



# Laboratory investigation of cyclic gas injection using CO<sub>2</sub>/N<sub>2</sub> mixture to enhance heavy oil recovery in a pressure-depleted reservoir

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## Abstract

CO<sub>2</sub> has strong abilities of oil swelling and viscosity reduction for heavy oil extraction, N<sub>2</sub> is a preferable gas media for pressure maintenance, and their mixture is then considered as an alternative method for enhanced oil recovery (EOR) in a pressure-depleted heavy oil reservoir. PVT analysis and cyclic gas injection experiments are conducted to reveal EOR mechanisms for CO<sub>2</sub>/N<sub>2</sub> mixture, and five different CO<sub>2</sub>/N<sub>2</sub> molar ratios (1:0 (pure CO<sub>2</sub>), 4:1, 7:3, 1:1, and 0:1 (pure N<sub>2</sub>)) are designed in this paper. PVT analysis shows that the changes of oil properties including saturation pressure, volume factor, and viscosity are highly related to CO<sub>2</sub>/N<sub>2</sub> ratio of the mixture, and a higher CO<sub>2</sub>/N<sub>2</sub> ratio can always lead to better gas/oil interactions. When CO<sub>2</sub>/N<sub>2</sub> ratio is higher than 7:3, the viscosity can reduce to less than 60% of the initial oil viscosity. Gas injection experimental results show that 4:1 mixture can achieve an oil recovery of 17.31%, which is close to the recovery obtained by pure CO<sub>2</sub>. For the pressure-depleted oil reservoir, simultaneous CO<sub>2</sub>/N<sub>2</sub> injection or N<sub>2</sub> followed by CO<sub>2</sub> injection is suitable injection mode for the mixture. With such a design of CO<sub>2</sub>/N<sub>2</sub> mixture, an optimized EOR effect can be achieved with gas/oil interactions dominated by CO<sub>2</sub> coupled with energy supplement provided by N<sub>2</sub>. A pilot test of CO<sub>2</sub>/N<sub>2</sub> mixture injection is successfully conducted in a test well, and an oil increment of 337 t is obtained after 40,000 m<sup>3</sup> of N<sub>2</sub> injection followed by 80,000 m<sup>3</sup> of CO<sub>2</sub> injection.

**Keywords** CO<sub>2</sub>-EOR · N<sub>2</sub>-EOR · Mixture gas · Heavy oil · Gas/oil interaction

## Introduction

Heavy oil reservoirs have become alternative resources as the decline of conventional oil resources, which account for 70% of total world oil reserves (Guo et al. 2016). Compared with the conventional oil, heavy oil usually has a high viscosity and an undesirable oil mobility, and the oil recovery using waterflooding is generally less than 20% (Shi et al. 2019). Thermal fluids including steams and hot-water are commonly used to heat up heavy oils for the improvement of oil mobility. However, problems such as heat loss, excessive gas emission, highly cost of post-treatment, and maintenance would limit the utilization of thermal fluids (Hascakir 2018).

Solvent gases can be used as alternative injecting media to enhance oil recovery (EOR), and a pure light hydrocarbon, a mixture of several light hydrocarbons, or CO<sub>2</sub> is usually treated as the solvent (Mokrys and Bulter 1993; Ivory et al. 2010; Jiang et al. 2014). Among those solvent, CO<sub>2</sub> is gaining more attention due to its special characteristics, which can be injected into the formation through a miscible operation or an immiscible operation. For the immiscible CO<sub>2</sub> injection, the oil viscosity can be dramatically reduced and the oil mobility can be effectively improved after CO<sub>2</sub> dissolved into the heavy oil. Oil swelling can also be caused after CO<sub>2</sub> interacts with the oil, which then induces an improvement of oil relative permeability for EOR (Miller and Jones 1981; Seyyedsar and Sohrabi 2017; Shokri and Babadagli 2017; Haddad and Gates 2017; Ahadi and Torabi 2018). For the miscible CO<sub>2</sub> injection, a miscibility development can be achieved through a multi-contact process of gas and oil. The light components of oil phase can be extracted or vaporized into the gas phase, and some heavy components of gas phase can also be condensed into the oil phase during CO<sub>2</sub>/oil multi-contact process. After a miscibility is formed, the interfacial tension (IFT) between oil and gas can be reduce to zero, and the

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flooding efficiency can be above 90% in the laboratory according to literatures (Srivastava et al. 2000; Wang and Gu 2011; Jia et al. 2019).

Although a remarkable oil increment can be obtained through CO<sub>2</sub> injection, its application in a pressure-depleted heavy oil reservoir still faces challenges. There are two critical factors for the development of this type of reservoir, one is the oil inherent property, and the other is the loss of pressure or energy. CO<sub>2</sub> would be a preferable injecting gas media with the consideration of heavy oil properties. While since the reservoir is lack of formation energy supplement, the pressure would decline gradually after years of exploitation, which then causes a low yield of oil production. Thus, energy supplement should also be considered to increase and maintain the formation pressure. Notwithstanding CO<sub>2</sub> can be utilized for pressurization through cyclic CO<sub>2</sub> injection, the pressure buildup rate of CO<sub>2</sub> is usually very low in the depleted oil reservoir according to the literatures (Bossie-Codreanu and Gallo 2004; Yoosook et al. 2017; Agartan et al. 2018). Compared with CO<sub>2</sub>, N<sub>2</sub> is a better injecting media for reservoir pressure maintenance; moreover, it is not corrosive and usually cheaper than CO<sub>2</sub> or hydrocarbon gas in EOR applications (Hudgins et al. 1990; Sadooni and Zonnouri 2015; Yuan et al. 2015). The mechanisms of CO<sub>2</sub> and N<sub>2</sub> for EOR are quite different which can be explained at the molecule level. First, the quadrupole-quadruple interaction between CO<sub>2</sub> and oil causes oil swelling and viscosity reduction. In contrast, N<sub>2</sub> is more stable that its Van der Waals force with oil which is very weak that the solubility in oil is very low. Second, N<sub>2</sub> has a higher capillary pressure with the oil phase compared with CO<sub>2</sub>. The high capillary pressure gradient pushes the hydrocarbons, methane, and pentane upward in the form of bulk or Darcy flow. The oil recovery mechanisms are like “sucked out” by the capillary pressure gradient for N<sub>2</sub> injection (Hu et al. 1991; Jia et al. 2019). Considering the EOR mechanisms of CO<sub>2</sub> and N<sub>2</sub> injections mentioned above, CO<sub>2</sub>/N<sub>2</sub> mixture is expected to achieve a complementary advantage for enhanced oil recovery in a pressure-depleted reservoir.

