

Research on the CO₂ Displacement and Sequestration Laws in Low Permeability Reservoir

Zhang Zhichao^{1,2}, Bai Mingxing^{1,2*}, Du Siyu^{1,2}

1 Northeast Petroleum University, Daqing, Heilongjiang 163318, China; 2 Key Laboratory of Ministry of Education for Enhanced Oil Recovery, Northeast Petroleum University, Daqing, Heilongjiang 163318, China (*Bai Mingxing: 1209712605@qq.com)

ABSTRACT

In the past, the attention of CO₂ flooding is merely paid to the CO₂ Enhanced Oil Recovery (CO₂-EOR) of low permeability reservoirs. However, facing the worldwide warming impact caused by excessive CO₂ emissions, improving the gas sequestration efficiency in a reservoir within the process of CO₂ displacement is becoming the research hotspot. In this work, we investigated the oil production characteristics and gas sequestration law in the pores of reservoirs by conducting several CO₂-induced experiments. The nuclear magnetic resonance (NMR) test is used to monitor the seepage law of oil and gas in the pores of core samples during CO₂ flooding. The underlying mechanisms of improving oil recovery and CO₂ storage efficiency in different water-cut reservoirs are also investigated through Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), and wettability angle analyses. The experiment results show that the CO₂ flooding and gas storage efficiency are mainly related to the factors of water-cut f_w of reservoirs, CO₂ flooding pressure, and the geophysical properties changes induced by the CO₂-brine-oil-rock reaction. Compared with the amount of oil extraction in the oil-saturated rock samples by CO₂ injection, much more formation oil can be produced, and laying more amount of CO₂ to be stored under the reservoir with $f_w=50\%$ by immiscible CO₂ flooding with the mechanism of gas breakthrough prevention. The oil yield and CO₂ storage efficiency in reservoirs can also be effectively enhanced by rising the CO₂ flooding pressure and prolonging the contact time of CO₂ with the formation brine and rocks. Compared with the reaction results of CO₂-brine-oil-rock that occurred in the reservoir with only bound water, the reaction that occurred in the reservoirs with $f_w=50\%$ is more intense, leading to more minerals dissolution, thus increasing the larger pore volume (PV) of rocks and making the rock surface more hydrophilic. Otherwise, the hydrophilic wettability modification of rocks can

improve the CO₂ displacement and gas storage effect within the reservoir due to the capillary resistance reduction in the process of CO₂ flooding oil. The experimental evidence additionally indicates that CO₂ flooding applied within the reservoir after a stage of water flooding is more suitable to boost the oil displacement and gas sequestration effect.

Keywords: CO₂ flooding and gas sequestration, oil recovery, gas sequestration efficiency, water-cut

NONMENCLATURE

Abbreviations

E_s	CO ₂ dissolution sequestration coefficient
S_{or}	Reminding oil saturation
R_o	Solubility of CO ₂ in oil, kg/kg
S_{wr}	Reminding saltwater saturation
R_w	Solubility of CO ₂ in saltwater, kg/kg
θ_{rough}	Wetting angle
θ_{smooth}	Wetting angle on an ideal surface
γ	Roughness ratio

1. INTRODUCTION

In recent years, the increasing CO₂ emissions and oil resources shortage has seriously constrained the sustainable economic development of all countries. However, CO₂ injection into oil reservoirs, either miscible or immiscible flooding, especially for the low permeability reservoirs with huge reserves is considered a promising approach to improve oil recovery and alleviate the poor effect of excessive greenhouse gas emissions. The improved oil recovery effect of reservoirs by CO₂ displacement was first proposed by Wharton et al.^[1], as early as 1950. By 2014, over 150 projects of CO₂-EOR had been carried out worldwide, and the application of this technology resulted in a cumulative daily oil increment of 292,735 barrels^[2]. Wei et al.^[3] studied the mechanism of CO₂ improving the oil recovery of low

permeability reservoirs by displacement experiments and believed that the essence of enhanced oil recovery by CO₂ injection is due to the nature of good solubility ability and lower Minimum Miscibility Pressure (MMP) of CO₂ with crude oil phase, which can significantly reduce crude oil viscosity, interfacial surface tension (IFT), and swelling crude oil. In previous studies, more attention to CO₂ displacement was put to its effect on improving oil recovery, and little concern was paid to the gas sequestration efficiency of CO₂ in reservoirs. However, due to the intensification of environmental pollution caused by excessive CO₂ emissions, nowadays, the international community began to put more attention to the sequestration effect during the CO₂ flooding process in reservoirs. Based on the dual goals of improving reservoir recovery and enhancing gas storage efficiency, a certain scale of CO₂ displacement and storage projects have also been constructed internationally. According to the research report of the Global Carbon Capture and Storage Institute (GCCSI), CO₂ capture, oil displacement, and sequestration are important ways to reduce carbon emissions. Presently, twenty-eight large-scale carbon emission reduction projects are running in the world, with an annual CO₂ storage capacity of approximately 38.2 million tons, of which twenty-two are the CO₂ oil displacement and storage projects, with an annual CO₂ storage capacity of 29.3 million tons^[4-5]. In 2021, seventy-one new CCUS demonstration projects were established for CO₂ resource utilization globally, most of which were aimed at injecting CO₂ into oil reservoirs for EOR and gas storage, and a target of CO₂ capture capacity of 150 million tons/a will reach after all projects were completed and put into operation. The International Energy Agency (IEA) has also evaluated the application prospects of CCUS technology and believed that by 2040, CCUS technology will contribute more than 9% in the scenario of controlling global temperature rise within 2 °C, and contribute 15% to the global goal of achieving zero net CO₂ emissions by 2070^[7]. Therefore, it is crucial to study the law of improving oil recovery and gas storage efficiency by CO₂ flooding in the low permeability reservoirs with huge reserves to ensure the safe and effective operation of the CCUS project.

The international community has also begun to pay more attention to the joint research of CCS-EOR by injecting CO₂ into oil reservoirs and achieving a win-win situation of CO₂ emission reduction and improving oil recovery^[8-9]. The earliest known project to use CO₂ for reservoir displacement and gas storage is the fault oilfield Weyburn in Canada. Due to the reduction of the formation pressure, the oil production of the oilfield

decreased from 45000 bbls/d in 1964 to 15000 bbls/d in 1980. To improve the oil recovery of the reservoir, the CO₂-EOR project has been carried out since 2000 with a CO₂ injection amount of 5000 tons/d. After the immiscible CO₂ flooding application in the oilfield, the oil production rate increased to 25000 bbls/d and maintained a long-term stable production effect^[10-11]. And by 2017, the oilfield had an accumulated CO₂ injection amount of 27 million tons^[10]. In addition, Klusman et al.^[12] also applied numerical simulation to evaluate the CO₂ flooding and sequestration project in a pilot experimental area in Rangey, Colorado, USA. They found that during the 20 years of CO₂ injection into the reservoir, most of the injected CO₂ was already dissolved in the remaining fluids of the reservoir without any risk of gas leakage. In China, with the proposal of the "dual carbon" goal, Chinese scholars have also conducted certain technical research on CO₂-EOR and gas sequestration technique, and have formed an industrial chain technology system integrating carbon capture, transportation, utilization, and sequestration. In 2020, China National Petroleum Corporation (CNPC) established several national-level pilot zones for the integration of CO₂ storage and oil displacement in four different types of oil reservoirs, including the low permeability of Daqing reservoirs, ultra-low permeability of Jilin reservoirs, ultra-low permeability of Changqing reservoirs, and conglomerate of Xinjiang reservoirs. A total of 4.5 million tons of CO₂ accounts for 75% of the cumulative CO₂ injection volume of CCS-EOR projects in oil fields nationwide has been injected into the four oil reservoirs, and has led to a 30% of oil recovery increase^[6]. In 2022, Sinopec Shengli Oilfield company also completed China's first million-ton level of CO₂ flooding and storage CCS-EOR demonstration project.

