Effect of Injection Pressure on CO2 Huff-n-Puff in Low-Permeability Sandstone Cores Using Nuclear Magnetic Resonance

Deyu Wang1, Yingjun Ju1, Songlin Feng1, Shidong Chen1, Wen Wei1, Jingyang Ma1, Tong Zhang1 and Jinsheng Zhao2*
1No.6 Oil Production Plant, Changqing Oilfield, Xi’an, China
2School of Petroleum Engineering, Xi’an Shiyou University, Xi’an, China

*Corresponding author email: jszhao@xsyu.edu.cn

Abstract. In order to figure out the micro-scale recovery degree of different pore sizes, the T2 spectrum of low-permeability sandstone cores before and after CO2 huff-n-puff is obtained using NMR technique. The results show that the micro-scale recovery degree increases with increase of pore sizes. Oil in macropores and medium pores is more easily produced, and Oil in micropores is difficult to recover at 7-12MPa. The total recovery degree of three cores increases with the increase of injection pressure. This study is expected to be significant for understanding the mechanisms of CO2 huff-n-puff for enhancing oil recovery in low-permeability sandstone reservoirs.

Keywords: CO2 huff-n-puff; Low-permeability sandstone; NMR technique; Pore size; Micro-scale recovery degree.

1. Introduction
In order to reduce CO2 emissions which can lead to the intensification of the greenhouse effect, the research on the capture, storage and utilization of CO2 has become a hot topic (Li et al. 2019). Because of the low natural energy, the development of low-permeability reservoirs usually relies on water injection or gas injection to replenish formation energy for a desired production (Alhuraishawy et al. 2018). CO2 injection can improves oil recovery through oil swelling, hydrocarbon extraction, viscosity reduction and relative permeability effects (Koorosh and Farshid, 2007), and it is an efficient method for enhancing oil recovery from low-permeability oil reservoirs. The methods of CO2 injection for enhanced oil recovery include CO2 flooding (CO2 miscible flooding, CO2 near-miscible flooding, and CO2 immiscible flooding), CO2 huff-n-puff, and CO2-water alternate injection (Li et al. 2019). In the above methods, since CO2 huff-n-puff is applicable in single well, it is also recognized as relatively low initial capital outlay and rapid payout (Haines and Monger, 1990). Low-permeability sandstone reservoirs typically contain a wide pore throat sizes ranging from the nano-scale to micro-scale (Lai et al. 2018), and have complex pore geometry and pore throat structure, which affects oil displacement efficiency during CO2 huff-n-puff. Above 7.38 MPa and 35°C, CO2 exhibits supercritical state, and in this state, CO2 has high density, high diffusivity and low viscosity (Zhao et al. 2019), which make CO2 enter the smaller pore and drive out the oil during CO2 huff-n-puff. Thereby, investigation of the residual oil variations in different size pores is beneficial for understanding the fundamental mechanisms of CO2 huff-n-puff for enhancing oil recovery in low-permeability sandstone reservoirs. Nuclear magnetic resonance (NMR) is used to detect the hydrogen-containing fluid distribution in porous media. Based on the mechanisms of NMR technique, the distribution of transverse relaxation time of hydrogen nucleus...
of fluid in pores can be represented by the measured $T_2$ spectrum (Zhao et al. 2018). The corresponding transverse relaxation time correlates the pore size, thereby NMR technique can be used in the oil industry to determine the pore size distribution (Lai et al. 2016). Several researchers have studied the performance of CO$_2$ huff-n-puff in micro-pore scale using NMR technique (Wei et al. 2019; Bai et al. 2019). Wei et al (2019) monitored the oil concentration in the matrix and fracture using a low-field nuclear-magnetic-resonance (NMR) technique. They found that the crude oil is mainly produced from the macropores and the remaining oil in the cores is mainly distributed in the small and medium pores. For CO$_2$ huff-n-puff in low-permeability sandstone reservoirs, although some studies have been carried to investigate the oil production performance of CO$_2$ huff-n-puff in micro-pore scale, the micro-scale recovery degree and remaining oil distribution in different pore sizes, i.e., micropores, small pores, medium pores, and macropores has not been systematic studied, which, however, is fundamental for understanding the mechanisms of CO$_2$ huff-n-puff for enhancing oil recovery in low-permeability sandstone reservoir.

