An Experimental Study of Combined Foam/ Surfactant Polymer (SP) Flooding for Carbone Dioxide -Enhanced Oil Recovery (CO₂-EOR)

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Highlights

- A novel EOR strategy coupling the foam flooding with the SP flooding was proposed
- Its pressure behaviour, water cut and accumulative oil recovery during core flooding were investigated under both miscible and immiscible conditions and compared with the other two conventional EOR methods
- Suggestions were made with regard to the applicability of this novel EOR method

Abstract

To better address the issue of viscous fingering and gravity segregation confronted in CO₂ flooding, a novel EOR method which coupled the SP flooding with the CO₂ foam flooding was presented. Its displacement performance was systematically evaluated and compared with the other two injections modes (i.e. direct foam flooding and CO₂/SP flooding) which applied the same amount of the gas and chemicals as the proposed mode. It had been found, if the injection pressure enabled the oil/CO₂ miscibility to occur, the foam/SP flooding was endowed with the highest blockage and lowest water cut. Moreover, its oil recovery factor was 5.8% and 12.6% greater than that of direct foam CO₂/SP flooding respectively; on the other hand, if the injection pressure was below the minimum miscibility pressure (MMP), the direct foam flooding and the SP flooding displayed comparable water cut and oil recovery factor. Although the foam/SP flooding still recovered the most crude oil, it was only 3.7% and 6.8% higher than that of the direct foam and SP flooding respectively, indicating the less evident displacement advantage. It was believed that the proposed method possessed huge EOR potential, especially in the reservoir whose pressure was well above the MMP.

Keywords: foam flooding; SP flooding; blockage; water cut; tertiary oil recovery

1. INTRODUCTION

Statistics suggests that global oil consumption grew by 1.4 million barrels per day (b/d) seen in 2013 and total world proved oil reserves can only satisfy 52.5 years of worldwide needs at current production rate (BP, 2015). On the other hand, it is well documented that significant amount of the original oil in place (OOIP) (approximately 60% to 70%) cannot be mobilized through conventional water floods no matter it is conducted in laboratory or field scale due to its poor sweep efficiency as well as the unfavourable displacement efficiency (Mohajeri et al., 2015; Hirasaki et al., 2011; Gharbi, 2000; Ahmadi and Shadizadeh, 2013; Andrianov, et al., 2012). Consequently, the subject of improving oil production after water floods becomes
more and more compelling both to the oil industry and to the governments, giving rise to the importance on the enhanced oil recovery (EOR) methods over the past decades.

Gas flooding, including immiscible and miscible displacement process, accounts for roughly half of the EOR production worldwide (Christensen, et al., 2001). Generally, fluids such as carbon dioxide, nitrogen and methane are injected into the target formation and interact with the residual oil in place, resulting in the tremendous increase in oil production through swelling effect, viscosity reduction or component extraction (Hao, et al., 2004; Grigg, et al., 1997). Despite the huge EOR potential, nearly all gas injections suffer from gravity segregation and viscous fingering due to the viscosity and density differences between displacing fluids and reservoir fluids, which, accordingly, detrimentally affect the EOR outcome ((Lescure and Claridge 1986, Rogers and Grigg 2001, Dugstad, Opel et al. 2011).

By introducing foamed gas, regardless of its phase (gas phase, dense phase or supercritical phase) into the reservoir, both the aerial and vertical sweep efficiencies are substantially improved. This stems from the improvement of the gas apparent viscosity and reduction in gas relative permeability thanks to the creation of thin foam films, namely, lamellae (Li, et al., 2010; Heller, et al., 1994; Farajzadeh, et al., 2012; Khalil, et al., 2006); yet, the recovery efficiency of foam flooding is severely hindered by foam instability and surfactant retention during the foam propagation in the porous medium, thereby, a number of investigations have been carried out to tackle these issues in recent years (Ma et al., 2013; Majidaie, et al., 2012; Yu, et al., 2012; Romero, et al., 2002; Dickson, et al., 2004).