The improved CCS-EOR project refers to the process of optimization of CO₂-EOR and CO₂ Enhanced Sequestration efficiency (CO₂-ESE) in a reservoir. By optimizing the technical parameters of CO₂ flooding, the oil recovery is improved while also maximizing the CO₂-ESE effect simultaneously, thereby achieving dual benefits of economic and environmental profits^[13]. According to the law of mass conservation during CO₂ flooding in reservoirs, assuming that the pressure and temperature of the reservoir remain unchanged and no CO₂ leakage during the CO₂ flooding, the greater the oil recovery of the reservoir flooded by CO₂, and the more oil and water are exchanged by the injected CO₂, resulting more CO₂ is stored under the reservoir. After oil displacement, the CO₂ retained in the reservoir pores will dissolve in the remaining fluids, forming dissolution

sequestration. During the long-term storage process after the CCS-EOR project, CO₂ is stored underground permanently by the mechanism of mineral sequestration induced by the CO₂-water-rock reaction. However, due to the density and viscosity differences between CO₂ and oil, the injected CO₂ will undergo gas breakthrough, gravity overlap, and other bad effects, which affect the oil recovery and gas storage effect in the reservoir^[14-15]. Li et al.^[16] conducted experimental research on the CO₂ displacement and sequestration patterns and found that the CO₂ water alternative gas (CO₂-WAG) scheme had the highest EOR effect but the lower gas sequestration coefficient SF_c for low-permeability cores than that of cyclic gas injection pattern. Wang et al.^[17] applied numerical simulation methods to assess the oil recovery and CO₂ storage efficiency of CO₂-WAG and continuous gas flooding in complex fault-block reservoirs of Jinnan, China. They found that the effect of CCS-EOR is much better by CO₂-WAG injection than that of continuous gas injection scenarios. The CO₂-WAG method can increase the oil recovery by more than 15% and can achieve an amount of 30.88% PV CO₂ underground storage. Assef et al.^[18] evaluated the effectiveness of CO₂ cyclic gas flooding in the Middle Bakken shale oil reservoir in the United States through numerical simulation. They believe that the mechanism for achieving the better effect of CCS-EOR is that the flow direction changes of CO₂ flooding in the process of the cyclic gas injection, thereby causing the hysteresis effect of the phase permeability of CO₂, which can prevent gas breakthrough earlier and get higher CO₂ adsorption saturation S_{cr} under formation. Gao et al.^[19-21] proposed an integrated factor f to characterize the optimization relationship between CO₂-EOR and CO₂-ESE in oil reservoirs. They believed that in the early stage of CO₂ flooding in oil reservoirs, a larger weight factor should be assigned to the oil displacement term and more attention should mainly be paid to the CO₂-EOR effect. After the gas breakthrough of CO₂ in the production well, a larger weight factor should be assigned to the CO₂ storage term, and the injection rate of CO₂ should be reduced to alleviate the impact of the gas breakthrough and improve the CO₂ storage effect. Yao et al.^[22] applied numerical simulation methods to study the effect of oil displacement and storage efficiency of CO₂ miscible flooding. They found that CO₂ miscible flooding can get better EOR and ESE effect than immiscible flooding. When miscible flooding was applied in the low permeability reservoirs, the oil recovery could reach 29.2%, and the CO₂ storage coefficient could reach 7.76. Hu et al.^[23] believe that the main theme to be mastered

during CO₂ flooding and storage is to maintain reservoir pressure and promote miscible flooding, and to develop efficient CO₂ plugging agents to prevent the gas breakthrough. In addition, when CO₂ is used for oil displacement in a reservoir, the CO₂-brine-oil-rock interaction will change the rock properties and also have an impact on CO₂-EOR and CO₂-ESE. Cui et al.^[24] found that CO₂ injection into the reservoir cores can improve the permeability of low-permeability reservoir rocks through experiments of CO₂-brine and sandstone core reaction of Xinjiang oil fields, thereby improving the oil displacement efficiency. Zhang et al.^[25] has determined the dissolved minerals in the reservoir induced by the CO₂-brine-rock reaction are mainly calcite and feldspar and the precipitated minerals are the more hydrophilic kaolinite, which not only improves the permeability of the reservoir but also reduces the capillary resistance of CO₂ flooding oil. Song et al.^[26] and Gamadi et al.^[27] also confirmed that the CO₂-brine-oil-rock interaction can change the surface wettability of rocks through indoor experiments, leading to a more hydrophilic rock surface. Through the 1.5-year CO₂-brine-sandstone reaction experiment, Rathnaweera et al.^[28] evaluated the long-term impact of the reaction on the core geophysical properties and found that the long-term CO₂ storage not only makes the calcite dissolution but also makes quartz and kaolinite dissolution, increasing core permeability by more than 10%. Arsyad et al.^[29] also found that the permeability of the Ainula Berea sandstone reservoir significantly increased during CO₂ storage.

Although current scholars have conducted some research on CO₂ displacement and storage techniques in low permeability reservoirs, the current research base is not yet sufficient for ensuring the mechanism and law of CO₂-EOR and CO₂-ESE during the CO₂ flooding process. Effective theoretical research on the impact law of CO₂-brine-oil-rock interaction occurred in different water-cut reservoirs during CO₂ displacement and sequestration is also lacking. Therefore, this paper takes the CYG low-permeability oil field in the Songliao Basin of China (with a reservoir depth of 1390m, reservoir pressure 14.3MPa, an average permeability of 25 mD, and porosity of 15%) as the research object^[30] to conduct research of CO₂ flooding and sequestration laws and determine the theory methods of improving the efficiency of CO₂-EOR and CO₂-ESE in low-permeability reservoirs.

2. THE EXPERIMENT DESIGN

2.1 The experimental materials and equipment

Experimental 2# and 3# core and the corresponding rock slices shown in Fig.1, Fig.2 are taken from well X6-

16 in the CYG oilfield, the geophysical parameters are listed in Table 1. Before the CO₂ flooding experiment, the core samples were repeatedly rinsed with acetone to remove the oil. The cleaned cores were then placed in an oven and heated to 100 °C for 24 hours of drying, after that, the cores were weighed separately. The brine of CaCl₂ type with a total salinity of 8515mg/L was taken from the target formation; The purity of CO₂ gas is 99.99%; The oil used in the experiment comes from the produced oil of well X6-16. Under surface conditions, the density of crude oil is 0.89 g/cm³, and the viscosity is 6.8 cP. The fluoride solution with 1600ml is also used as the annular pressure boosting fluids in the flooding experiment for the online nuclear magnetic resonance (NMR) test.

An NMR scanner(MesoMR12-060H-I, Jiangsu, China) with a magnetic field strength of 0.5T was used in the online CO₂ flooding experiment. The mineral compositions and morphology of the reservoir rocks have been identified with a scanning electron microscope (SEM) and X-ray diffraction meter(XRD) (S360, Cambridg company, UK; STOE company, Germany); The displacement backpressure is controlled through the manual pump (HDS-50, Jiangsu, China); The weight of rock and other experimental materials was weighed by a precision balance (AU120, Japan); Gas pressurization was supported by the CO₂ displacement system(TES-92, Jiangsu, China); The wettability of the reservoir rock was tested separately through wetting angle tester (SZ100-JC2000C, Beijing, China); The density and viscosity of formation oil and water were measured by the density – viscosity meter (DMA 4200 M, Anton Paar, USA); In the online NMR testing, a heat shrink tubing was used to enclose a reservoir rock to separate the fluoride solution and fluids inside and outside the core (Jiangsu, China). The non-magnetic core holder (Jiangsu China); The confining pressure outside the experimental rock sample was established by the control system of confining pressure (TDSH-1, Jiangsu, China); And the rock sample was saturated with oil and water with the saturation device (TDS-80, Jiangsu, China).