Shayegi (1997) first introduced CO<sub>2</sub>/N<sub>2</sub> mixture as a solvent for cyclic injection process in her PhD thesis. She used core-flooding experiments to investigate the effect of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, and their mixture, and pointed out that a preferable oil recovery can be achieved using CO<sub>2</sub>/N<sub>2</sub> mixture. Then, Farias et al. (2009) focused on the effects of different CO<sub>2</sub>/N<sub>2</sub> mixtures on oil components using a PVT cell, and then pointed out that CO<sub>2</sub> has a higher hydrocarbon vaporization effect than N<sub>2</sub>, and more hydrocarbon extraction can be attained with a higher CO<sub>2</sub> concentration for the mixture. Habibi et al. (2017) also analyzed the gas-oil interactions using a visual PVT cell. Their results showed that CO<sub>2</sub>-oil interactions are much stronger than N<sub>2</sub>-oil interactions under formation conditions. Pure CO<sub>2</sub> injection would usually cause severe asphaltene precipitation/deposition due to the extraction of light and medium components, CO<sub>2</sub>/N<sub>2</sub> mixture is then

proposed as a solution to relieve this problem (Zanganeh et al. 2012; Hemmati-Sarapardeh et al. 2014). Shang et al. (2017) measured the IFT for paraffin + CO<sub>2</sub> and (CO<sub>2</sub> + N<sub>2</sub>) mixture gas at different temperatures and pressures, and pointed out that the IFT of paraffin + (CO<sub>2</sub> + N<sub>2</sub>) mixture is higher than the IFT of paraffin + CO<sub>2</sub> system, which will then influence the EOR process of gas injection. Wang et al. (2018) simulated the composition change of oil and CO<sub>2</sub>/N<sub>2</sub> mixture using PVTsim Nova. Their results showed that the deposition pressure range will transfer when the CO<sub>2</sub>/N<sub>2</sub> injection ratio reaches 1:1, and asphaltene deposition is unlikely to occur using CO<sub>2</sub>/N<sub>2</sub> mixture injection in a buried-hill reservoir.

Although plenty of researches have been conducted on gas/oil interactions, gas injection experiments using CO<sub>2</sub>/N<sub>2</sub> mixture are still limited, and most are focused on enhanced coalbed methane (ECBM) processes (Seomoon et al. 2016; Liu et al. 2016; Li et al. 2018). Recently, Zhao et al. (2018) conducted a CO<sub>2</sub>/N<sub>2</sub> huff-n-puff experiment in a fractured-cavity model, and their results showed that the mixture can increase the formation pressure after bottom-water energy depletion, and then obtains an oil recovery of 17.85%. These previous researches mentioned above give an enlightenment for the EOR utilization of CO<sub>2</sub>/N<sub>2</sub> mixture in the pressure-depleted heavy oil reservoir.

In order to study the EOR mechanisms of gas injection using CO<sub>2</sub>/N<sub>2</sub> mixture, PVT analysis and laboratory experiments are utilized in this paper. For the PVT experiments, different CO<sub>2</sub>/N<sub>2</sub> molar ratios for the mixtures are designed as 1:0, 4:1, 7:3, 1:1, and 0:1, respectively, and high-pressure property changes including saturation pressure ( $P_b$ ), volume factor ( $B_o$ ), and viscosity ( $\mu_o$ ) are compared with different injecting gas media. Then, a series of outcrop cores are used to simulate a depleted reservoir condition (the initial pressure is below  $P_b$ ), and cyclic gas injection experiments are conducted using different CO<sub>2</sub>/N<sub>2</sub> mixture. With the consideration of both oil recovery factor and pressure complement, a suitable CO<sub>2</sub>/N<sub>2</sub> ratio and injection mode are determined for the mixture. The EOR mechanisms for CO<sub>2</sub>/N<sub>2</sub> mixture are then discussed based on the results of PVT analysis and gas injection experiments. A successful pilot test of CO<sub>2</sub>/N<sub>2</sub> mixture injection is also introduced in this paper, which may give a guidance for the application of CO<sub>2</sub>/N<sub>2</sub> mixture in the pressure-depleted heavy oil reservoir.

## Experiments

### Materials

The oil and water samples are collected from a depleted oil reservoir, Jidong Oil Field, China. The density of formation oil is 0.89 g/cm<sup>3</sup>, and the oil viscosity is 52.13 mPa s under formation conditions (65 °C, 16.24 MPa), which belongs to a

conventional heavy oil. The compositions of formation oil are detailed in Table 1. The minimum miscibility pressure (MMP) of the oil measured by a slim tube is 27.4 MPa. The salinity of the formation water is 1937 mg/L. Both of the injected CO<sub>2</sub> and N<sub>2</sub> are with purities of 99.99 mol%.

The cores used in the gas injection experiments are outcrop cores with an average size of 300 × 45 × 45 mm<sup>3</sup>. The average permeability of the cores is 497.3 × 10<sup>-3</sup> μm<sup>2</sup>, and the average porosity is 17.02%. The petrophysical properties are shown in Table 2.

### PVT analysis for gas-oil system

CO<sub>2</sub>-oil tests, N<sub>2</sub>-oil tests, and CO<sub>2</sub>-N<sub>2</sub>-oil tests with CO<sub>2</sub>/N<sub>2</sub> molar ratios of 4:1, 7:3, and 1:1 are first investigated in the PVT analysis. Constant composition expansion (CCE) tests and viscosity measurements are conducted to evaluate high-pressure properties of the gas-oil system. CCE tests are conducted using a PVT apparatus as shown in Fig.1. The PVT apparatus is consisted of a visual PVT cell, a thermostat air bath, a pressure sensor, a temperature sensor, and an operation system. The volumetric capacity of the cell is 250 mL, the operation pressure is 200 MPa, and the operation temperature is 200 °C. The viscosity measurements are conducted using a viscometer as shown in Fig.2, which has a viscosity measurement ranges from 0.3 to 20,000 mPa s.

The changes of saturation pressure (*P<sub>b</sub>*) and swelling factor (*B<sub>o</sub>*) after gas injection can be evaluated using the CCE tests, and the changes of oil viscosity (*μ<sub>o</sub>*) can be measured through the viscosity tests. Since the mass of CO<sub>2</sub>, N<sub>2</sub>, and formation oil is always constant at all conditions, and the density of CO<sub>2</sub>, N<sub>2</sub>, and oil can also be determined at a reference pressure and temperature (65 °C, 16.24 MPa), a specific gas/oil volume ratio can then be derived from the gas/oil molar ratio (as shown in Table 3). With the determination of gas/oil volume ratio, the injection volume of gas and oil can be calculated for

the PVT analysis. It is more convenient to use volumetric parameters during injection procedures of the tests, while it is more commonly used with molar parameters for the post-PVT data analysis.

The detailed sequences of PVT analysis for gas-oil system are as follows: ① The PVT cell and the viscometer are cleaned and evacuated using a vacuum pump separately. ② Set a value of gas/oil volume ratio for the gas-oil system. A specific volume of formation oil is then injected into the PVT cell and the viscometer separately, followed by a specific volume of gas. ③ Increase the pressure and temperature of the cell, and stir the gas-oil mixture for 12 h until the gas is completely dissolved into the formation oil. ④ Decrease the pressure step by step, and record the oil volume at a specific pressure. The saturation pressure (*P<sub>b</sub>*) of the gas-oil system can be determined when the first gas bubble is observed in the PVT cell, and the oil viscosity (*μ<sub>o</sub>*) can be measured when the pressure reaches 16.24 MPa at the temperature of 65 °C. ⑤ Change the injecting gas/oil volume ratio to another value, and repeat ① to ④, then another *P<sub>b</sub>* value and *μ<sub>o</sub>* value can be obtained. ⑥ After the changes of gas/oil ratio for five to eight times, a series of *P<sub>b</sub>* values and a series of *μ<sub>o</sub>* values can be obtained. ⑦ During the experiment procedure, the oil and gas volumes under different pressures can also be recorded, and then a series of volume factor (*B<sub>o</sub>*) values can also be obtained. *B<sub>o</sub>* can be calculated as the ratio of subsurface oil volume to surface oil volume. ⑧ Change the CO<sub>2</sub>/N<sub>2</sub> volume ratio for the gas phase as 1:0, 2:1, 1:1, 1:2, and 0:1, and repeat ① to ⑦, then the changes of *P<sub>b</sub>*, *B<sub>o</sub>*, and *μ<sub>o</sub>* versus CO<sub>2</sub>/N<sub>2</sub> ratio can be obtained. The detailed measurements of PVT analysis are also listed in Table 3.