Another intriguing EOR technique is the injection of surfactant-polymer blend into water-flooded reservoir, accordingly, this method is referred to as surfactant/polymer flooding or SP flooding. Its displacement mechanisms include: (1) surfactant can interact with the reservoir fluids (formation brine and crude oil) and generate microemulsion in situ. If the brine salinity locates within the optimum salinity region at which the Winsor Type III microemulsion can be yielded, then the interfacial tension (IFT) between displacing phase and crude oil would attain ultralow value. As a result, high capillary number is achieved and the residual oil can be readily mobilized based on the capillary desaturation curve (CDC) (Dean, 2011; Healy et al., 1976); (2) the polymer mitigates the permeability variation effect and modifies the mobility ratio through thickening the displacing phase, thus the overall sweep efficiency is greatly improved (Yang, 2010). And also, the presence of the polymer assists in reducing the surfactant adsorption onto reservoir rock (He et al., 2015; Wang et al. 2015). In other words, the effectiveness of SP flooding largely depends on the synergy of these mechanisms. However, very few SP flooding projects have been reported in modern chemical EOR. The major concerns are: (1) practically, the optimum brine salinity is hard to be maintained taking into consideration the complexity of displacement process and reservoir environment; thereby, the ultralow IFT can hardly be achieved. Although the addition of alkali in to SP solution (i.e. ASP flooding) facilitates the IFT reduction, precipitation and corrosion of surface equipment will take place by the presence of alkali (Elraies and Kalwar, 2013); (2) generally, the surfactant and polymer are not likely to advance through the porous medium at the same superficial velocity, because the polymer will flow ahead of the surfactant due to the polymer
inaccessible pore volume, which was referred to as “chromatographic effect” (Lotsch et al., 1985), making the synergism effect far less effective than expected.

In this work, we present a new chemical EOR method combining the foam flooding and SP flooding, on the purpose of maximize the EOR capability of SP flooding and foam flooding. On one hand, the adsorbed surfactant in foam flooding process can be compensated by SP solution through material exchange, then to some extent, the foaming ability of foam flooding will be maintained if not enhanced; on the other hand, the polymer in the SP solution barely flows ahead of the surfactant. In this hybrid process, SP and foam slug were injected in an alternative manner with the SP solution being followed by CO\textsubscript{2} foams. It is noted the polymer concentration in the foam floods is lower than that in the SP floods due to the dilution effect of supercritical CO\textsubscript{2} so the polymers in the SP slug would be “dragged” due to the polymer concentration gradient between SP and foam slugs, which to some extent relieves the chromatographic effect in the formation and leads to significant mobility reduction. To assess the displacement efficiency of the combined foam/SP flooding, three modes (Mode A, Mode B and Mode C) which utilize the same amount of CO\textsubscript{2} and chemicals are included in this research. Their illustrations are shown in Fig. 1 and the corresponding descriptions are as follows:

1) Mode A. 0.8 pore volume (PV) foam consisting of 0.4 PV CO\textsubscript{2} and 0.4 PV SP solution is fed into the core with the assistance of a foam generator located ahead of the core holder.

2) Mode B. The SP solution and CO\textsubscript{2} are introduced alternately into the core plug by two cycles in order to create foam \textit{in situ}. In each cycle, 0.2 PV CO\textsubscript{2} and 0.2 PV SP solution are applied.

3) Mode C. Instead of CO\textsubscript{2}, the foam is combined with SP solution and they are injected alternately by two cycles as well. In each cycle, 0.3 PV foam (comprising 0.2 PV CO\textsubscript{2} and 0.1 PV SP solution) and 0.1 PV SP solution are used.

The supercritical CO\textsubscript{2} will be applied for all experiments. Section 2 presents the materials, experimental setup and procedures. Section 3 shows the results of two sets of the core flooding experiments. One set is conducted under miscible condition (P= 2500 psi), while the other set is carried out when CO\textsubscript{2} is immiscible with crude oil (P= 1200 psi). Discussions and interpretations have also been made in this section. The paper is end up with concluding the remarks in section 4.
Fig. 1 The illustration of Mode A (a), Mode B (b) and Mode C (c)