Table 1 The physical parameters of core samples

Sample	Diameter/ cm	Length/c m	Permeability/ mD	Porosity/ %
2#	2.5	10	65.38	22.8
3#	2.5	7	35.09	22.6



Fig.1 The low permeability sandstone core sample

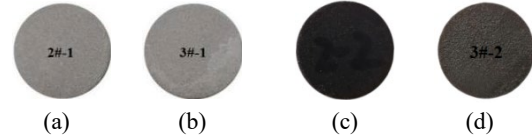


Fig.2 The core slices for CO₂-brine-oil-rock reaction experiment(a,b,Dried core slices;c, Oil-saturated core slice;d, Core slice with water-cut $f_w=50\%$)

2.2 Experimental Process

2.2.1 The oil displacement experiment of CO₂

The water-cut of the reservoir can affect CO₂ oil displacement and gas storage effect. Therefore, CO₂ flooding experiments were conducted on cores with different water-cut rock samples(oil-saturated and water-cut $f_w=50\%$), the experimental process mainly includes the steps: ① Rinse the 2# and 3# cores with distilled water, and then dry them at 100 °C for 24 h. ② Saturate the two cores with a 7% mass fraction of manganese chloride water and formation oil in sequence. When oil is produced regularly from the outlet face of the core, the oil-saturated process ends; ③ Seal the rock core sample with a heat shrink tube and place it in the non-magnetic core holder. Heat the core to the temperature of 70 °C, and select the CPMG sequence to test the T2 spectrum and images of the core as the basic comparative data. ④ Conduct CO₂ displacement experiments on two rock cores with a flooding pressure of 15MPa. During the displacement process, the nuclear magnetic resonance T2 spectra and images were tested every 10 minutes, and the amount of oil and water expelled from the cores were also recorded by the test tube at the end flooding until 120 minutes of CO₂ displacement time. ⑤ By comparing the T2 spectra and images at different CO₂ flooding times, the oil production and gas sequestration characteristics in reservoir pores were analyzed. ⑥ After repeating the oil washing and drying operations on the tested core, saturate the manganese water and oil in sequence, and continue the manganese water(7% mass fraction) displacement until the water-cut f_w of the produced liquid reaches 50%. ⑦ Afterwards, CO₂ displacement experiments were conducted and T2 spectra and images were tested every 10 minutes to record the oil pore development

characteristics and CO₂ storage effect of cores with $f_w=50\%$.

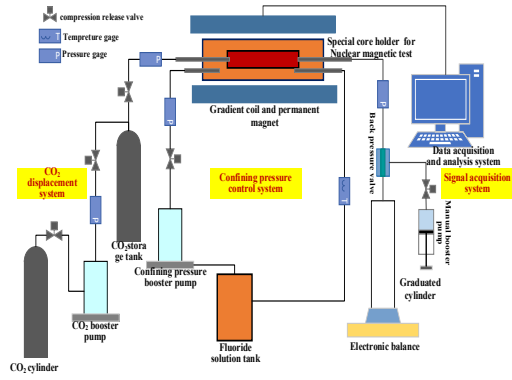


Fig. 3 The NMR online scanning equipment of CO₂ flooding
2.2.2 The CO₂ dissolution experiment

After CO₂ is injected into the pores of the formation to displace formation fluids, it will occupy the pore space of the displaced fluids and form displacement (structure+adsorption) sequestration. In addition, the retained CO₂ in pore spaces also dissolves in the remaining oil and water, forming the dissolution sequestration of CO₂. Therefore, to analyze the dissolution sequestration law of CO₂ in reminding formation fluids under different reservoir temperatures and pressure conditions, the solubility experiment is conducted and the experimental process is shown in Fig.4, which includes the following steps: ① Weigh the mass of 60ml of formation fluids(oil/water) with an electronic balance, then pour fluid into the HT-HP PVT test cylinder, and tighten the top cover of the cylinder with a wrench. ② Adjust the temperature of the HT-HP cylinder to the experimental temperature of (30 °C, 50 °C, 70 °C, 90 °C, 100 °C, 110 °C). After the temperature in the cylinder stabilizes, CO₂ is injected into it through the boosting system to achieve the experimental pressure (3MPa, 5MPa, 7MPa, 10MPa, 15MPa, 20MPa, 25MPa, 30MPa). Afterward, turn on the magnetic stirrer to stir the fluid inside the cylinder, allowing CO₂ to quickly dissolve and balance with the formation fluid inside the cylinder. ④ Close the gas inlet and outlet valves of the cylinder. After the pressure inside the cylinder stabilizes for 30 minutes, open the drainage valve at the bottom of the cylinder to discharge the liquid at a low speed. At the same time, pressurize the cylinder by adjusting the pump speed of the manual pump to keep the pressure stabilized, preventing the dissolved gas from separating from the liquid phase. ⑤ The gas-liquid mixed phase is discharged into the separator for gas-liquid separation and metering, and the solubility of CO₂ in oil or water under different

formation temperatures and pressure conditions is obtained by the results.

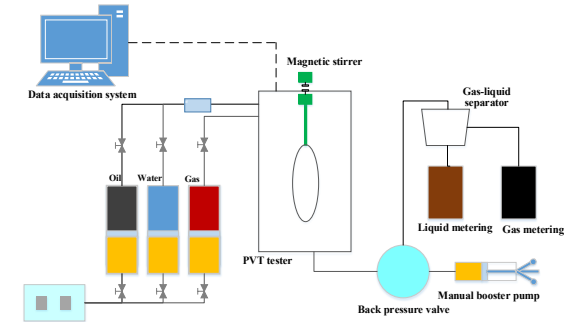


Fig.4 The experimental process for determining the solubility of CO₂ in formation fluids

2.2.3 The CO₂-brine-oil-rock reaction experiment

After CO₂ is injected into the different water-cut reservoirs, it will induce different degrees of CO₂-brine-oil-rock reaction, which can bring out different changes in the wettability, porosity, and permeability of the reservoir rock, thus changing the oil production characteristics and gas storage effect in pores by CO₂ flooding. Therefore, the CO₂-brine-oil-rock interaction experiment was carried out to clarify the reaction mechanism and law on the effect of CO₂ oil displacement and sequestration. The experimental scenarios are listed in Table 2, and the reaction device is shown in Fig.5, and the experiment steps are as follows: ① Wash the 2# and 3# cores after the CO₂ flooding experiment with organic solvent toluene repeatedly for 24 hours, and then rinse all cores with deionized water repeatedly. Place the washed cores in an oven, and heat them at 100 °C for 24 hours. ② Cut two sections of 0.5cm thin core slices from both ends of the dried experimental core and name as 2#-1, 2#-2, and 3#-1, 3#-2, respectively. ③ Afterward, the wetting angles of 2#-1 and 3#-1 slices were measured, and the mineral morphology and type of the core slices were determined by SEM. ④ After crushing half of the samples from core slices 2#-2 and 3#-2 to the powder of 200 mesh, the XRD analysis was conducted to determine the various mineral contents in the slices before the reaction of CO₂-brine-oil-rock. ⑤ Inject 600ml of formation water into the high temperature and high pressure (HT-HP) cylinder reactor, put the oil-saturated 2# and the water-cut $f_w=50\%$ 3# cores with and their slices into the cylinder reactor and seal the top cap of it. ⑤ After heating the reactor to 90 °C, CO₂ from the gas cylinder is pressurized to 15MPa to inject into the reactor through an injection system for the reaction of CO₂-brine-oil-rock for 16 days. ⑥ Rinse the experimental cores and all slices after the reaction and use toluene to remove the absorbed oil. Then, rinse the

surface of the rock samples repeatedly with deionized water, and finally dry them in an oven at 100°C for 24 hours. ⑦ Analyze the mineral morphology, compositions, and wetting angle of drying core slices 2#-1 and 3#-1 after the reaction by SEM-EDS, XRD, and wetting angle tester. ⑧ The core of 2# after the reaction was saturated with oil and the oil-saturated rock 3# was flooded by manganese water until the $f_w=50\%$ again. ⑨ The CO₂ flooding experiments with cores after reaction were conducted repeatedly with the same temperature and pressure of 70 °C and 15MPa, respectively for 120 minutes. ⑩ The NMR T2 spectra and images of the flooded cores were also measured every 10 minutes to record the law of fluids extraction in different pore radii of rock samples and a comparison of the T2 spectra and images with that in chapters 1.2.1 was conducted to analyze the influence mechanism of the CO₂-brine-oil-rock interaction on the oil displacement characteristics and CO₂ sequestration laws in different water-cut reservoirs.