### Cyclic gas injection experiments

A series of cyclic gas injection experiments are designed to optimize the CO<sub>2</sub>/N<sub>2</sub> ratio and the injection mode for the CO<sub>2</sub>/

**Table 1** Compositions of the formation oil

Component	mol%	Component	mol%	Component	mol%	Component	mol%
N <sub>2</sub>	1.80	C <sub>8</sub>	0.24	C <sub>18</sub>	2.36	C <sub>28</sub>	1.94
C <sub>1</sub>	20.31	C <sub>9</sub>	0.83	C <sub>19</sub>	2.08	C <sub>29</sub>	1.86
C <sub>2</sub>	6.523	C <sub>10</sub>	0.45	C <sub>20</sub>	1.77	C <sub>30</sub>	1.62
C <sub>3</sub>	1.152	C <sub>11</sub>	0.88	C <sub>21</sub>	1.67	C <sub>31</sub>	1.15
iC <sub>4</sub>	0.384	C <sub>12</sub>	1.42	C <sub>22</sub>	1.53	C <sub>32</sub>	0.90
nC <sub>4</sub>	0.256	C <sub>13</sub>	1.97	C <sub>23</sub>	1.42	C <sub>33</sub>	0.72
iC <sub>5</sub>	0.026	C <sub>14</sub>	2.35	C <sub>24</sub>	1.31	C <sub>34</sub>	0.61
nC <sub>5</sub>	0.033	C <sub>15</sub>	2.17	C <sub>25</sub>	1.38	C <sub>35</sub>	0.56
C <sub>6</sub>	0.066	C <sub>16</sub>	2.33	C <sub>26</sub>	1.52	C <sub>36+</sub>	27.93
C <sub>7</sub>	0.15	C <sub>17</sub>	2.55	C <sub>27</sub>	1.78		
						Total	100

**Table 2** Physical parameters of the outcrop cores

No.	Apparent volume/mL	Pore volume /mL	Permeability $/\times 10^{-3} \mu\text{m}^2$	Porosity/%	Initial oil saturation/%
S1	593	106	515	17.88	64.5
S2	605	110	452	18.18	69.2
S3	574	96	573	16.72	53.4
S4	587	102	454	17.38	62.1
S5	599	95	477	15.86	51.9
S6	569	92	591	16.16	59.7
S7	601	102	419	16.97	61.2

$\text{N}_2$  mixture. The experimental setup consists of five sub-systems as shown in Fig. 3: an injection system, a displacement system, a production system, a temperature control system, and a data acquisition system. In the injection system, the formation water, formation oil,  $\text{CO}_2$ , and  $\text{N}_2$  are stored in transfer cylinders and then injected into the core by constant pressure and rate pumps. In the displacement system, an outcrop core is placed in a coreholder with a confining pressure. In the production system, a backpressure regular (BPR) is used to control the production pressure. The produced oil is recorded by test tubes, and the gas is measured by a gas flow meter. The thermostat is used to maintain the experimental temperature, and the injection and production pressures are obtained by the data acquisition system.

The optimization experiments of  $\text{CO}_2/\text{N}_2$  ratio are designed to compare the oil extraction ability for different injecting gas media. Pure  $\text{CO}_2$ , pure  $\text{N}_2$ , and  $\text{CO}_2/\text{N}_2$  mixtures with  $\text{CO}_2/\text{N}_2$  volume ratios of 2:1, 1:1, and 1:2 are utilized in the experiments, which are consistent with the PVT analysis. The outcrop cores used in the experiments are S1, S2, S3, S4, and S5 as listed in Table 2. First, epoxy resins are coated on the surface of the core to avoid  $\text{CO}_2$  corruption, and the bulk volume

of the core is measured before the experiment. The core is placed into the coreholder and evacuated using a vacuum pump. After the core is saturated with formation water, the porosity is determined as the ratio of brine saturation volume to the bulk volume. Brine is then injected into the inlet and produced from the outlet to measure the permeability of the core. After the permeability measurement, the core is displaced by formation oil to reach a residual water saturation, and the initial oil saturation is calculated as the ratio of injected oil volume to the pore volume.

The inlet of the outcrop core is set as both the injector and the producer for the gas injection experiment, and the sequences are detailed as follows: ① The initial temperature is set as  $65^\circ\text{C}$ . The initial pressure is set as 5 MPa using the BPR, which is a pressure-depleted condition. ② Gas is injected into the core with a rate of 0.3 mL/min until the injection volume reaches

**Fig. 1** Picture of PVT analysis apparatus**Fig. 2** Picture of the viscometer

**Table 3** detailed measurements for PVT analysis (65 °C, 16.24 MPa)

	Pure CO <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub> mixture			Pure N <sub>2</sub>
CO <sub>2</sub> /N <sub>2</sub> molar ratio	1:0	4:1	7:3	1:1	0:1
CO <sub>2</sub> /N <sub>2</sub> volume ratio	1:0	2:1	1:1	2:1	0:1
Gas/oil ratio/%	0	0	0	0	0
	10	10	10	10	5
	20	20	20	20	10
	30	30	30	30	15
	40	40	40	35	20
	50	50	45	/	/
	60	60	/	/	/
	65	/	/	/	/

$\rho_{CO_2} = 0.595 \text{ kg/cm}^3$ ,  $\rho_{N_2} = 0.156 \text{ kg/cm}^3$  at 60 °C, and 16.24 MPa

0.05 PV (under formation conditions). ③ The inlet is shutoff with a soaking time of 12 h, and then opened to start a producing process. When the pressure drops to 5 MPa again, 1 cycle is terminated. ④ Repeat ② and ③ for another three times, and the whole experimental process is terminated after 4 cycles of gas injection. The pressure and the production of oil and gas are measured during the experiments.

During the process of pure CO<sub>2</sub> injection and pure N<sub>2</sub> injection, the gas can be injected into the core through either CO<sub>2</sub> cylinder or N<sub>2</sub> cylinder, and one constant rate and pressure pump is enough. While for the mixture injection, CO<sub>2</sub> and N<sub>2</sub> should be injected into the core simultaneously, and two pumps need to be used in this case. Different injection rate for each pump is set according to the CO<sub>2</sub>/N<sub>2</sub> ratio. Taking the scenario of 2:1 (CO<sub>2</sub>/N<sub>2</sub> volume ratio) as an example, the injection rate of CO<sub>2</sub> and N<sub>2</sub>