Note: 1. oil bank 2. Foam 3. SP solution 4. CO₂

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Materials

Core plug: Berea samples with length around 6.9 cm and diameters of 3.8 cm are cut from quarried sandstone blocks (Ohio, USA) and are used as supplied. The porosity and permeability of these plugs are about 18% and 400 mD respectively and their composition are determined by XRD technique and tabulated in Table 1 and 2. Scanning electron microscope (SEM) image of the sample powder is given in Fig. 2.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Quartz</th>
<th>Albite</th>
<th>Kaolin</th>
<th>Muscovite</th>
<th>Feldspar</th>
<th>Anothite</th>
<th>Illite</th>
<th>Dolomite</th>
<th>Ankerite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight%</td>
<td>74.9</td>
<td>0.8</td>
<td>0.8</td>
<td>0.6</td>
<td>8.9</td>
<td>3.0</td>
<td>1.0</td>
<td>5.1</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Table 2 The oxides composition of the core plug

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO₂</th>
<th>CaO</th>
<th>CO₂</th>
<th>Na₂O</th>
<th>Al₂O₃</th>
<th>H₂O</th>
<th>MgO</th>
<th>K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight%</td>
<td>83.15</td>
<td>2.15</td>
<td>2.44</td>
<td>0.09</td>
<td>3.45</td>
<td>0.14</td>
<td>1.12</td>
<td>1.59</td>
</tr>
</tbody>
</table>
Gas: CO₂ gas with purity of 99.99% is supplied by BOC (Australia) and applied in the entire research process.

Crude oil: Oil sample is sourced from an oil reservoir located on North West Shelf of Western Australia and its properties are listed in Table 3. Its minimum miscibility pressure (MMP) with CO₂ was estimated to be around 1500 ~ 1700 psi (Li et al., 2012). It is noted that the oil sample is filtered before any use.

<table>
<thead>
<tr>
<th>Test</th>
<th>Unit</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density @ 15°C</td>
<td>Kg/L</td>
<td>0.9428</td>
</tr>
<tr>
<td>API gravity</td>
<td>°API</td>
<td>18.5</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>%mass</td>
<td>0.14</td>
</tr>
<tr>
<td>Arsenic</td>
<td>mg/kg</td>
<td>2.3</td>
</tr>
<tr>
<td>Kinematic Viscosity @40°C</td>
<td>cSt</td>
<td>37.26</td>
</tr>
<tr>
<td>Sulphur-Total</td>
<td>%mass</td>
<td>0.14</td>
</tr>
<tr>
<td>Total Acid Number</td>
<td>mg KOH/g</td>
<td>0.50</td>
</tr>
<tr>
<td>Water Content</td>
<td>%volume</td>
<td>0.150</td>
</tr>
</tbody>
</table>

Brine: Synthetic brine A with the salinity of 5,000 ppm (NaCl) is employed for the SP blend preparation. Brine B with the salinity of 20,000 ppm (NaCl) is used in the core flooding experiments.

Foam formula: The sodium alpha olefin sulfate (AOS C₁₄-₁₆) with 35% active matter is supplied by Stepan Chemical Co. (USA) and used as surfactant or foaming agent. Additive N70K-T is able to boost the liquid membrane strength in the foaming system and purchased from Solvay Chemicals Inc. (USA), its properties are listed in Table 4. AVS, a ter-polymer product with a molecular weight of $10 \times 10^6$ g/mol and hydrolysis degree of 22%, is provided by the Research Institute of Petroleum Exploration & Development (RIPED, China) as a thickener in the SP solution. The schematic of
AVS molecule is illustrated in Fig. 3. The SP formulation in this study is determined as 0.5 wt. % AOS + 0.15 wt. % AVS + 0.5 wt. % N70K-T.

Fig. 3 Molecular structure of the ter-polymer AVS

Table 4 Properties of the additive N70K-T

<table>
<thead>
<tr>
<th>Property</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form</td>
<td>Gel</td>
</tr>
<tr>
<td>Colour</td>
<td>Clear</td>
</tr>
<tr>
<td>pH</td>
<td>7.0-8.0 (g/L) Aqueous solution</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>33 hPa (25°C)</td>
</tr>
<tr>
<td>Density</td>
<td>1.03 g/cm³</td>
</tr>
<tr>
<td>Boiling point</td>
<td>104 °C (1013 hPa)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>20 mPa·s</td>
</tr>
<tr>
<td>Water solubility</td>
<td>55g/L</td>
</tr>
</tbody>
</table>

Note: R1 and R2 are different long chain alkyl groups.