Table 1 The physical parameters of core samples

Experimental scenario	Flooding pressure/MPa	Experimental temperature/°C	Reaction Time/d
Oil-saturated rock 2#	15	90	16
Rock 3# with $f_w=50\%$	15	90	16

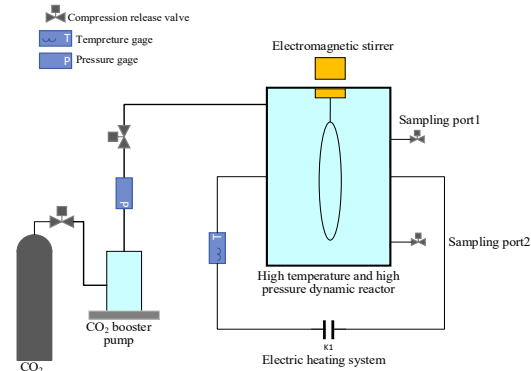


Fig.5 The HT-HP reactor system for CO₂-brine-oil-rock reaction

3. RESULTS

3.1 The oil extraction characteristics of CO₂ flooding

At the reservoir temperature and pressure (T=70 °C, P=15MPa) condition, the CO₂ displacement characteristics of 2# and 3# core with water-cut $f_w=50\%$ are shown in Figs 6-7. We found the formation oil is mainly produced from the pores with the radius over 0.05 μm and 0.06 μm in the two rock samples by the CO₂ immiscible displacement. However, the lower pore production limit of formation oil for the oil-saturated 2#

and 3# cores is 0.04 μm and 0.02 μm with CO₂ immiscible displacement respectively, as shown in Figs 8-9, indicating with the water-cut f_w of reservoir decreases, the immiscible CO₂ can extract the formation oil from the lower radius pore and stored in the smaller rock pores.

After 120 minutes of CO₂ immiscible displacement, the liquid recovery (LR) of core 2# with $f_w=50\%$ is 62.2% and the oil recovery (OR) is 53%. For the 3# core with $f_w=50\%$, the LR and the OR after CO₂ displacement is 65.8% and 57%, respectively. For the oil-saturated 2# core, after 120 minutes of CO₂ displacement, the LR and OR are the same is 51.2%, and that for the 3# core is 52.8%.

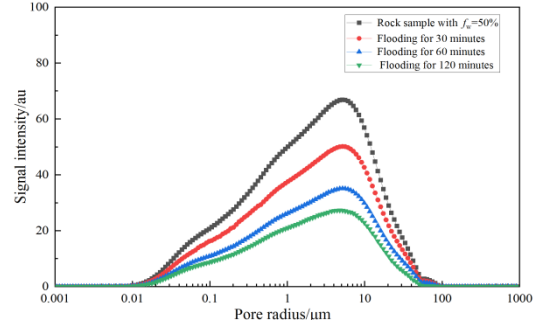


Fig.6 The oil production characteristics in pores of 2# reservoir core with water-cut $f_w=50\%$ by CO₂ flooding

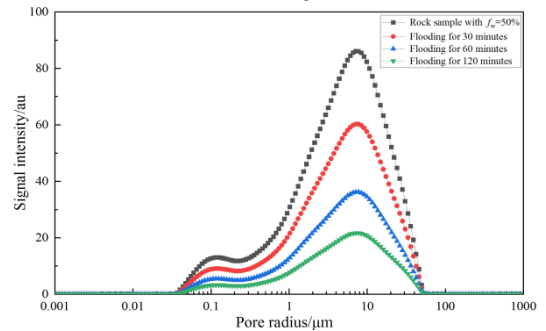


Fig.7 The oil production characteristics in pores of 3# reservoir core with water-cut $f_w=50\%$ by CO₂ flooding

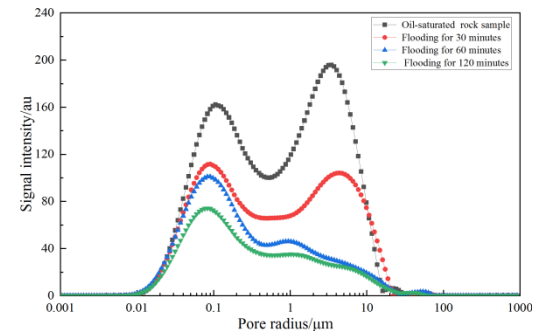


Fig.8 The oil production characteristics in pores of oil-saturated 2# core by CO₂ flooding

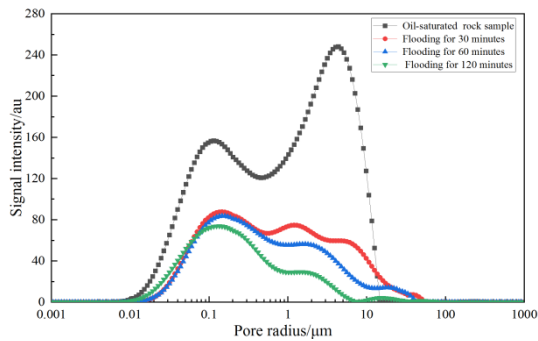


Fig.9 The oil production characteristics in pores of oil-saturated 3# core by CO₂ flooding

3.2 The oil extraction laws of different reservoirs

The NMR images of the 2# and 3# core samples saturated with oil, and water flooding until with water-cut $f_w=50\%$ were tested at different times of immiscible CO₂ flooding. Analyzed in Fig.10, the oil and water in the two experimental cores are gradually extracted and therefore the brightness of the NMR images shows gradually darkens. After a continuous displaced time of 120 minutes, the brightness of the image of the tested reservoir cores with $f_w=50\%$ is significantly lower than that of the image of the oil-saturated core samples, indicating that the oil extraction effect of the core samples with a degree of water-cut by CO₂ immiscible displacement is better compared with flooding the oil-saturated rock samples. The different CO₂ displacement effects may be owing to that the oil-saturated cores can bear additional viscous fingering during CO₂ immiscible flooding, resulting in a lower oil recovery compared to the partly saturated oil cores.

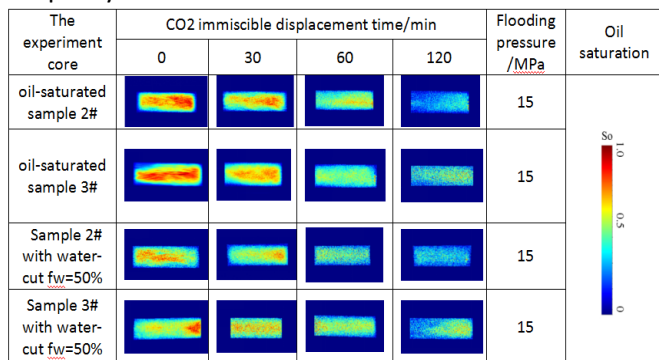


Fig.10 The NMR image of the displaced cores at different stage of CO₂ flooding

3.3 The CO₂ dissolution sequestration laws in the reminding fluids

In the stage of short-term CO₂ injection into the reservoir, the CO₂ sequestration mechanism mainly includes displacement (structure+adsorption) and dissolution sequestration with a low amount of mineral sequestration due to a slow reaction rate for CO₂-brine-

oil-rock. The effect of displacement sequestration can be characterized by CO₂-EOR according to the law of material conservation, expressed by the phenomenon of the higher the oil displacement recovery by CO₂ injection, the more the amount of CO₂ is stored under a reservoir. Otherwise, the dissolution sequestration ability of CO₂ is related to the amount and type of residual fluids in reservoirs after CO₂ flooding. Based on the test results of CO₂ solubility in the formation of saline water and oil under different reservoir temperatures and pressures, as shown in Figs 11-12, we can see that the solubility of CO₂ in the formation of oil and saltwater will increase with the pressure rise and temperature decrease. But before the contact pressure of the two phases is less than 7MPa, the solubility rate of CO₂ in saltwater rapidly increases with the pressure rising. However, the growth rate of CO₂ solubility slows down when the pressure is over 7MPa with the reason that the solubility of CO₂ in saline water is close to saturation after this critical pressure. However, the solubility of CO₂ in the formation oil phase still increases after 7MPa, chiefly due to the rise in pressure, which accelerates the CO₂ extraction effect to light-weight hydrocarbons in the oil phase, strengthens the mass transfer between CO₂ and oil, leading to a quicker increase rate of the solubility of CO₂ in the formation oil.