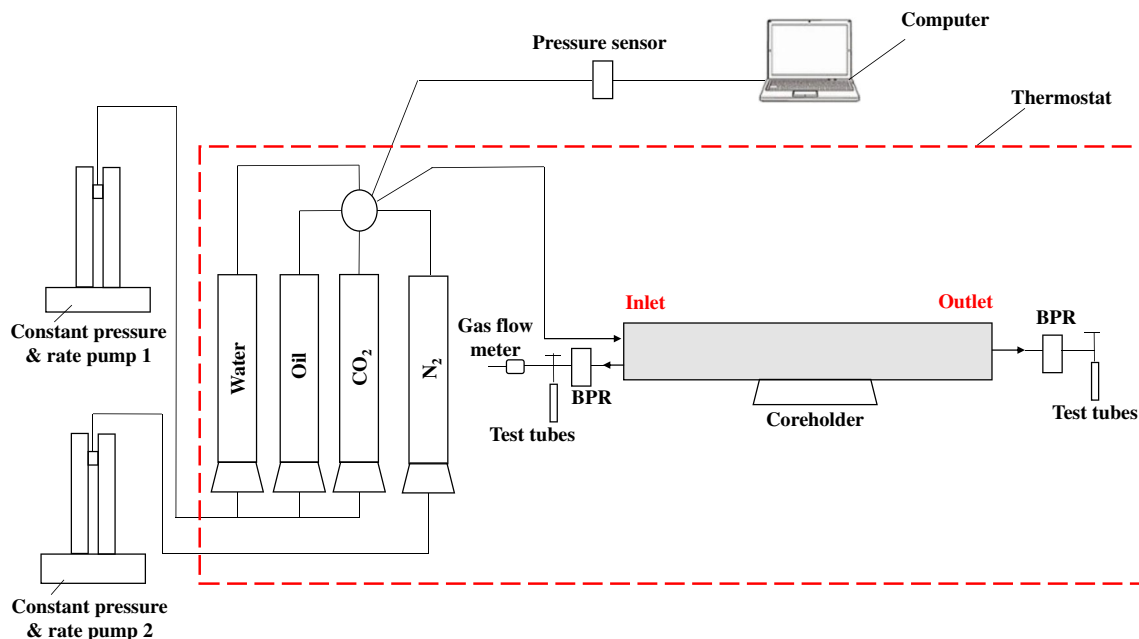
need to be set as 0.2 mL/min and 0.1 mL/min during procedure ②. Other experimental procedures and measurement parameters are the same as mentioned above.

After the determination of injecting CO<sub>2</sub>/N<sub>2</sub> ratio, the injection mode for CO<sub>2</sub>/N<sub>2</sub> mixture is also optimized through the gas injection experiments. Three injection modes are designed as follows: simultaneous CO<sub>2</sub>/N<sub>2</sub> injection, N<sub>2</sub> followed by CO<sub>2</sub>, and CO<sub>2</sub> followed by N<sub>2</sub>. The outcrop cores of S2, S6, and S7 are used in the experiments, and the experimental preparations are the same as the CO<sub>2</sub>/N<sub>2</sub> ratio optimization experiments. Since CO<sub>2</sub> and N<sub>2</sub> are injected into the Core S2 simultaneously, it can be treated as simultaneous CO<sub>2</sub>/N<sub>2</sub> injection. For the N<sub>2</sub> followed by CO<sub>2</sub> injection, 0.017 PV of N<sub>2</sub> is firstly injected into Core S6, and then followed by 0.033 PV of CO<sub>2</sub> in procedure ②. While for the CO<sub>2</sub> followed N<sub>2</sub> injection, 0.033 PV of CO<sub>2</sub> is firstly injected into Core S7, and then followed by 0.017 PV of N<sub>2</sub>. The CO<sub>2</sub>/N<sub>2</sub> volume ratio remains the same as 2:1 for the experiments with different injection mode, and the total volume is also 0.20 PV after 4 cycles of gas injection. Other experimental procedures and measurement parameters are the same as the CO<sub>2</sub>/N<sub>2</sub> ratio optimization experiments.

## Results and discussions

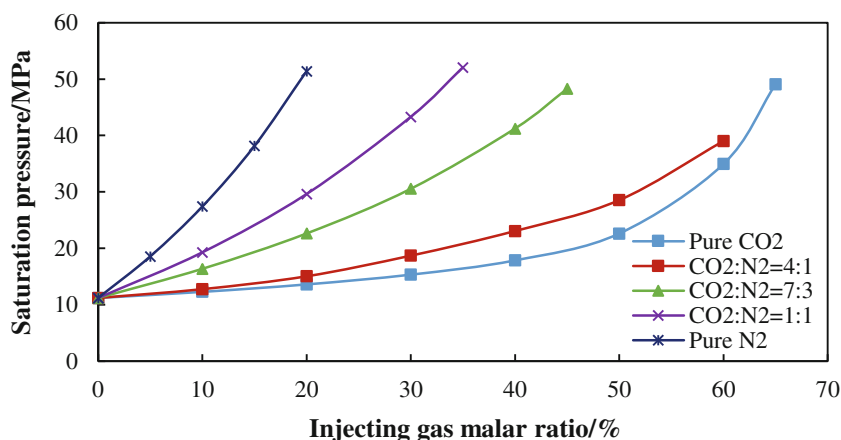
### PVT comparisons of CO<sub>2</sub>-oil, N<sub>2</sub>-oil, and CO<sub>2</sub>-N<sub>2</sub>-oil systems

The high-pressure property changes for CO<sub>2</sub>-oil, N<sub>2</sub>-oil, and CO<sub>2</sub>-N<sub>2</sub>-oil systems are firstly compared through the PVT analysis. Figure 4 shows the plot of saturation pressure ( $P_b$ )



**Fig. 3** Flow chart for the gas injection experiments

**Fig. 4** Changes of saturation pressure ( $P_b$ ) for the gas-oil system at 65 °C



versus injecting gas molar ratio for the gas-oil system. The initial value of  $P_b$  for the formation oil is 11.2 MPa, which will raise as the increase of injecting gas molar ratio. Compared with pure CO<sub>2</sub> and pure N<sub>2</sub>,  $P_b$  of the heavy oil is more sensitive with N<sub>2</sub>. When the gas molar ratio increases from 0 to 20 mol%,  $P_b$  influenced by pure N<sub>2</sub> will increase from 11.2 to 51.39 MPa, while  $P_b$  influenced by pure CO<sub>2</sub> just increases from 11.2 to 13.6 MPa. The saturation pressure influenced by CO<sub>2</sub>/N<sub>2</sub> mixture is between pure CO<sub>2</sub> and pure N<sub>2</sub> and is also influenced by CO<sub>2</sub>/N<sub>2</sub> molar ratio of the mixture. For example, with 20 mol% of CO<sub>2</sub>/N<sub>2</sub> mixture injection,  $P_b$  influenced by the mixture with a CO<sub>2</sub>/N<sub>2</sub> ratio of 4:1, 7:3, and 1:1 is 19.62 MPa, 22.63 MPa, and 15.04 MPa, respectively.

The dissolving capacity for different injecting gas media can also be interpreted from Fig. 4. For example, when the pressure is 30 MPa, about 12 mol% of N<sub>2</sub> can be dissolved in 88 mol% of oil, and 57 mol% of CO<sub>2</sub> can be dissolved in 43 mol% of oil. CO<sub>2</sub> has a much better dissolving capacity into the heavy oil compared with N<sub>2</sub>. As a result, the dissolving capacity of CO<sub>2</sub>/N<sub>2</sub> mixture is closely related to the CO<sub>2</sub>/N<sub>2</sub> molar ratio for the mixture. When the pressure is 30 MPa, CO<sub>2</sub>/N<sub>2</sub> mixture dissolved into the oil with a CO<sub>2</sub>/N<sub>2</sub> ratio of 1:1, 7:3, and 4:1 is 18 mol%, 29 mol%, and 52 mol%, respectively. The dissolving capacity of CO<sub>2</sub>/N<sub>2</sub> mixture is enhanced dramatically as the increase of CO<sub>2</sub>/N<sub>2</sub> molar ratio.