2.2 Core Flooding Experiment

The schematic of the core flooding setup is presented in Fig. 4. As shown, the setup consists of displacement pumps, a foam generator which has been illustrated in Fig. 5, fluids accumulators, core holder, pressure transmitters, data acquisition system, back pressure regulator, etc. The displacement pump feeds varying fluids into the core holder and is set for constant flow rate. The foam generator (Haian Oil Scientific Research Apparatus Co., Ltd., China) is made from hastelloy and can resist extreme chemical corrosion. The core holder (Core Lab, U.S.A.) is placed horizontally and contains the core plug while allowing fluids to flow in and out under elevated temperature and pressure. The differential pressure at different times during experiment is monitored and recorded by pressure transmitters (KELLER, Switzerland) which are mounted at the inflow and outflow end of the core holder. The
temperature and pressure history during core flooding process can be recorded and stored by the data acquisition system (Control Center Series 30). The experiments are carried out at 323 K unless otherwise specified and the experimental procedures are as follows:

1. The initial core plug is dried out at 338 K for four days and its porosity and gas permeability are determined by AP-608 Automated Permeameter-Porodimeter (Coretest systems, Inc., U.S.A.) before it is loaded horizontally into the core holder. Then confining pressure up to 4000 psi is applied to the core plug which, afterward, is vacuumed for at least 12 hours to remove the air from the core holder.

2. The core plug is fully saturated with brine B until steady-state flow is achieved. Then its liquid permeability can be obtained by applying single-phase Darcy’s Law.

3. Crude oil is pumped into the core holder at 0.3 ml/min until the water cut reaches 1% to attain the residual water saturation; afterwards, the core plug is aged for 24 hours.

4. Water floods with brine B at 0.5 ml/min is conducted to allow the residual oil saturation to be established, which is indicated by the 99% water cut.

5. Given amount of supercritical CO\textsubscript{2} and chemicals are injected into the core plug (Mode A, B or C) under either miscible or immiscible condition, which is followed by the chase waterfloods at 0.5 ml/min until 99% water cut is reached.

![Fig. 4 The setup of the core flooding experiments](image)

1- CO\textsubscript{2} Tank 2- Gas Mass Flow Control System 3- Foam Generator 4- Brine B or Surfactant/polymer Solution 5- Curde oil 6- Injection Pump 7- Pressure Transducer 8-
3. RESULTS AND DISCUSSION

3.1 Core Flooding Experiments under Miscible Condition.

One set of experiments consisting of three runs (one run for each Mode) are conducted under miscible condition, which is the first part of this research. Apart from the way in which the supercritical CO$_2$ and chemicals are introduced into the core plug, the experimental conditions and procedures are consistent for the three experiments. The results are summarized in Table 5.

| Table 5 Summary of the core flooding experiments under miscible condition (323K, 2500 psi) |
|---------------------------------------------------------------|-----------------|-----------------|-----------------|
| Experiment                                                   | #1              | #2              | #3              |
| Porosity (%)                                                 | 18.45           | 18.16           | 18.66           |
| Gas permeability (mD)                                        | 483             | 476             | 470             |
| Brine permeability (mD)                                      | 384             | 369             | 374             |
| Tertiary mode                                                | A               | B               | C               |
| Total amount of gas and chemicals used                       | 0.4 PV supercritical CO$_2$ + 0.4 PV SP solution | 0.4 PV supercritical CO$_2$ + 0.4 PV SP solution (0.2 PV CO$_2$ + 0.2 PV SP solution) *2 | 0.4 PV supercritical CO$_2$ + 0.4 PV SP solution (0.3 PV foam$^a$ + 0.1 PV SP solution) *2 |
| Injection scheme                                             | 0.8 PV foam$^a$ | (0.3 PV foam$^a$ + 0.1 PV SP solution) *2 |
| Initial oil saturation (%)                                   | 69.4            | 67.8            | 70.1            |
| Water floods recovery (%)                                    | 37.8            | 35.9            | 36.7            |
| Tertiary oil recovery (%)                                    | 30.8            | 25.9            | 37.7            |
| Max. pressure drop (psi)                                     | 87.6            | 65.1            | 103.4           |
| Overall oil recovery (%)                                     | 68.6            | 61.8            | 74.4            |

