO2 flooding at different pressures are presented in Table 5. Therefore, the reduction of water permeability was caused by pore clogging and wettability alteration. If the CO2-EOR technique is applied, it is necessary to injection chemical inhibitor into the reservoir to reduce the risk of asphaltene precipitation.

**Table 5.** The relative variation of the $T_2$ spectrum in condition of water saturation and oil saturation respectively.

<table>
<thead>
<tr>
<th>Core no</th>
<th>Injection pressure (MPa)</th>
<th>$D_w$ (%)</th>
<th>$D_o$ (%)</th>
<th>$I_{WA}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2–1</td>
<td>9.1</td>
<td>3.67</td>
<td>1.96</td>
<td>1.70</td>
</tr>
<tr>
<td>2–3</td>
<td>16.2</td>
<td>8.20</td>
<td>4.12</td>
<td>4.08</td>
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<tr>
<td>2–5</td>
<td>22.1</td>
<td>13.75</td>
<td>9.79</td>
<td>3.97</td>
</tr>
</tbody>
</table>

**4 Conclusion**

In this paper, five CO2 coreflood tests were conducted at immiscible, near-miscible and miscible conditions. For each test, the ORF, the viscosity and the asphaltene contents of the produced oil were analyzed. Then, the distribution of asphaltene precipitation in the pores and wettability alteration was quantitatively evaluated.

It is found that, the extraction effect of the CO2 played a more dominant role in the CO2-EOR process with higher injection pressure. So that more light components are extracted and recovered by the CO2 and more heavy components including asphaltene were left in the core at higher injection pressure. And, the asphaltene precipitated in the core had little increase in the CO2 miscible flooding stage.

The severity of formation damage influenced by asphaltene precipitation increased with the increasing of injection pressure. And, the asphaltene precipitation had a greater influence on the medium and large pores due to the sufficient interaction between the CO2 and crude oil. Furthermore, the asphaltene precipitation not only caused pore clogging, but also induced rock wettability alteration towards oil-wet direction. If the CO2-EOR technique is applied, it is necessary to injection chemical inhibitor into the reservoir to reduce the risk of asphaltene precipitation.

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