Volume factor ( $B_o$ ) is used to evaluate oil swelling capacity, which is caused by the dissolved gas in the oil under formation conditions. Volume factor is the ratio of subsurface oil volume to surface oil volume. Because of the degassing of surface oil, the volume of subsurface oil is usually higher than the volume of surface oil, and the value of  $B_o$  is usually higher than 1. Since there are huge differences of the dissolving capacity for different injecting gas media, the oil swelling capacity for different gas media is then discussed as shown in Fig. 5. The initial value of  $B_o$  for the heavy oil is 1.058 under formation conditions of 65 °C and 16.24 MPa, which also raises as the increase of injecting gas molar ratio. CO<sub>2</sub> has a better oil swelling capacity for the heavy oil compared with N<sub>2</sub>. For

example, when the injecting gas is 20 mol%,  $B_o$  is 1.095 and 1.075 for the CO<sub>2</sub> and N<sub>2</sub>, respectively. The volume factor influenced by CO<sub>2</sub>/N<sub>2</sub> mixture is between pure CO<sub>2</sub> and pure N<sub>2</sub> and is also related to CO<sub>2</sub>/N<sub>2</sub> molar ratio of the mixture.  $B_o$  raises as the increase of CO<sub>2</sub>/N<sub>2</sub> molar ratio, and a better oil swelling capacity can be obtained with a higher CO<sub>2</sub> concentration for the CO<sub>2</sub>/N<sub>2</sub> mixture.

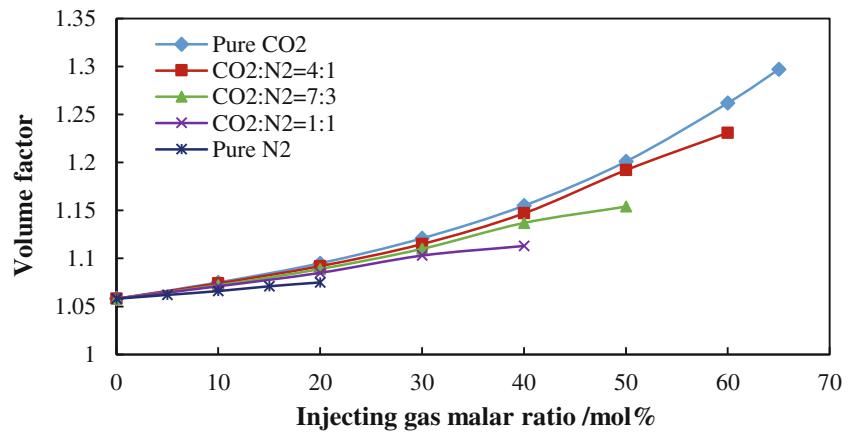
Another important factor for gas-EOR is oil viscosity ( $\mu_o$ ) reduction, and the measurement results are shown in Fig. 6. The initial value of  $\mu_o$  for the formation oil is 52.13 mPa s, which will decrease as the increase of injecting gas molar ratio. As more gas is dissolved into the formation oil, the viscosity reduction by the injecting gas is more obvious. However, the capacity of viscosity reduction is much different between CO<sub>2</sub> and N<sub>2</sub>. For example, when the injecting gas molar ratio increases from 0 to 20 mol%, the viscosity drops from 52.13 to 27.02 mPa s for the CO<sub>2</sub>-system, while the viscosity only drops from 52.13 to 45.49 mPa s for the N<sub>2</sub>-system. CO<sub>2</sub> has a much better viscosity reduction capacity for the heavy oil. For the CO<sub>2</sub>/N<sub>2</sub> mixture, the capacity of viscosity reduction is closely related to the CO<sub>2</sub>/N<sub>2</sub> molar ratio of the mixture. With a higher CO<sub>2</sub>/N<sub>2</sub> ratio, a better viscosity reduction capacity will be obtained for the mixture. When the injection gas molar ratio exceeds 20 mol% with a pure CO<sub>2</sub> or a 4:1 mixture or a 7:3 mixture, the viscosity can reduce to less than 60% of the initial oil viscosity.

The PVT analysis reveals that CO<sub>2</sub> has better interactions with the heavy oil compared with N<sub>2</sub>. For the CO<sub>2</sub>/N<sub>2</sub> mixture, its interactions with formation oil are always between pure CO<sub>2</sub> and pure N<sub>2</sub>. A higher CO<sub>2</sub>/N<sub>2</sub> molar ratio for the mixture can always lead to better capacities of dissolution, oil swelling, and viscosity reduction, which are the dominant mechanisms for the heavy oil extraction.

### Optimization of CO<sub>2</sub>/N<sub>2</sub> ratio for cyclic gas injection

To study the feasibility of EOR using CO<sub>2</sub>/N<sub>2</sub> mixture, several cyclic gas injection experiments using pure CO<sub>2</sub>, pure N<sub>2</sub>, and

**Fig. 5** Changes of volume factor ( $B_o$ ) for the gas-oil system at 65 °C and 16.24 MPa



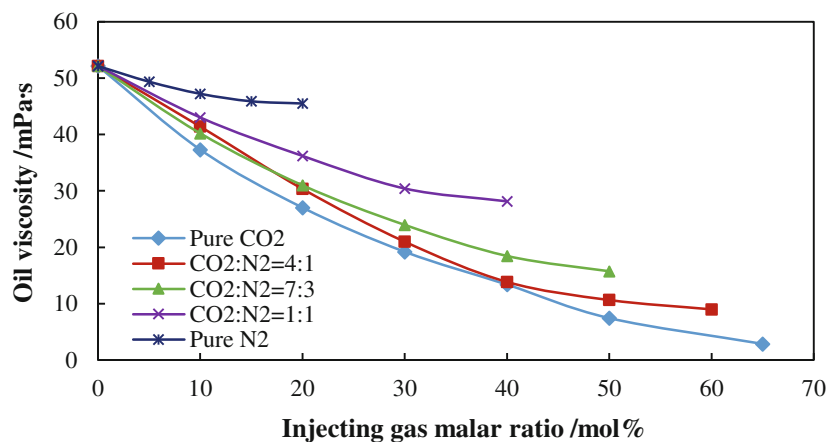
$CO_2/N_2$  mixture are designed after the PVT analysis. Four cycles of gas injections are conducted with a total volume of 0.20 PV in each experiment. The  $CO_2/N_2$  volume ratio for the mixture is 1:0, 2:1, 1:1, 1:2, and 0:1, respectively, which is equal to 1:0, 4:1, 7:3, 1:1, and 0:1 for the  $CO_2/N_2$  molar ratio.

Figure 7 shows the oil recovery factors of cyclic gas injections using different gas media. After 4 cycles of gas injections, pure  $CO_2$  and the 2:1 mixture achieve higher oil recovery factors. The oil recovery of 2:1 mixture is 17.31%, which is close to the oil recovery of 19.03% achieved by pure  $CO_2$ . 1:1 mixture achieves the middle oil recovery of 13.27%, while 1:2 mixture and pure  $N_2$  achieve the lowest oil recovery factors, which are less than 10%.

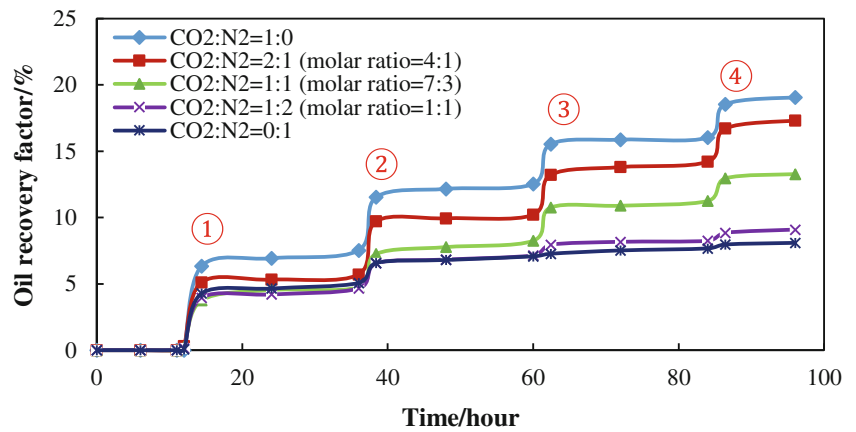
As discussed above, the oil extraction mechanisms for  $CO_2/N_2$  mixture is strongly related to the injecting  $CO_2/N_2$  ratio. Since the concentration of  $N_2$  component increases as the  $CO_2/N_2$  ratio decreases for the mixture, the interactions between gas and oil are weakened, which then affect the oil extraction of the  $CO_2/N_2$  mixture. For the mixture with a  $CO_2/N_2$  volume ratio of 2:1 ( $CO_2/N_2$  molar ratio is 4:1),  $CO_2$  accounts for a large proportion of the mixture, and the superior performances of gas dissolution, oil swelling, and viscosity reduction dominated by  $CO_2$  are highly reserved for enhanced oil recovery.