#Note: The foam is produced with the assistance of a foam generator. The created foams are comprised of 0.4 PV supercritical CO$_2$ and 0.4 PV SP solution, and 0.2 PV supercritical CO$_2$ and 0.1 PV SP solution in experiments #1 and #3 respectively.
3.1.1 Pressure drops

The pressure drops across the core plugs during secondary and tertiary recovery of various injection modes are plotted in Fig. 6, 7 and 8 as a function of injected PV. It has been found that, irrespective of the modes, differential pressure rose rapidly immediately after the brine was injected, indicating the oil bank was moving towards the outlet end of the core holder. Nonetheless, the differential pressure dropped after 0.1 PV brine was pumped. This could be attributed to early brine breakthrough resulting from the density and viscosity difference between the brine and crude oil, consequently, the oil could not be displaced evenly. After water breakthrough, the pressure drops tended to become steady until residual oil saturation was established. At this point, differing tertiary recovery methods were initiated.

In mode A, the CO$_2$ foam was injected directly into the core plug with the assistance of a foam generator. As expected, the pressure drop increased dramatically up to 87 psi. Two mechanisms might have contributed to the tremendous increase in pressure drop. Firstly, the introduced foam possessed extremely high apparent viscosity and thus was able to make the oil bank move forward. Secondly, the foam preferred to enter the large throats and then block them, accordingly, the relatively small pores and throats which could not be reached in the brine injection process due to the capillary force effect might have been swept by the CO$_2$ foam. One noticeable phenomenon was the pressure drop fluctuation in foam flooding process. This could be due to the collapse and regeneration of the CO$_2$ foam in the porous medium. The chase brine was injected at the end of foam injection in order to make full use of the CO$_2$ and chemicals those had already existed in the pores. Therefore, the pressure drop increased at the beginning of the chase waterfloods because of the blockage caused by adsorbed polymer and recreated foam. With more and more chase brine being injected into the system, the blockage became less and less, which arose from the loss of chemicals. As a result, the pressure drop declined gradually until steady-state flow was attained.

When it came to mode B, the pressure drop changed in a different manner. Compared to mode A, the differential pressure increased relatively slowly and the fluctuation was pronounced, with the maximum value only 65 psi, which was a clear indication of the inadequate foam generation. This poor performance was primarily caused by the insufficient interaction between CO$_2$ and SP solution, a consequence of their mobility difference. Another intriguing feature in the foam generation process was that, generally, the pressure drop increased when the CO$_2$ was introduced, while the SP solution injection was found to make the pressure drop decrease. It was observed that this fluctuation took place in both injection cycles, which validated that the foam creation in porous medium was not instant and that it required some amount of time for the foam creation and propagation to occur. Unlike in mode A, the differential pressure in mode B continually dropped when chase waterfloods was initiated. Again, this phenomenon verified the low efficiency of foam production in mode B. To some extent, the adsorbed polymer and foaming agent which was able to facilitate the foam regeneration in the core plug were capable of prohibiting the decline of pressure drop which, like in mode A, became relatively steady after 2.0 PV chase brine was fed into the system.
In the case of mode C, the scenario was completely different from those in mode A and B. It was found that the differential pressure across the core plug rose significantly after the foam injection phase began. Although the introduction of SP solution did cause the pressure drop to be unstable somehow, the maximal pressure drop was able to reach 100 psi and it fluctuated around 80 psi, indicating the oil bank kept moving forward in the foam and SP solution injection process. The distinguishing displacement performance might stem from the following reasons: (1) the foam stability was greatly improved because of the presence of the SP solution. The surfactant could assist in maintaining the foamability, while the polymer was helpful in terms of making the foam more robust; (2) the existence of the foam alleviated the problem of chromatographic separation of SP solution; (3) the mass transfer between the foam and SP solution eased the chemicals loss to a great extent; (4) the synergism of the foam and chemicals aided the mobility reduction of supercritical CO$_2$ and considerably improved the displacement efficiency of CO$_2$ flooding. In a word, its remarkable blockage was largely attributed to the enhanced foam flooding as well as the modified SP flooding. After the chase brine was introduced, as expected, the differential pressure tended to decrease; nonetheless, compared to mode A and B, the decline was quite slow and smooth as illustrated in Fig. 8. As discussed earlier, the interaction between CO$_2$ foam and SP solution in the porous medium were quite strong, therefore, the residual resistance during the chase waterfloods phase was evident and this prevented the differential pressure from quick drop. The differential pressure became relatively steady after 2.2 PV chase brine was injected, which meant residual oil saturation had been attained at this stage.