In this work, the oil production performance of CO$_2$ huff-n-puff at different injection pressure is investigated by the NMR technique. Based on the measured $T_2$ spectrum before and after huff-n-puff, the recovery degree and remaining oil distribution in different pores size, i.e., micropores, small pores, medium pores, and macropores, are discussed. This study can help to understand the fundamental mechanisms of enhancing oil recovery through CO$_2$ huff-n-puff in low-permeability sandstone oil reservoirs.

2. Experiment Section

2.1. Materials

In this study, three sandstone core samples are from Houbei oilfield in Chang 6 reservoir of China, and the parameters of core samples is summarized in Table 1. The oil is made up of kerosene and dehydrated crude oil at a volume ratio of 3:1, with a viscosity of 2.16 mPa·s and density of 0.8 g/cm$^3$ at 323.15 K. Water used for saturating cores is Mncl$_2$ solution with a mass concentration of 25000mg/l, which can eliminate hydrogen signals in the water. CO$_2$ used in this experiment has a purity of 99.99 mol% (Xi’an Guodu Gas Supply Station, China).

Table 1. Core samples parameters and operation parameters of CO$_2$ huff and puff.

| Core No. | Length (cm) | Radius (cm) | Permeability (mD) | Pore (%) | Injection pressure (MPa) | Injection volume (PV) | Soaking time (h) | Cycle numer |
|----------|-------------|-------------|-------------------|----------|-------------------------|----------------------|-----------------|-------------|
| 1        | 3.84        | 2.50        | 3.17              | 11.03    | 7.0                     | 0.3                  | 10              | 1           |
| 2        | 4.02        | 2.50        | 3.38              | 10.89    | 9.0                     | 0.3                  | 10              | 1           |
| 3        | 4.17        | 2.50        | 3.51              | 11.15    | 12.0                    | 0.3                  | 10              | 1           |

2.2. Experimental Setups

The schematic of CO$_2$ huff-n-puff setup is shown in Figure 1. NMR apparatus (Mini-MR, Niumag, China) is used to obtain the $T_2$ spectrum of the low-permeability sandstone cores. The confinement pressure and back pressure are maintained by a syringe pump (Hai’an Co., Ltd., China) and a back-pressure valve (Hai’an Co., Ltd., China). The system temperature is controlled by a thermostat. A core-saturation equipment (Hongbo Co., Ltd., China) is used to saturate distilled water into core samples.
2.3. Experimental Procedures

In this experiment, CO\textsubscript{2} is first injected into the oil-saturated core samples for huff-puff experiment. NMR technique is then used to investigate the remaining oil distribution of core samples by comparing the measured $T_2$ spectrum before and after CO\textsubscript{2} huff-n-puff. The detailed experimental procedures are described as follows:

Before the experiment, we use benzene to clean the core samples for removing the oil. The cleaned core samples are then dried at 373.15K for 24 hours to remove the moisture. A permeability meter is then employed to measure the permeability of the core samples. Core samples are then vacuumed to saturate with the aqueous solution of MnCl\textsubscript{2} using a core-saturation equipment. The core samples saturated with water are weighed and then put into the core holder for oil displacing water experiment until the core outlet was 100% oil. NMR apparatus is then used to scan the core samples saturated with oil to obtain the $T_2$ spectrum. The measured $T_2$ spectrum is analysed to estimate the original oil distribution in different pore sizes of core samples.

Next, CO\textsubscript{2} huff-n-puff experiment is conducted. First, the outlet of the core holder is closed, and then CO\textsubscript{2} is injected into the core samples at the injection rate of 0.1ml/min until the injection volume reach the volume presented in Table 1.

After that, the inlet of the core holder is closed, and the core is aged for soaking time which presented in Table 1. The inlet of the core holder is opened, and the oil is produced at a certain pressure fall gradient. The temperature is kept a constant of 50°C during the experiment.

After CO\textsubscript{2} huff-n-puff experiment, the core samples are scanned to obtain the $T_2$ spectrum, which is used to determine the remaining oil distribution of core samples after CO\textsubscript{2} huff-n-puff. On the basis of the $T_2$ spectrum before and after CO\textsubscript{2} huff-n-puff, the recovery degree of different pore sizes can be calculated according to the following formula.

$$R = \frac{S_0 - S}{S_0} \times 100\%$$

Where $R$ is recovery degree after CO\textsubscript{2} huff-n-puff; $S_o$ is the area surrounded by $T_2$ spectrum of core saturated with oil and X-axis; $S_o$ is the area surrounded by $T_2$ spectrum after CO\textsubscript{2} huff-n-puff and X-axis. Finally, by analyzing the $T_2$ spectrum before and after CO\textsubscript{2} huff-n-puff, micro-scale recovery degree in different pore sizes is discussed.