Figure 8 shows the oil recovery for each cycle during gas injection experiments. It can be observed that although the oil recovered by 2:1 mixture is less than the oil recovered by pure  $CO_2$  during the first and the second cycle, a better oil recovery can still be obtained for the 2:1 mixture during the third and the fourth cycle. Figure 9 shows the pressure of cyclic gas injection using different gas media. After gas is injected into the core in each cycle, the pressure declines at the beginning of the soaking time both for the pure  $CO_2$  injection and for the 2:1 mixture injection. This pressure declines can be attributed to several factors. First, oil swelling occurs after  $CO_2$  dissolves into the oil phase, which is expected to increase pressure of the system. However, molecular diffusion between  $CO_2$  and oil will reduce the gas/oil interfacial tension, which overwhelms the effect of oil swelling. Second, the pressure propagation also occurs after gas injection with the pressure declines near the inlets and pressure increases away from the inlets (Jia et al. 2018). It can also be observed that the pressure of 2:1 mixture is much higher than the pressure of pure  $CO_2$  after the same volume of gas is injected, especially for the third and the fourth cycle. Although  $N_2$  has poor interactions with the heavy oil, it can otherwise effectively complement formation energy. The gas/oil interactions dominated by  $CO_2$  coupled

**Fig. 6** Change of viscosity ( $\mu_o$ ) for the gas-oil system at 65 °C and 16.24 MPa



**Fig. 7** Oil recovery factors of cyclic gas injections using different gas media

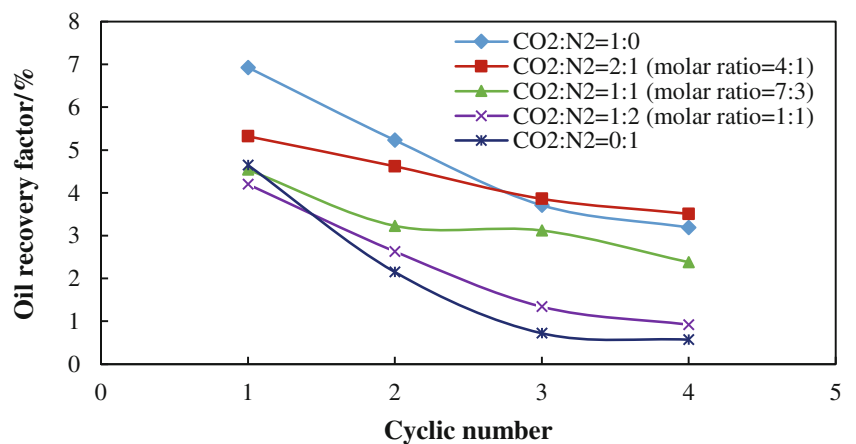


with the pressure supplement by N<sub>2</sub> lead to a remarkable oil recovery for the 2:1 mixture injection.

For the mixture with a CO<sub>2</sub>/N<sub>2</sub> volume ratio of 1:1, a higher energy supplement is obtained due to the increase of N<sub>2</sub> concentration, and gas/oil interactions can still be observed with pressure declines as shown in Fig.9. However, this energy supplement cannot fully compensate the loss of gas/oil interactions, which then weaken the ability of oil extraction for the 1:1 mixture. The 1:2 mixture and pure N<sub>2</sub> achieve the highest pressures after gas injections with the same gas volume, and merely pressure declines can be observed as shown in Fig.9. N<sub>2</sub> is the major component for 1:2 mixture and pure N<sub>2</sub>, and since N<sub>2</sub> has poor interactions with the heavy oil, energy supplement will become the dominant EOR mechanism under those circumstances, which leads to the poor oil extractions for the 1:2 mixture and the pure N<sub>2</sub>.

Since the oil extraction is sensitive to the proportions of CO<sub>2</sub> and N<sub>2</sub> components, the injecting CO<sub>2</sub>/N<sub>2</sub> ratio should be carefully studied for the mixture injection. A CO<sub>2</sub>/N<sub>2</sub> volume ratio of 2:1 (CO<sub>2</sub>/N<sub>2</sub> molar ratio is 4:1) is optimized through the laboratory experiments in this paper. With such a design of injecting CO<sub>2</sub>/N<sub>2</sub> ratio, a remarkable oil recovery can be obtained under the dominant EOR mechanisms of CO<sub>2</sub> coupled with pressure supplement of N<sub>2</sub>.

**Fig. 8** Oil recovery factor for each cycle during different gas injection experiments



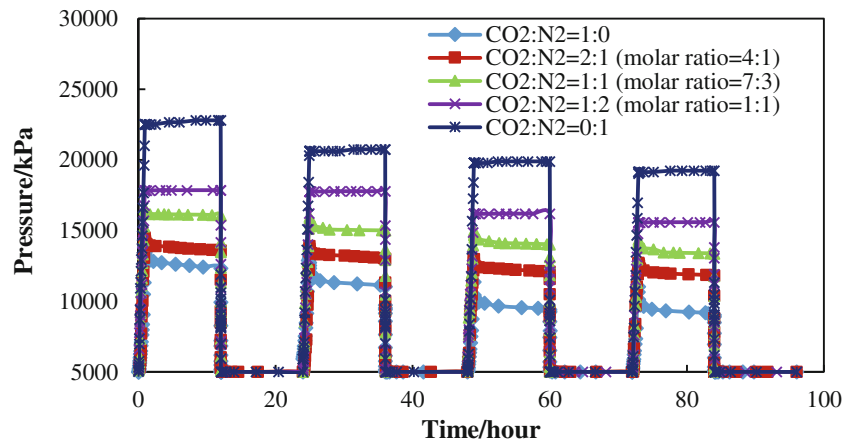
### Injection mode of CO<sub>2</sub>/N<sub>2</sub> mixture for the cyclic gas injection

Besides the CO<sub>2</sub>/N<sub>2</sub> ratio for the mixture, the injection mode should also be studied for a better oil extraction. Three injection modes are designed as follows: simultaneous CO<sub>2</sub>/N<sub>2</sub> injection, N<sub>2</sub> followed by CO<sub>2</sub>, and CO<sub>2</sub> followed by N<sub>2</sub>. The injected CO<sub>2</sub>/N<sub>2</sub> volume ratio is set as 2:1, and the results are shown in Fig.10. After 4 cycles of gas injection, the total oil recovery of N<sub>2</sub> followed by CO<sub>2</sub> is 16.60%, which is close to the recovery of 17.03% achieved by simultaneous CO<sub>2</sub>/N<sub>2</sub> injection. While the CO<sub>2</sub> followed by N<sub>2</sub> injection obtains the lowest oil recovery of 12.38% with the same gas injection volume.