3.1.2 Cumulative oil recovery and water cuts

The cumulative oil recoveries during core flooding processes are presented in Fig. 9, 10 and 11. The core plugs after the core flooding are shown in Fig. 12. Prior to any tertiary methods, the brine floods (secondary recovery) recovered nearly 36% of the initially saturated oil when the water cut reached 99%. At this point, brine injection stopped and various EOR methods comprising mode A, B and C commenced. As illustrated in the Table 4, the most amount of incremental oil (38.7%) was found to be produced by applying mode C, followed by mode A (32.8%), while the least amount of incremental oil (28.9%) was recovered by mode B after brine injection. As a consequence, if taking into consideration the secondary oil recovery, the cumulative oil recoveries (i.e. overall oil recoveries) of mode A, B and C were 70.6%, 62.8% and 75.4% respectively. Apparently, the tertiary recovery difference arose from the varying injection modes. In mode A, direct foam which was created with the aid of a foam generator, was injected into the core plug and dramatically reduced the water/oil mobility ratio. Accordingly, the displacement efficiency of the miscible CO$_2$ flooding was maximized. However, due to the foam collapse caused by oil invasion and lamellae breakdown, and also because of the chemicals adsorption onto the rock surface, the foams became weaker and weaker, especially in the chase waterfloods phase. This, with no doubts, would greatly affect the tertiary oil recovery. In mode B, as stated before, the contact between supercritical CO$_2$ and SP solution was inadequate, leading to insufficient amount of foam production in the porous medium. Despite the relatively high performance of the foam flooding, the tertiary oil recovery of mode B was the lowest among the three modes, indicating the detrimental impact
imposed by this injection mode on the oil recovery. Under the miscible condition, the alternate injection of CO₂ foam and SP solution, namely mode C, possessed the highest tertiary oil recovery. The combination of foam flooding and SP flooding was capable of overcoming the problems existing in the direct foam injection through the synergism mechanism, and this might explain the tertiary oil recovery advantage of mode C over that of mode A.

With regards to the water cut, it was found that, irrespective of the tertiary modes, the water breakthrough took place only after 0.2 PV or 0.3 PV brine was injected. As mentioned earlier, this was caused by unfavourable mobility ratio due to the viscosity difference between the injected brine and crude oil. After the breakthrough, the water cut increased substantially and crude oil could barely be recovered. At the end of the brine injection, the water cut was nearly constant at 99%, indicating the establishment of residual oil saturation. At this point, the supercritical CO₂ and chemicals were fed into the system through various injection modes and led to the considerable reduction in the water cut. In mode A, as illustrated in Fig. 10, the water cut dropped significantly as the foam was directly injected and it could decrease to as low as 56%. Reasonably, the enhanced oil production in the foam injection process contributed to the reduction in the water content in the produced effluent. After the injection of around 0.2 PV foam, however, the water cut began rising unceasingly even with continuous foam injection. This phenomenon matched the earlier fact that the oil production would drop at certain point of the foam injection owing to the pronounced foam collapse which had negative impact on the blockage capability. Consequently, the water cut increase to 90% at the end stage of direct foam flooding. When it came to the mode B, similar to that in the mode A, the water cut went down initially, but at a far lower rate. With the alternate injection of supercritical CO₂ and chemicals, the water cut fluctuated dramatically, which again validated the low efficiency of the foam generation by this way. The lowest water cut during this tertiary recovery process was only 68%, which was in good agreement with the less incremental oil production in comparison with that of mode A. Moreover, the water production rate increased noticeably at the late stage of the CO₂ and chemicals injection and the water cut reached 95% quickly. Afterwards, the water cut hardly changed and stayed around 98% in the entire chase waterfloods phase. In the case of the mode C, the water cut also varied over time. Nevertheless, unlike in mode B, the water production rate declined quickly as soon as the foam/SP solution were introduced until the lowest value (48%) was attained. Although the fluctuation existed somehow, its extent was less evident than that of mode B. Furthermore, it could be found this mode was endowed with the lowest average water cut among the three injection modes, reflecting its highest blocking capacity. As expected, the water cut increased by a great extent as the foam/SP solution injection ceased and chase waterfloods began. However, compared to the other two counterparts, its water content changed more slowly in the chase waterfloods phase, which might result from the huge relative permeability reduction of the chase brine. To sum up, the remarkable capability of the water control could have validated the strong synergism arising from the combined use of the foam flooding and SP flooding.
Fig. 6 The pressure drop history of Mode A under miscible condition