Take the 2# core of respective oil-saturated and water-cut $f_w=50\%$ after the CO₂ displacement experiment in Section 2.1 as an example to research the dissolution sequestration laws, the remaining oil saturation for the oil-saturated rock after CO₂ flooding $S_{or}=0.488$; and the remaining oil saturation $S_{or}=0.288$, the remaining water saturation $S_{wr}=0.09$ for the core with a water-cut of $f_w=50\%$ after CO₂ flooding. According to the CO₂ dissolution sequestration coefficient E_s in the remaining fluids proposed by us as Formula (1), the variation law of CO₂ dissolution within the reminding formation fluids can be obtained as shown in Figs 13-14. The E_s of CO₂ in the remaining fluid is the highest after CO₂ displaces the completely saturated oil core, followed by the partly saturated oil core ($f_w=50\%$). Otherwise, considering the oil recovery of various styles of reservoirs after CO₂ flooding, the partly saturated oil rock samples($f_w=50\%$) after CO₂ flooding have the highest oil recovery. Therefore, CO₂ flooding ought to be carried out at the reservoir after an explicit stage of water flooding, which may simultaneously improve the dual effects of CO₂-EOR and CO₂-ESE.

$$E_s = S_{or}R_o + S_{wr}R_w \quad (1)$$

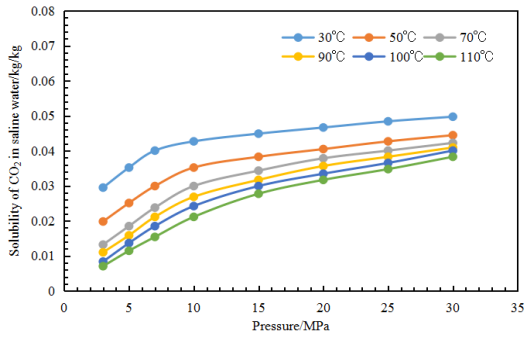


Fig.11 The solubility of CO₂ in saline water kg/kg

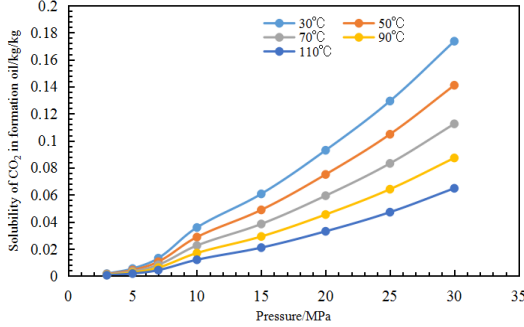


Fig.12 The solubility of CO₂ in formation oil kg/kg

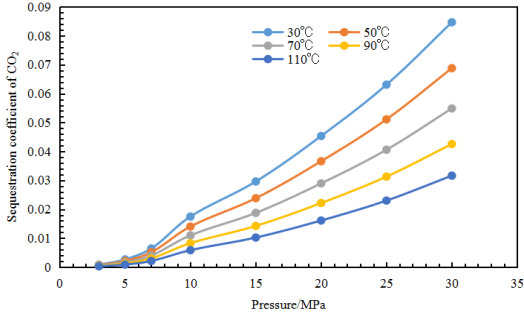


Fig.13 The dissolution sequestration coefficient of CO₂ (oil-saturated core sample 2#, the $S_{or}=0.488$)

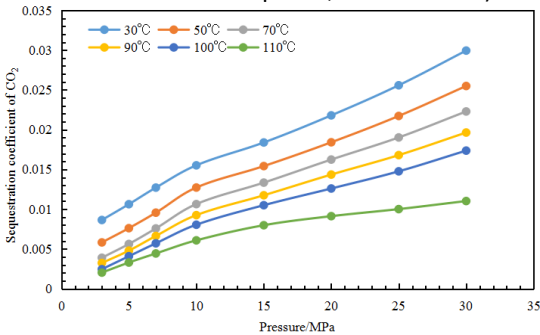


Fig.14 The dissolution sequestration coefficient of CO₂ in residual fluids (core sample 2#, $f_w=50\%$, $S_{or}=0.288$, $S_{wr}=0.09$)

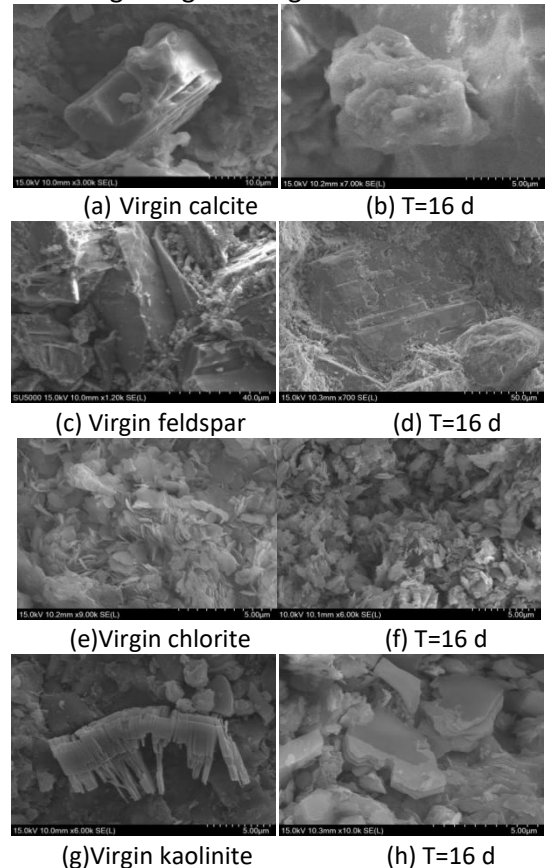
3.4 The physical properties change law of CO₂ induced reaction

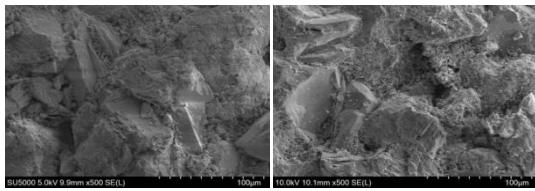
3.4.1 The changes of mineral morphology

From the SEM results of the rock surface of the oil-saturated 2# slice containing only bound water before and after the CO₂-brine-oil-rock reaction, as shown in Fig.15 (a-j). The dissolution of calcite and feldspar minerals on the rock surface has occurred but is not

obvious, and there are horizontally layered secondary minerals of like book-page kaolinite crystal formation. The ratio rate of pore/surface area increases from 7% to 10%, and the pore size of the rock sample increases from 0.3 μm ~130 μm to 0.7 μm ~135.0 μm , indicating that the dissolved minerals caused by the CO₂-water-oil rock reaction are mainly calcite and feldspar, and feldspar dissolution will lead to its kaolinization. In addition, a small amount of clay minerals of chlorite in the rock sample has also undergone dissolution after the reaction.

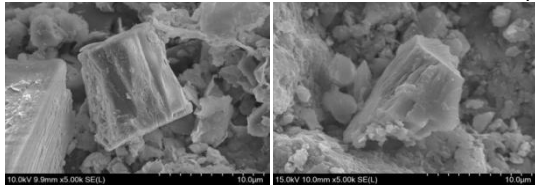
The SEM test results of the mineral morphology changes before and after the CO₂-brine-oil-rock reaction from the 3# core slice with water-cut $f_w=50\%$ are shown in Fig.16 (k-t). We found that a larger corrosion pit of calcite crystal is formed on the rock surface after the reaction, and the feldspar mineral also has formed a zigzag irregular dissolution boundary. Otherwise, a larger ratio of pore/surface area of the rock sample 3# has been found, which increases from 8% to 15%, and the pore size changes from 0.3 μm ~67 μm to 0.3 μm ~174 μm . The dissolution degree of feldspar and calcite is higher than that of oil-saturated 2# core, which indicates that the increase of water-cut in the reservoir will increase the degree of CO₂-water-oil-rock reaction, increase the pore volume and pore connectivity, thus improving the effect of CO₂ flooding and gas storage.