Figure 11 compares the pressure data of different gas injection mode. As discussed above, the pressure declines shows a gas/oil interaction process, which can be observed both in simultaneous CO<sub>2</sub>/N<sub>2</sub> injection and in N<sub>2</sub> followed by CO<sub>2</sub> injection. It can also be observed that the pressure of N<sub>2</sub> followed by CO<sub>2</sub> injection is higher than the pressure of simultaneous injection. When the CO<sub>2</sub> and N<sub>2</sub> are injected into the core simultaneously, the pressure supplement mainly provided by N<sub>2</sub> is likely to be weakened by CO<sub>2</sub>. While with a pre-injected slug of N<sub>2</sub>, the molecular diffusion between N<sub>2</sub>



**Fig. 9** Pressure data of cyclic gas injections using different gas media



and oil can form a higher capillary pressure at the inlet of core. This capillary pressure rapidly increases the inlet pressure, and then force the gas phase move inside of the core to contact with more oil (Hu et al. 1991). When the pressure is enhanced above the saturation pressure ( $P_b$ ), the successive  $CO_2$  slug can fully interact with the formation fluid to extract the heavy oil. With those mechanisms mentioned above,  $N_2$  followed by  $CO_2$  injection can achieve the best oil recovery for the first, second, and third cycle as shown in Fig.10.

Unlike the pressure declines for the simultaneous  $CO_2/N_2$  injection and  $N_2$  followed by  $CO_2$  injection, a slight increase of pressure is observed during the soaking time for the  $CO_2$  followed by  $N_2$  injection as shown in Fig.11. Since the initial pressure of the core is lower than the saturation pressure ( $P_b$ ),  $CO_2$  cannot be dissolved into the oil until the pressure reaches  $P_b$ , which sacrifices a large concentration of  $CO_2$ . After the pressure reaches  $P_b$ , only a small proportion of  $CO_2$  is left for oil extraction. Furthermore, the pre-injected  $CO_2$  also hinders the molecular diffusion between  $N_2$  and oil. The successive  $N_2$  is remained at the inlet of the core for oil swelling, thus the pressure inclines during the soaking time for the  $CO_2$  followed by  $N_2$  injection.

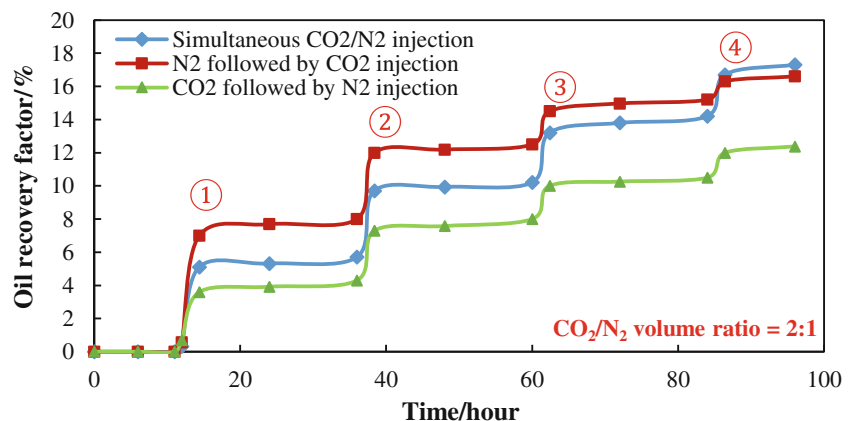
Both simultaneous  $CO_2/N_2$  injection and  $N_2$  followed by  $CO_2$  injection are suitable injection modes for the mixture. When the formation pressure is under saturation pressure,

the primary work is to increase the formation energy using  $N_2$ , which can be effectively achieved by simultaneous  $CO_2/N_2$  injection and  $N_2$  followed by  $CO_2$  injection. After the pressure reaches and exceeds the initial saturation pressure, the injected gas can fully interact with the heavy oil, and then recovers plenty of crude oil from the depleted oil reservoir.

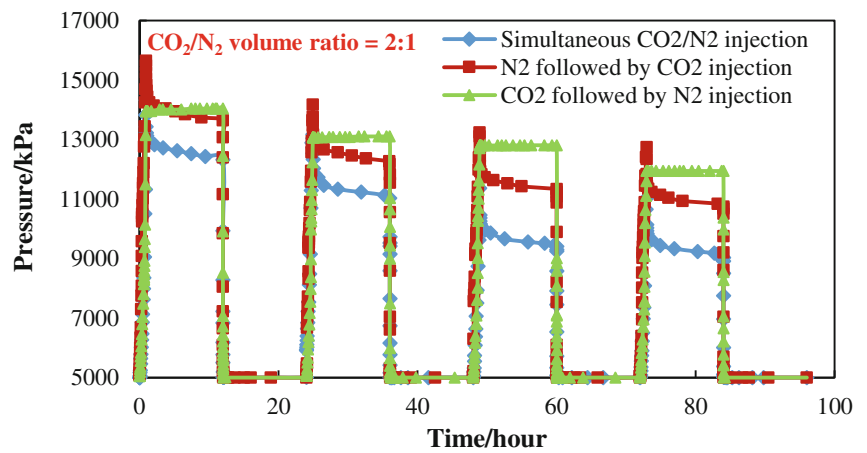
A test of  $CO_2/N_2$  mixture injection is also conducted in the pilot. LN5-3 is chosen as the test well, which is located in Liunan Block, Jidong Oil Field, China. Natural depletion was applied for the test well before the mixture injection, and the formation energy is insufficient after years of exploitation. From August 15, 2015 to April 24, 2016, the dynamic liquid level declined from - 1333.28 to - 1906 m, and the tubing and casing pressures were both less than 1 MPa. When the well was opened at August 15, 2015, the water cut dropped sharply from 89.61 to 43.35%, and then slowly increased to 70.49% before the mixture injection. The daily production rates also decreased during the natural exploitation, and the average oil, water, and liquid rate was only 0.36 m<sup>3</sup>/d, 0.84 m<sup>3</sup>/d, and 1.20 m<sup>3</sup>/d, respectively.

One cycle of  $CO_2/N_2$  mixture injection was then conducted in the test well.  $CO_2/N_2$  volume ratio of the mixture was 2:1, and the injection mode was  $N_2$  followed by  $CO_2$  injection, which were in accordance with the laboratory results. The gas injection started from April 25 to May 18, 2016.  $N_2$  was