3. Results and Discussion

Figures 2-4 present the $T_2$ spectrum distribution of core sample 1#, 2# and 3# before and after CO\textsubscript{2} huff-n-puff with the injection pressure of 7MPa, 9MPa and 12MPa. From eq 4, we know that the distribution of $T_2$ spectrum represents the distribution of pore size. Based on the $T_2$ spectrum distribution, the pores of core samples can be divided into four grades, i.e., micropores (<1ms), small pores (1-10 ms), medium pores (10-100 ms) and macropores (>100ms). We calculated the recovery degree of CO\textsubscript{2} huff-n-puff in different pores size according to eq 1, which are summarized in Table 2.
Table 2. The CO2 huff and puff efficiency of different pores size at different injection pressure.

| Core No. | Experimental conditions | T2 distribution | Micropores | Small pores | Medium pores | Macropores | All pores |
|----------|-------------------------|----------------|------------|-------------|--------------|------------|----------|
|          |                         |                | 0.1-1ms    | 1-10ms      | 10-100ms     | 100-1000ms |          |
| 1        | Initial Oil Saturation  | 87.16          | 425.41     | 218.09      | 77.35        | 808.01     |          |
|          | After CO2 huff and puff(7MPa) | 82.63       | 269.78     | 34.64       | 2.02         | 389.07     |          |
|          | Recovery Efficiency(%)  | 5.20           | 36.58      | 84.12       | 97.39        | 51.85      |          |
|          | Initial Oil Saturation  | 45.29          | 313.67     | 252.06      | 202.04       | 813.06     |          |
| 2        | After CO2 huff and puff(9MPa) | 47.69       | 186.61     | 88.11       | 0            | 322.41     |          |
|          | Recovery Efficiency(%)  | -5.30          | 40.51      | 65.04       | 100.00       | 60.35      |          |
|          | Initial Oil Saturation  | 43.02          | 279.61     | 226.55      | 214.11       | 763.29     |          |
| 3        | After CO2 huff and puff(12MPa) | 49.24       | 161.85     | 47.01       | 0            | 258.1      |          |
|          | Recovery Efficiency(%)  | -14.46         | 42.12      | 79.25       | 100.00       | 66.19      |          |

It can be seen from Figure 2-4, the T2 spectrum of three core samples after CO2 huff-n-puff decreases significantly compared with the T2 spectrum of initial oil saturation. With the increase of injection pressure, the decrease range of T2 spectrum after CO2 huff-n-puff increase, which indicate that the injection pressure was a major factor affecting the effect of CO2 huff-n-puff. The micro-scale recovery degree increases with the increase of pore size. Oil in macropores and medium pores is more easily produced, and for the three cores sample, the total recovery degree of macropores and medium pores reach 87.6%, 80.6% and 89.33%, respectively, which can be calculated from Table 2. As for the macropores, the recovery degree is 97.39% with the injection pressure of 7MPa, and when the injection pressure is 9MPa and 12 MPa, the recovery degrees in macropores reach 100%. For the medium pores, the recovery degree at the injection pressure of 7MPa is 84.12% which is higher than that of the injection pressure of 9MPa (65.04%) and 12MPa (79.25%). The reason may be that the pore-throat connectivity in medium pores of the core sample #1 is better than that of core sample #2 and #3. The recovery degree of the small pores increases with the increase of injection pressure, and when the pressure is 7MPa, 9MPa and 12MPa, the corresponding recovery degree of the small pores is 36.58%, 40.51% and 42.12%, respectively. Exceptionally, as for the three cores sample, the recovery degree of the micropores is very low, indicating that the oil in the micropores is difficult to recover at such three injection pressures. Moreover, in the interval of micropores, the T2 spectrum after CO2 huff-n-puff is higher than that before CO2 huff-n-puff in Figure 3 and Figure 4, which resulting in a negative recovery degree at the injection pressure of 9MPa and 12MPa (See Table.2). It may be because that the dissolution reaction between the supercritical CO2 and rock minerals, which increases the number of the pores, additionally, the secondary migration of crude oil leads to the increase of the oil in the micropores. In general, after CO2 huff-n-puff, with the increase of injection pressure, the total recovery degree of the three cores sample increased, 51.85%, 60.35% and 66.19%, respectively.
Figure 2. Measured T2 spectrum distribution of core sample 1# before and after CO2 huff and puff with the injection pressure of 7MPa.