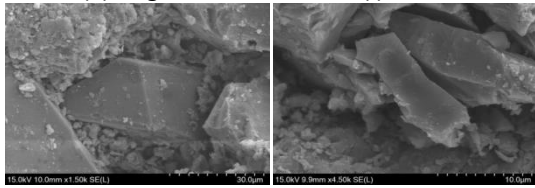


(i) Virgin pore (j) T=16 d

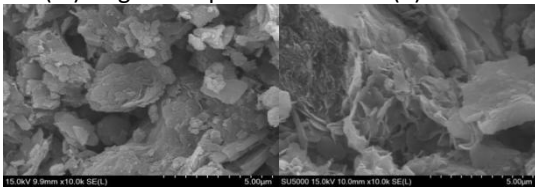
Fig.15 The morphology and of minerals before and after CO₂-brine-oil-rock reaction for the oil-saturated rock sample 2#



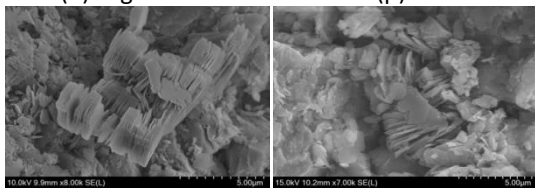
(k) Virgin calcite (l) T=16 d



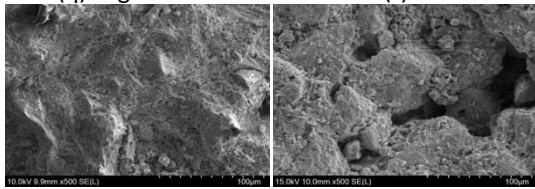
(m) Virgin feldspar (n) T=16 d



(o) Virgin chlorite (p) T=16 d



(q) Virgin kaolinite (r) T=16 d



(s) Virgin pore (t) T=16 d

Fig.16 The morphology and pore of minerals before and after CO₂-brine-oil-rock reaction for the rock sample 2# with water-cut $f_w=50\%$

3.4.2 The mineral composition changes induced by CO₂ flooding

The mineral composition modification of the core samples 2# and 3# with the XRD test before and after the CO₂-brine-oil-rock reactions show is shown in Figs 17-18. The dissolved minerals caused by reactions of CO₂ with oil-saturated cores 2# and rock 3# with water-cut $f_w=50\%$ are all mainly calcite and feldspar, and the precipitated minerals are mainly kaolinite and quartz. Compared to the CO₂-induced reaction that occurred within oil-

saturated reservoir rock 2#, the modification amount of reaction minerals is more significantly proceeded within the formation rock 3#. The diffraction peak heights of calcite and feldspar tested by XRD were minimized by 2.5% and 1.2% respectively, the peak heights of chlorite content decreased to a certain extent, and the peak heights of kaolinite and quartz inflated by 0.9% and 1.3% severally for the oil-saturated core 2# after reaction, which is consistent with the conclusions of the corrosion pit of calcite and zigzag corrosion boundary of feldspar observed by the results of SEM analysis. The mineral amount change in the rock samples 2#, 3# before and after the CO₂-induced reaction can be characterized with Formulas (2) - (7), the content increase of kaolinite and quartz mainly comes from the dissolution of feldspar and chlorite minerals, in addition, a certain quantity of ankerite is additionally formed within the precipitated minerals. However, the content of calcite in core 3# with water-cut $f_w=50\%$ decreased by 4.8%, feldspar content decreased by 2.5%, chlorite mineral content also decreased to a certain extent, quartz content increased by 2.4%, and kaolinite content increased by 1.5% before and after the reaction. Analyzing the results of mineral reactions, we found that with the reduction of water-cut f_w of the reservoir, the reaction degree between CO₂, formation water, and rocks decreases, which also leads to a decreasing tendency in the improvement of the reservoir physical properties such as the porosity, permeability, and wettability.

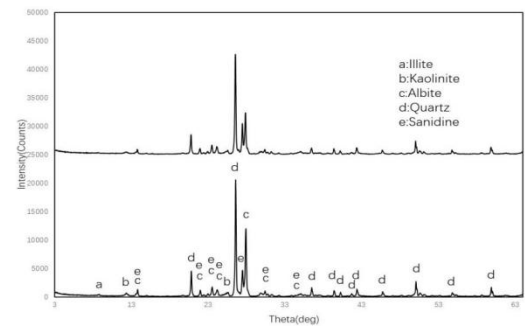
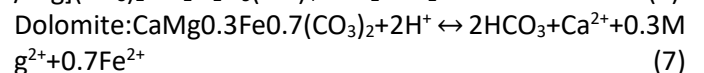
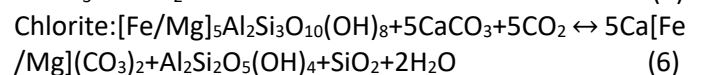
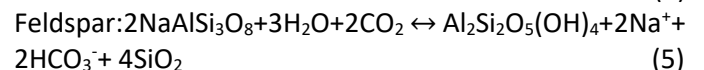
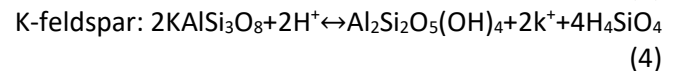
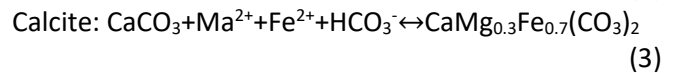
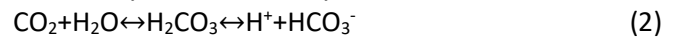


Fig.17 The XRD spectrum of mineral composition of 2 # core sample before and after reaction

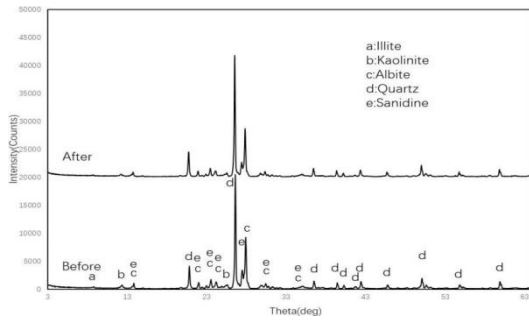


Fig.18 The XRD spectrum of mineral composition of 3# core sample before and after reaction

3.4.3 The effect of CO₂ injection on the wettability of reservoir rock

After sixteen days of HT-HP reactor reaction with CO₂, saltwater, and different water-cut of reservoir rock samples, the oil-saturated 2# core slice and the 3# core slice with water-cut $f_w=50\%$ were washed and dried in a high-temperature oven with 100 °C for 24 hours, and also the wetting angles of these slices were compared as shown in Figs 19 (a-d). We found that after the CO₂-brine-oil-rock reactions, the wetting angles of the 2# and 3# core sections decreased from 125.3 ° to 116.7° and 123.7° to 69°, respectively. The decreased degree of wetting angles of the 3# slice was bigger than that of the 2# slice. Therefore, we judge the reaction degree of CO₂-brine-oil-rock reaction in part water-cut reservoir is higher than that in a fully oil-saturated reservoir, which also leads to a stronger hydrophilicity transformation for the reservoir with a degree of water-cut. However, according to the capillary resistance theory, the rise of the hydrophilicity of rocks is beneficial to the oil displacement, which conjointly cut back the adhesion work of oil drops on the reservoir rock pore surface, thus improving the oil displacement and sequestration effect of CO₂. For the mechanism of improving the wettability of reservoir rocks by CO₂ injection, Iglauer et al.^[31] and Wenzel et al.^[32] planned the link between roughness and wettability of rock surface, as shown in Formula (8). They believe that the CO₂-water-rock reaction can increase the roughness of the rock surface, whereas the rise of roughness for the rock surface can cut back the wetting angle and increase the water wettability of the rock. Through SEM and XRD test experiments, Zhang et al.^[25] also found CO₂-water-rock reaction, on the one hand, magnified the roughness of the rock surface, and more hydrophilic minerals such as kaolinite and quartz were generated on the rock surface after the reaction, which led to the improvement of the hydrophilicity of rock slices.

$$\cos\theta_{rough} = \gamma \cos\theta_{smooth} \quad (8)$$

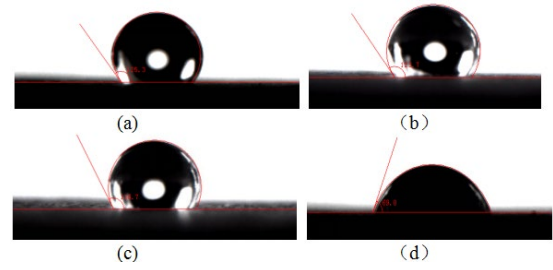


Fig.19 The changes in the wettability of rock before and after CO₂-induced reactions(a, b, wetting angle of 2# and 3# dry core slice; c, wetting angle of the washed oil-saturated 2# slice; d, wetting angle of the washed 3# slice with water-cut $f_w=50\%$)