**Fig. 10** Oil recovery factors of cyclic gas injections using different gas injection modes

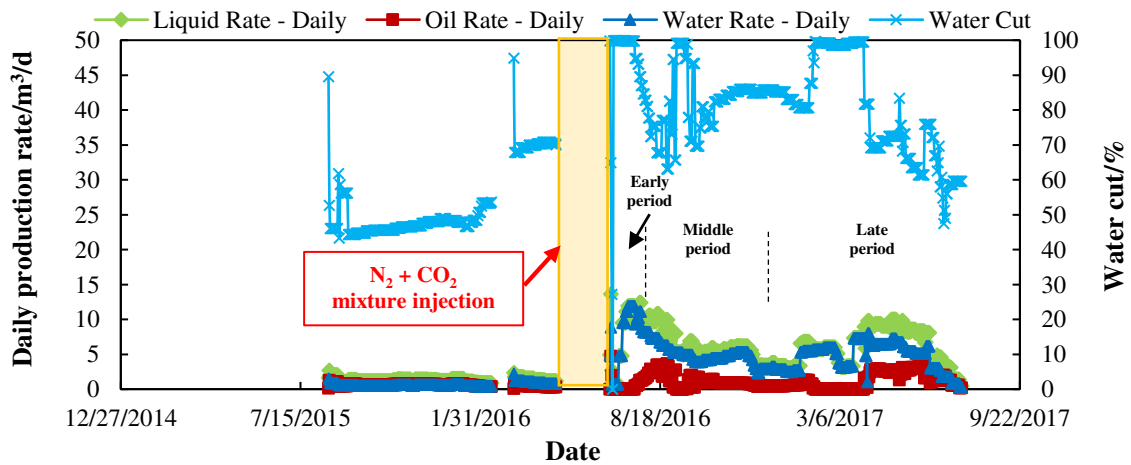


**Fig. 11** Pressure data of cyclic gas injections using different gas injection modes

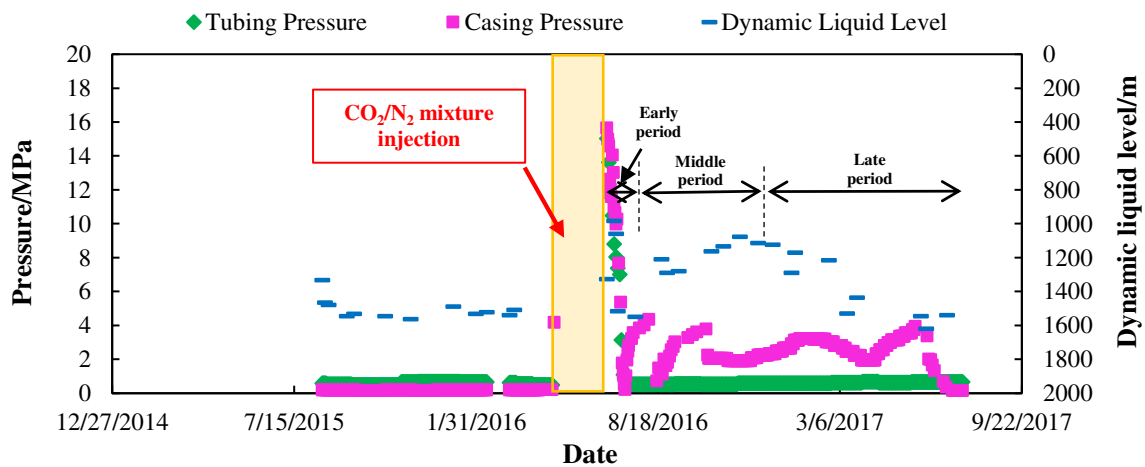


firstly injected with an injection flowrate of 5000 m<sup>3</sup>/d and an injection pressure of 5 MPa, then CO<sub>2</sub> was injected with the same operation parameters. After 24 days of gas injection, 40,000 m<sup>3</sup> of N<sub>2</sub> and 80,000 m<sup>3</sup> of CO<sub>2</sub> were injected into

the formation. Then the well was shut-in for 35 days and re-produced at June 23, 2016. Figure 12 shows the production performance of CO<sub>2</sub>/N<sub>2</sub> mixture injection, which can be subdivided into three periods as follows.



**(a) Daily production performance and water cut**



**(b) Pressure data and dynamic liquid level**

**Fig. 12** Production performance of CO<sub>2</sub>/N<sub>2</sub> mixture injection for the test well

(1) Early production period: Gas mixture was firstly produced when the well was re-produced. The tubing and casing pressures were both higher than 15 MPa, and the dynamic liquid level was increased to  $-988$  m, which indicated that the mixture successively supplemented the near-wellbore energy. After a short period of free gas production, water near the wellbore was mainly produced for nearly a month. The maximum daily water rate was enhanced up to  $12.44$  m<sup>3</sup>/d, which indicated that the mixture effectively improved the well production performance.

(2) Middle production period: The EOR of CO<sub>2</sub>/N<sub>2</sub> mixture was reflected with a remarkable oil increment and an obvious water decline during this period. The water cut dropped from 94.78 to 63.12%, and then gradually increased during the successive production period. The daily oil rate was dramatically enhanced from 0.36 to a maximum of 3.68 m<sup>3</sup>/d, and then decreased to 1.16 m<sup>3</sup>/d. It can also be observed that the dynamic liquid level and the casing pressure increased during the middle production period as shown in Fig. 12b. With the convective flux and molecular diffusion, the injected CO<sub>2</sub> and N<sub>2</sub> moved deeply into the formation and dissolved with the residual oil. The dissolved gas pushed the oil out during this period, which attributed most to the total oil recovery.

(3) Late production period: After the dissolving gas driving period, the formation was lacking of energy again with pressure and liquid level declines. The daily production rates of water, oil, and liquid dropped to the similar rates of natural exploitation. The water cut also dropped to less than 60% at July 18, 2017, which represented the end of the production period.

After 288 days of production, the CO<sub>2</sub>/N<sub>2</sub> mixture recovered 337 t of heavy oil from the test well. This successful pilot test shows a potential application of CO<sub>2</sub>/N<sub>2</sub> mixture injection. For a depleted heavy oil reservoir, CO<sub>2</sub>/N<sub>2</sub> mixture can be considered as an optional gas media for enhanced oil recovery. With a suitable injecting CO<sub>2</sub>/N<sub>2</sub> ratio and a proper injection mode, the mixture can dramatically enhance the formation pressure, and then interact with heavy oil for the oil extraction.

## Conclusions

A feasibility study of CO<sub>2</sub>/N<sub>2</sub> mixture is evaluated to enhance the heavy oil recovery in a depleted reservoir. CO<sub>2</sub>-oil interactions, N<sub>2</sub>-oil interactions, and CO<sub>2</sub>-N<sub>2</sub>-oil interactions are firstly compared using PVT analysis. Then, several experiments of cyclic gas injections using different gas media are conducted in the laboratory. Some conclusions can be summarized as follows.

(1). The oil saturation pressure, volume factor, and viscosity are highly related to CO<sub>2</sub>/N<sub>2</sub> ratio of the gas mixture. CO<sub>2</sub>-N<sub>2</sub>-oil interactions are usually between CO<sub>2</sub>-oil

interactions and N<sub>2</sub>-oil interactions, and a higher CO<sub>2</sub>/N<sub>2</sub> ratio can always lead to better capacities of dissolution, oil swelling, and viscosity reduction.

- (2). Pure CO<sub>2</sub> can achieve the best oil recovery of 19.03% due to the strong interactions between CO<sub>2</sub> and oil. While the mixture with a CO<sub>2</sub>/N<sub>2</sub> volume ratio of 2:1 can achieve an oil recovery of 17.31%, which is near the oil recovery of pure CO<sub>2</sub> injection. The remarkable oil recovery achieved by 2:1 mixture is due to the gas/oil interactions dominated by CO<sub>2</sub> coupled with energy supplement provided by N<sub>2</sub>.
- (3). For a depleted heavy oil reservoir, simultaneous CO<sub>2</sub>/N<sub>2</sub> injection and N<sub>2</sub> followed by CO<sub>2</sub> injection are suitable modes for the mixture. The formation pressure can be rapidly enhanced with N<sub>2</sub> pre-injected or injected simultaneously, and then a fully CO<sub>2</sub>/oil interactions can be ensured for a better oil extraction.
- (4). A pilot test of CO<sub>2</sub>/N<sub>2</sub> mixture injection is successfully conducted in a test well, and an oil increment of 337 t is obtained after 40,000 m<sup>3</sup> of N<sub>2</sub> injection followed by 80,000 m<sup>3</sup> of CO<sub>2</sub> injection. The pilot result shows a potential EOR application of CO<sub>2</sub>/N<sub>2</sub> mixture in the depleted heavy oil reservoir.

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