Figure 3. Measured T2 spectrum distribution of core sample 2# before and after CO2 huff and puff with the injection pressure of 9MPa.

Figure 4. Measured T2 spectrum distribution of core sample 3# before and after CO2 huff and puff with the injection pressure of 12MPa.

4. Conclusions
In this work, the CO2 huff-n-puff effect at different injection pressure in low-permeability sandstone core samples is investigated using NMR technique. Based on the measured T2 spectrum before and after CO2 huff-n-puff, the micro-scale recovery degree in different pore sizes, i.e., micropores, small pores, medium pores, and macropores, are discussed. The detailed conclusions are summarized as follows:
By comparing the $T_2$ spectrum before and after CO$_2$ huff-n-puff one cycle, the micro-scale recovery degrees increase with the increase of pore sizes. Oil in macropores and medium pores is more easily produced. Oil in micropores is difficult to recover at the three injection pressures 7MPa, 9MPa and 12MPa.

(2) With the increase of injection pressure, the recovery degree of small pores increases, resulting in the total recovery degree of the three cores sample after CO$_2$ huff-n-puff one cycle increase, 51.85%, 60.35% and 66.19%, respectively.

(3) Due to the dissolution reaction between the supercritical CO$_2$ and rock minerals, which increases the number of the pores, additionally, the secondary migration of crude oil leads to the increase of the oil in the micropores. Thereby, the recovery degree of micropores decreases with the increase of injection pressure.

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References
[1] Alhuraishawy, A., B. Bai, M. Wei, J. Geng, and J. Pu. Mineral dissolution and fine migration effect on oil recovery factor by low-salinity water flooding in low-permeability sandstone reservoir. *Fuel*, No. 220: 898-907(2018).
[2] Bai, H., Q. Zhang, Z. Li, B. Li, D. Zhu, L. Zhang, and G. Lv. Effect of fracture on production characteristics and oil distribution during CO$_2$ huff-n-puff under low-permeability and low-permeability conditions. *Fuel*, No.246: 117-125(2019).
[3] Haines, H. K., and T. G. Monger. A Laboratory Study of Natural Gas Huff ‘N’ Puff. In CIM/SPE International Technical Meeting, Calgary, AL, June 10-13(2019).
[4] Koorosh, A., and T. Farshid. Laboratory Experimental Results of Huff-and-Puff CO$_2$ Flooding in a Fractured Core System. In SPE Annual Technical Conference and Exhibition, Anaheim, CA, November 11-14(2007).
[5] Li, B., H. Bai, A. Li, L. Zhang, and Q. Zhang. Experimental investigation on influencing factors of CO$_2$ huff-n-puff under fractured low-permeability conditions. *Energy Science & Engineering* No.7:1621 - 1631 (2019).
[6] Lai, J., G. Wang, Z. Wang, J. Chen, X. Pang, S. Wang, Z. Zhou, Z. He, Z. Qin, and X. Fan. A review on pore structure characterization in low-permeability sandstones. *Earth-Science Reviews*. No.177: 436–457(2018).
[7] Lai, J., G. Wang, Z. Fan, J. Chen, S. Wang, Z. Zhou, and X. Fan. Insight into the pore structure of low-permeability sandstones using NMR and HPMI measurements. *Energy & fuels*. No.30: 10200–10214(2016).
[8] Wei, B., K. Gao, T. Song, X. Zhang, W. Pu, X. Xu, and C. Wood. Nuclear-Magnetic-Resonance Monitoring of Mass Exchange in a Low-Permeability Matrix/Fracture Model During CO$_2$ Cyclic Injection: A Mechanistic Study. *SPE Journal*. https://doi.org/10.2118/199345-PA(2019).
[9] Xiao L., J. Li and Z. Mao. A method to determine nuclear magnetic resonance (NMR) $T_2$ cut off based on normal distribution simulation in low-permeability sandstone reservoirs. *Fuel*. No.225: 472-482(2018).
[10] Zhao J., X. An, and S. Qiao. The extraction effect of CO$_2$ injection on the flow properties of crude oil. *Petroleum Science and Technology*. 37, No.6:710-717(2019).
[11] Yao, Y., Liu, D. Comparison of low-field NMR and mercury intrusion porosimetry in characterizing pore size distribution of coals. *Fuel*. No.95, 152-158(2012).
[12] Cai, Y., Liu, D., Pan, Z. Petrophysical characterization of Chinese coal cores with heat treatment by nuclear magnetic resonance. *Fuel*. No.108, 292-302(2013).