Fig. 7 The pressure drop history of Mode B under miscible condition
Fig. 8 The pressure drop history of Mode C under miscible condition

Fig. 9 The water cut and cumulative oil recovery of Mode A under miscible condition
Fig. 10 The water cut and cumulative oil recovery of Mode B under miscible condition

Fig. 11 The water cut and cumulative oil recovery of Mode C under miscible condition
3.2 Core Flooding Experiments under Immiscible Condition.

In order to investigate the effect of injection pressure on the displacement performance, another set of core flooding experiments are conducted under immiscible condition as the second part of this research. Like the first set of the experiments, apart from the way in which the supercritical CO₂ and chemicals are introduced into the core plug, the experimental conditions and procedures are consistent for this set of experiments. The results are presented in Table 6.

**Table 6  Summary of the core flooding experiments under immiscible condition**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
</tr>
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<tbody>
<tr>
<td>Porosity (%)</td>
<td>18.12</td>
<td>17.65</td>
<td>18.37</td>
</tr>
<tr>
<td>Gas permeability (mD)</td>
<td>463</td>
<td>443</td>
<td>468</td>
</tr>
<tr>
<td>Brine permeability (mD)</td>
<td>369</td>
<td>354</td>
<td>373</td>
</tr>
<tr>
<td>Tertiary mode</td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>Total amount of gas and</td>
<td>0.4 PV supercritical CO₂ + 0.4 PV SP solution</td>
<td>0.4 PV supercritical CO₂ + 0.4 PV SP solution</td>
<td>0.4 PV supercritical CO₂ + 0.4 PV SP solution</td>
</tr>
<tr>
<td>chemicals used</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Injection scheme</td>
<td>0.8 PV foam*</td>
<td>(0.2 PV CO₂ + 0.2 PV SP solution) *2</td>
<td>(0.3 PV foam* + 0.1 PV SP solution) *2</td>
</tr>
<tr>
<td>Initial oil saturation (%)</td>
<td>67.3</td>
<td>69.4</td>
<td>70.1</td>
</tr>
<tr>
<td>Water floods recovery (%)</td>
<td>33.8</td>
<td>34.5</td>
<td>31.4</td>
</tr>
</tbody>
</table>
#Note: The foam is produced with the assistance of a foam generator. The created foams are comprised of 0.4 PV supercritical CO$_2$ and 0.4 PV SP solution, and 0.3 PV supercritical CO$_2$ and 0.1 PV SP solution in experiments #4 and #6 respectively.