4. DISCUSSION

4.1 The oil production characteristics in pores of different reservoirs

The oil extraction characteristics of the oil-saturated 2# core sample with different CO₂ flooding pressure as is shown in Fig.20, the lower oil development limit of pores drops from 0.08 μm at 10 MPa to 0.04 μm at 15 MPa, which results in the extraction degree of oil and the storage effect of CO₂ changing better. When 2# core sample with water-cut $f_w=50\%$ is flooded with CO₂, shown in Fig.21, the rise of CO₂ injection pressure also led to a lower production limit of the pore radius of formation oil from 0.07 μm under the pressure of 10MPa drops to 0.05 μm at 15 MPa. Compared with the pore production limit of oil in different water-cut reservoirs by CO₂ flooding, the amount of oil extraction in smaller pores increases with the rise of CO₂ flooding pressure, but the increased amplitude of oil extraction in fully oil-saturated rock samples is higher. According to the NMR images of rock samples tested during the process of CO₂ flooding as shown in Fig.22, the effect of CO₂ flooding on the reservoir core with water-cut $f_w=50\%$ is better than that of CO₂ flooding the fully oil-saturated core. The reason for the lower oil extraction limit of pores with flooding pressure increase can be explained by Li et al (2021) [16] and Li et al (2016) [33] through the IFT analysis between the CO₂-saltwater and the CO₂-oil phases. They believed that as the displacement pressure increases, the diffusion rate of CO₂ molecules towards oil and water accelerates, resulting in quicker dynamic equilibrium and more CO₂ dissolution into the oil and water phases, which decreases the IFT between CO₂-oil and CO₂-saline water. However, the decreased degree of IFT between the CO₂ and oil phase is greater than that between the CO₂ and water phase, resulting in lower capillary resistance for the oil-saturated reservoir with CO₂ flooding. However, the poor gas breakthrough effect is more serious than the IFT improvement effect caused

by CO₂ flooding.

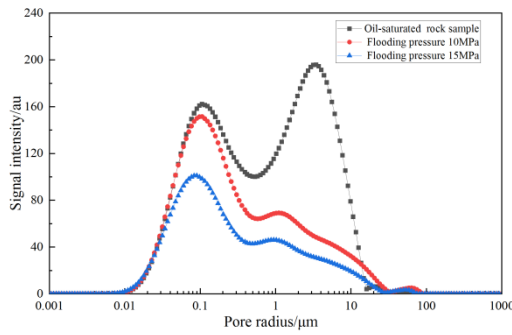


Fig.20 The pore development of oil-saturated 2# core by CO₂ flooding(T=120min)

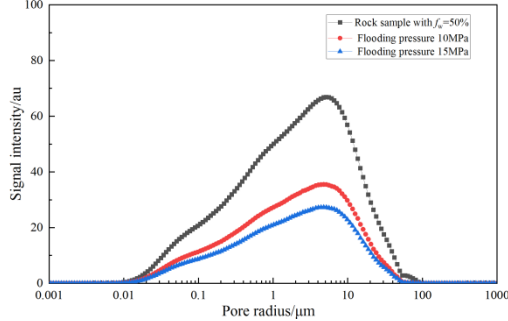


Fig.21 The pore development characteristics of 2# core with $f_w=50\%$ by CO₂ flooding(T=120min)

The experiment core	CO ₂ flooding pressure/MPa			Flooding time/min	Oil saturation S_o
	0	10	15		
Oil-saturated sample 2#				120	
Sample 2# with $f_w=50\%$					

Fig.22 The comparison of NMR images of CO₂ displacement effects on different types of reservoirs

4.2 The CO₂-induced improvement effect of oil displacement and sequestration

The oil extraction characteristics from the pores of the oil-saturated 2# rock sample before and after the CO₂-induced reaction in the HT-HP reactor are shown in Fig.23. We found that the peak area of the NMR spectra curve from core 2# testing increases and the amplitude of oil extraction spectra curve reduces as a whole, which indicates that the CO₂-brine-oil-rock reaction during the extraction of the reservoir with a partial water-cut can increase the pore volume of formation rock, also thus improve the seepage ability of fluids, and eventually result in a better and CO₂ flooding and sequestration efficiency. From the results of SEM, XRD, and wetting angle tests, we found the essential mechanism of enhanced oil extraction and gas sequestration effect was the dissolution of the minerals within the reservoir rock,

which increased pore volume and connectivity of the reservoir pore. The reaction also improves the rock sample surface more hydrophilic, which reduces the capillary resistance of CO₂ flooding formation oil. In short, CO₂ injected into reservoirs for a period can improve the displacement efficiency of oil and increase the amount of underground sequestration of CO₂.

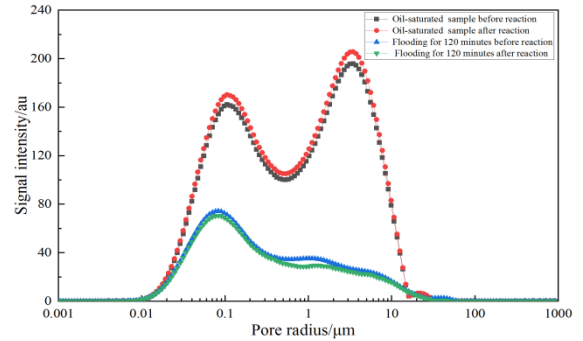


Fig.23 The changes in pore development characteristics of the oil-saturated core 2# before and after CO₂-brine-oil-rock reaction (P=15MPa, T=120min)

4.3 The CO₂ displacement and sequestration efficiency of different reservoirs

Combination of the changes of the peak area of the NMR spectrum curves and oil and water yield measured within the test tube during CO₂ flooding, the CO₂ displacement and sequestration efficiency in various water-cut reservoirs was obtained, as shown in Fig.24. We find that the CO₂-EOR and CO₂-ESE efficiency in the completely oil-saturated reservoir cores after CO₂ flooding is the lower than that in the rock sample with water-cut $f_w=50\%$. The production effect variations of oil in different core samples can be analyzed by the pore development characteristics during CO₂ flooding, as shown in Figs 6 and 8. When CO₂ is used to flood oil in part water-cut reservoir, the effective oil extraction time is longer with CO₂ flooding because of the gas breakthrough prevention effect with a lower viscosity ratio μ_w/μ_{CO_2} . However, in the process of CO₂ flooding with the oil-saturated reservoir, the gas breakthrough impact is serious because of the higher viscosity ratio μ_o/μ_{CO_2} , thus the displacement efficiency and gas sequestration efficiency of CO₂ in the part water-cut reservoir are higher, which indicates the most suitable reservoir site for improving CO₂ flooding and sequestration efficiency should be the reservoir after a certain period of water flooding.

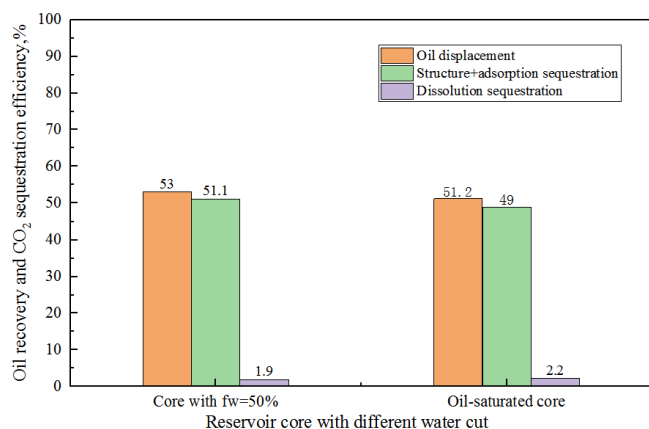


Fig.24 The oil recovery and CO₂ sequestration efficiency with CO₂ flooding in different formations (Rock sample 2#, P=15MPa, T=120min)

5. CONCLUSIONS

(1) For the 2# core with saturated oil, water-cut f_w up to 50%, respectively, the oil development lower limit in pores of the rock sample by CO₂ immiscible displacement is 0.04 μm and 0.05 μm , with oil recovery 51.2% and 53%, respectively. For the 3# core with saturated oil, water-cut f_w up to 50%, the development lower limit of oil in pores with CO₂ displacement is 0.02 μm , and 0.06 μm , respectively and the oil recovery of the rock sample is 52.8% and 57%, respectively. We find that the development lower limit of oil in the pores of rock samples decreases with the reduction of water-cut of the reservoir in the process of CO₂ immiscible flooding. However, considering the more serious gas breakthrough that occurred in the oil-saturated rock sample, the reservoir rock with a degree of water-cut is more suitable for the application of CO₂ oil displacement and sequestration.