### 3.2.1 Pressure drops

This subsection described and interpreted the pressure drop histories during core flooding processes which were performed under immiscible condition. The assessment results were illustrated in Fig. 13-15. It was noted that the pressure behaviour and the corresponding mechanism behind it in the water floods phase was pretty much the same as that in miscible condition, consequently, the special focus was given to the differential pressure variations in differing tertiary modes. As expected, the pressure drop substantially increased right after initiating the direct foam flooding (mode A). However, it quickly decreased by a huge extent as only a few quantity of CO$_2$ foam was injected, which was not observed in the case of miscible condition. It was well known that the foam would break down when touching the crude oil even if the formula was well designed to make foams oil-tolerance somehow. As a result, the CO$_2$ could become a continuous phase and advance through the porous medium; yet, the released CO$_2$ was not capable of being miscible with the residual oil in place because of the relatively low pore pressure. Instead, the CO$_2$ could only swell the oil and make it less viscous. Thus, the CO$_2$ mobility was much greater than that under the miscible condition, which explained the fast drop of the differential pressure. Another intriguing feature was that the pressure drop across the core plug fluctuated noticeably in the chase waterfloods phase. The more mobile CO$_2$ flowing in the pores and throats allowed the regeneration of foams with adsorbed surfactant, which slowed down the decline of the pressure drop to some extent. The scenario of mode B injection seemed interesting, because it was found that its highest pressure drop during the alternate injection of supercritical CO$_2$ and chemicals was not much lower than that under miscible condition. This phenomenon was largely associated with the impact imposed by the SP solution on supercritical CO$_2$: although the CO$_2$ could still escape from the ruptured foams and form a continuous phase, its mobility was greatly modified by the alternately injected SP solution, taking into consideration that the chemicals would not completely interact with the injected CO$_2$. Thus it served like a piston somehow to make the immiscible CO$_2$ advance relatively evenly. When it came to mode C, the impact of the SP solution on CO$_2$ was still evident. However, it appeared that the foam/SP synergism became weaker than that under miscible condition if the maximum as well as the average differential pressures were compared in these two conditions. This might arise from the foam instability caused by the lower pore pressure, although mode C was still endowed with the best pressure behaviour among these injection modes even under immiscible condition.

### 3.2.2 Water cut and oil recovery

The water cuts during the core flooding experiments are also presented in Fig. 13-15. The core plugs after core flooding are shown in Fig. 16. Likewise, the attention was paid to the
tertiary recovery phase. Generally, regardless of the injection mode, the water content changed in a similar manner compared to that under the counterpart miscible conditions. That was, the introduction of supercritical CO₂ and chemicals could significantly reduce the water production. On the other hand, the lower injection pressure negatively affected the water control performance of the various modes, making their water cuts not as low as the previous condition. Nonetheless, the mode C produced the least amount of the water, while the water produced by mode A and B were comparable in the tertiary recovery phase.

The oil recovery curves were not included in the figures in order to make them concise and clear. As seen in table 5, due to the worse blockage and the higher water content in the effluent, the overall oil recoveries of the three modes all decreased by some extent, reflecting the less encouraging displacement efficiency of the core flooding experiments under immiscible condition. Furthermore, it had been found that although mode B still had the lowest total oil recovery, the oil recovery difference among them were narrowed. Especially for mode A and B, they nearly recovered the same amount of crude oil if the system errors were neglected, while their recovery factors differed under miscible condition. In agree with the water production, mode C yielded the most oil in the flooding process. However, as clearly illustrated in Fig. 17, its advantage of the accumulative oil recovery over the other two modes became less evident under this condition.

![Fig. 13 The water cut and pressure drop history of Mode A under immiscible condition](image)
Fig. 14 The water cut and pressure drop history of Mode B under immiscible condition

Fig. 15 The water cut and pressure drop history of Mode C under immiscible condition
Fig. 16 Core plugs after core flooding experiment (323K, 1200 psi)

Note: (a) Mode A; (b) Mode B; (c) Mode C

Fig. 17 Comparison of accumulative oil recovery under different injection pressure

4. CONCLUSIONS
Under the injection pressure which allowed the CO₂ and the crude oil to be completely miscible, the combined foam/SP flooding exhibited remarkable blocking ability which could be validated by its pressure behaviour in the core flooding, while both the direct foam flooding and the CO₂/SP flooding showed worse blockage either due to the foam instability or the low efficiency of the foam generation.

Moreover, above the MMP, the foam/SP flooding possessed the best capacity of water control among these injection modes. Accordingly, its accumulative oil recovery was the highest and the its advantage of the accumulative oil recovery over the other two counterparts was evident.

Below the MMP, the foam/SP flooding still displayed the best performance with regards to the blockage, water cut and oil recovery, but the differences were greatly narrowed as a consequence of the less pronounced synergism compared to that in the miscible condition.

The average water cuts of the direct foam flooding and CO₂/foam were close, resulting in the nearly same recovery factor below the MMP.

It was suggested that the combined foam/SP flooding was more applicable to the reservoirs whose formation pressures were above the MMP. This injection mode was also capable of significantly enhancing oil recovery below MMP, but the displacement efficiency was not as encouraging as that above MMP. And also it could not display evident advantage over the other two injection modes in the immiscible condition.

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