(2) The reaction of CO₂-brine-oil-rock can induce the mineral's dissolution and precipitation during the process of CO₂ flooding, therefore improving the pore volume, permeability, and wettability of the rock surface. From the peak area of the NMR curves of the oil-saturated and a degree of water-cut cores, we find an overall increase of the fluid signal amplitude in pores of the saturated cores after the CO₂-induced reaction, which indicates the dissolution of the minerals induced by CO₂ injection leads to an increase of the pore volume of the reservoir, but the increment of PV of the cores with a degree of water-cut is higher than that in the oil-saturated reservoir. Otherwise, the oil extraction amplitudes of all cores are all enhanced after the CO₂-brine-oil-rock reactions, which indicates that CO₂ injection into the formation with a degree of water-cut can enhance the CO₂-EOR and CO₂-ESE efficiency.

(3) During the short-term period of CO₂ injection into the oil reservoir, the quantity of mineral sequestration caused by the CO₂-brine-oil-rock reaction is little. The main CO₂ sequestration mechanism in this stage is displacement (structure and adsorption) and dissolution. In the comparison of CO₂ storage amount with the displacement and dissolution sequestration in different formations, the amount of CO₂ displacement sequestration occupies exceeding 40% of the reservoir pore volume, but the dissolution quantity of CO₂ sequestration is lower than 2% of the reservoir PV. Moreover, the CO₂-EOR and CO₂-ESE of CO₂ flooding in oil-saturated reservoirs are poor compared to that in the reservoir with a degree of water-cut. Therefore, CO₂ immiscible flooding may be appropriately utilized in a reservoir after a degree of initial water flooding stage for enhancing the CO₂-EOR and CO₂-ESE efficiency. And the effect of CO₂ flooding and sequestration will also improve with the rise of CO₂ flooding pressure and CO₂-brine-oil-rock contact time prolonging.

ACKNOWLEDGEMENT

This work was financially supported by the National Natural Science Foundation of China (grant no.: 51774095) and Heilongjiang Postdoctoral Fund (grant no.: LBH-Q20010). Furthermore the authors would like to thank all members of the research team.

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

REFERENCE

- [1] Whorton LP, Eugene RB, Alvin BD. Method for producing oil by means of carbon dioxide. U.S. Patent No. 2,623,596. 30 Dec. 1952.
- [2] Koottungal L. 2014 worldwide EOR survey. Oil & Gas Journal 2014; 112(4):79-91.
- [3] Wei Bing, Gao H, Pu WF, et al. Interactions and phase behaviors between oleic phase and CO₂ from swelling to miscibility in CO₂-based enhanced oil recovery (EOR) process: A comprehensive visualization study. J Mol Liq 2017; 232: 277-284.
- [4] GCCSI. Global status of CCS 2021 [R]. Melbourne: Global CCS Institute, 2021.
- [5] GCCSI. Global status of CCS 2020 [R]. Melbourne: Global CCS Institute, 2020.

- [6] Song XM, Wang F, Ma DS, et al. Progress and prospect of carbon dioxide capture, utilization and storage in CNPC oilfields. *Petrol Explor Dev* 2023; 50(1):206-218.
- [7] IEA. Energy technology perspectives 2020: Special report on carbon capture, utilization and storage [R]. Paris: 2020.
- [8] British Petroleum Company. BP statistical review of world energy[R]. London: BP Company, 2018.
- [9] Izgec O, Demiral B, Bertin HJ, et al. Experimental and numerical modeling of direct injection of CO₂ into carbonate formations. In: the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA, September 2006.
- [10] Brown K, Whittaker S, Wilson M, et al. The history and development of the IEA GHG Weyburn-Midale CO₂ Monitoring and Storage Project in Saskatchewan, Canada (the world largest CO₂ for EOR and CCS program). *Petroleum* 2017; 3: 3-9.
- [11] Preston C, Monea M, Jazrawi W, et al. IEA GHG Weyburn CO₂ monitoring and storage project. *Fuel Process Technol* 2005; 86(14–15):1547–68.
- [12] Klusman RW. A geochemical perspective and assessment of leakage potential for a mature carbon dioxide-enhanced oil recovery project and as a prototype for carbon dioxide sequestration; Rangely field, Colorado. *AAPG Bulletin*, 2003; 87 (9):1485-1507.
- [13] He LP, Shen PP, Liao XW, et al. Potential evaluation of CO₂ EOR and sequestration in Yanchang oilfield. *J Energy Inst* 2016; 89(2): 215-221.
- [14] Zhao FL, Hao HD, Hou JR, et al. CO₂ mobility control and sweep efficiency improvement using starch gel or ethylenediamine in ultra-low permeability oil layers with different types of heterogeneity. *J Petrol Sci Eng* 2015; 133: 52-65.
- [15] Zhang Y, Gao MW, You Q, et al. Smart mobility control agent for enhanced oil recovery during CO₂ flooding in ultra-low permeability reservoirs. *Fuel* 2019; 241:442-450.
- [16] Li DC, Saraji S, Jiao ZS, et al. CO₂ injection strategies for enhanced oil recovery and geological sequestration in a tight reservoir: An experimental study. *Fuel* 2021;284:119013.
- [17] Wang H, Ji BY, Zhao SX, et al. Feasibility study on the CO₂ flooding and storage in the complex fault-block tight oil reservoir. *Journal of Shaanxi University of Science & Technology* 2022; 40(3):115-122.
- [18] Assef Y, Apostolos K, Almao PP. Numerical modelling of cyclic CO₂ injection in unconventional tight oil resources; trivial effects of heterogeneity and hysteresis in Bakken formation. *Fuel* 2019; 236:1512-1528.
- [19] Gao R, Lv CY, Lun ZM. Integrated evaluation method of CO₂ flooding and storage. *Thermal Power Generation* 2021; 50(1): 115-122.
- [20] Gao R, Lv CY, Lun ZM, et al. Integrated Numerical Simulation of Carbon Dioxide Displacement and Sequestration. *Special Oil & Gas Reservoirs* 2021; 28(2):102-107.
- [21] Gao R, Lv CY, Zhou K, et al. A CO₂ flooding dynamic storage potential calculation method based on compositional flash calculation. *Oil Drilling & Production Technology* 2021;43(1):70-75.
- [22] Yao YD, Li XF. A Study on CO₂ flooding effectiveness and its geologic storage. *Xinjiang Petroleum Geology* 2009; 30(4):493-495.
- [23] Hu YL, Hao MQ, Chen GL, et al. Technologies and practice of CO₂ flooding and sequestration in China. *Petrol Explor Dev* 2019;46(4):716-727.
- [24] Cui GD, Yang LH, Fang JC, et al. Geochemical reactions and their influence on petrophysical properties of ultra-low permeability oil reservoirs during water and CO₂ flooding. *J Petrol Sci Eng* 2021(203): 108672.
- [25] Zhang X, Wei B, Shang J, et al. Alterations of geochemical properties of a tight sandstone reservoir caused by supercritical CO₂-brine-rock interactions in CO₂-EOR and geosequestration. *J CO₂ Util* 2018; (28) : 408-418.
- [26] Song CY, Yang DY. Performance evaluation of CO₂ huff-npuff processes in tight oil formations. In: the SPE Unconventional Resources Conference Canada, Calgary, Alberta, Canada, November 2013.
- [27] Gamadi TD, Sheng JJ, Soliman MY, et al. An experimental study of cyclic CO₂ injection to improve shale oil recovery. In: the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA, April 2014.
- [28] Rathnaweera TD, Ranjith PG, Perera MSA. Experimental investigation of geochemical and mineralogical effects of CO₂ sequestration on flow characteristics of reservoir rock in deep saline aquifers. *SCI Rep-UK* 2016;6:19362.
- [29] Arsyad A, Mitani Y, Babadagli T. Comparative assessment of potential ground uplift induced by injection of CO₂ into Ainoura, and Berea sandstone formations. *Earth Planet. Sci* 2013; 6:278–286.
- [30] Yin DY, Xiang JH, Wang DQ. Classification of Fuyang oil reservoir with ultra-low permeability around placanticline of Daqing Oilfield. *Lithologic Reservoirs*, 2018, 30(1):150-154.
- [31] Iglauer S. CO₂-water-rock wettability: variability, influencing factors, and implications for CO₂ geostorage. *Acc. Chem. Res* 2017; 50(5):1134-1142.

- [32] Wenzel R N. Surface roughness and contact angle. The Journal of Physical Chemistry 1949;53(9):1466-1467.
- [33] Li BF, Ye JQ, Li Zm, et al. Phase interaction of CO₂-oil-water system and its effect on interfacial tension at high temperature and high pressure. Acta Petrolei Sinica 2016; 37(10):1265-1272.