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The Difference in Damage to Low-Permeability Reservoirs by Different Injection Methods of CO_2 Flooding

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Abstract: Low-permeability reservoirs have become an important field of oil and gas development in China. CO_2 flooding technology is an effective technical means for tertiary oil recovery. Although the asphaltene in the system is deposited in the form of a solid after CO_2 injection into the reservoir in contact with crude oil, which causes a certain blockage to the reservoir, the dissolution during the injection process improves the seepage capacity of the reservoir as a whole, and the damage degree of CO_2 flooding to low-permeability reservoirs under different injection modes is different. In this paper, the damage degree of asphaltene precipitation to low-permeability reservoirs under different injection modes of CO_2 flooding is quantitatively characterized. The mechanism experiment of organic scale plugging after continuous CO_2 flooding and CO_2–water alternate flooding, the wettability experiment of reservoirs, and the evaluation experiment of CO_2–water solution on rock dissolution are carried out, and the variation characteristics of relative permeability curve parameters are evaluated. In this paper, the damage degree of asphaltene precipitation to low-permeability reservoirs under different injection modes of CO_2 flooding is quantitatively characterized. The mechanism experiment of organic scale plugging after continuous CO_2 flooding and CO_2–water alternate flooding, the wettability experiment of reservoirs, and the evaluation experiment of CO_2–water solution on rock dissolution are carried out. The variation characteristics of relative permeability curve parameters are evaluated. The results show that the organic scale produced by CO_2 flooding will block the pore throat of the rock, but, on the whole, the dissolution caused by the reaction of CO_2 and chlorite is stronger, which makes the recovery rate of low-permeability reservoirs effectively improved. The organic scale blockage caused by CO_2–water alternating flooding is weaker than that caused by continuous CO_2 flooding. The dissolution effect is better and the permeability is higher. It can achieve a better oil displacement effect in pores with a pore size greater than 0.2 μm. On the whole, it can increase the core pore space and seepage channel, so that the recovery rate of low-permeability reservoirs can be effectively improved. This study has important theoretical and practical significance for improving oil recovery in low-permeability reservoirs.

Keywords: CO_2 flooding; CO_2–water alternate flooding; organic scale; dissolution; the relative permeability curve; enhanced oil recovery

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1. Introduction

In recent years, many oil fields at home and abroad have entered a period of high water cut development. CO_2 flooding technology is an effective technical means for tertiary oil recovery in high-water cut reservoirs. Using the existing well pattern to inject CO_2 is an economically feasible development method at low oil prices. In the process of CO_2 flooding, CO_2 is dissolved in crude oil, or the extraction of light components of crude oil causes the composition of the fluid in the reservoir and the thermodynamic conditions of the system to change, destroying the fluid phase balance in the original system, and precipitating the heavy components such as asphaltene and resin in crude oil, causing damage to the formation. The heavy components that were precipitated seriously reduce the formation permeability, resulting in formation damage, a wellbore, and wellbore blockage [1–3]. The selection of the CO_2 injection mode is one of the important problems in the effective development of oil fields.

The methods of CO_2 injected into reservoirs mainly include: CO_2 huff and puff, continuous injection, water and gas alternating injection (WAG), gravity stable flooding, and separate but simultaneous water and CO_2 injection (SSWG), among which CO_2–water alternating injection is one of the most commonly used injection methods [4,5]. After CO_2 is injected into the reservoir and in contact with the crude oil, the stability of the mutual solubility of the components in the crude oil system is destroyed. The asphaltene precipitation is deposited in the form of a solid, which causes blockage or adsorption on the rock at the pore throat, changes the wettability of the rock, increases the flow resistance of the crude oil in the reservoir, and reduces the reservoir permeability [6,7]. Qian et al. [8] found that with the increase in CO_2 injection pressure, the viscosity and asphaltene content of the produced crude oil decreased continuously, and the asphaltene content in the remaining oil increased continuously. The higher the CO_2 injection pressure, the more serious the asphaltene precipitation, and the greater the damage to the porosity and permeability of the low-permeability reservoir. Compared with continuous CO_2 flooding technology, CO_2–WAG injection technology can reduce the amount of asphaltene precipitation to a certain extent, and the continuity of the remaining oil distribution after displacement is better. The injected formation water is distributed in the center of medium and large pores, which is conducive to the dissolution and diffusion of CO_2 to crude oil with small pores, and effectively improves the effect of CO_2 flooding. When CO_2 enters the reservoir, it reacts with water, rock, and crude oil in the reservoir. Carbonate minerals can react with carbonate solution under acidic conditions. During the reaction, carbonate minerals are subject to certain dissolutions. Mineral dissolution increases the pore space of the reservoir, changes the porosity and permeability of the reservoir, increases the permeability of the reservoir to a certain extent, and improves the recovery factor [9].

In this paper, based on the collection and analysis of the field data of the target oil area, field sampling is carried out to quantitatively characterize the damage degree of asphaltene precipitation to low-permeability reservoirs under different injection modes of CO_2 flooding. Based on the core displacement experiment and combined with nuclear magnetic resonance technology, the organic scale plugging mechanism experiment of continuous CO_2 flooding and CO_2–water alternating flooding, the dissolution experiment of CO_2–aqueous solution on rock, and the reservoir wettability experiment are carried out. The variation characteristics of relative permeability curve parameters are evaluated, the influence of CO_2 flooding on reservoir seepage capacity is studied, and the advantages of CO_2–water alternating flooding are analyzed. It has important theoretical and practical significance for enhanced oil recovery of water injection wells.

2. Experimental Materials and Conditions

2.1. Experimental Materials and Instruments

Kerosene consists of light and medium crude components and is free of asphaltenes. Regarding ground raw oil at the wellhead in the Jinglou 8 area of Henan Oilfield, crude oil density is 0.8956~0.9024 g/cm^3, and the viscosity of ground-degassed crude oil is 21.71~31.27 mPa·s at 70 °C. The content of gum asphalt is 15.24~36.39%, wax is 14.90~31.32%, sulfur is 0.03~0.22%, and the freezing point is −5~27 °C. In the simulation formation water, the total salinity is about 8700 mg/L, and the content of Cl^- is 2900~3600 mg/L. Regarding CO_2, purity is 99.999%, Beijing Huayuan Gas Chemical Company Ltd., Beijing, China. It is taken from the natural core column with a diameter of 25 mm in Henan Oilfield. The physical parameters are shown in Table 1, and the mixed wetting index and initial oil saturation before the core experiment are shown in Table 2.

Table 1. Experimental core and its basic physical parameters.

Core Number	Length/cm	Diameter/cm	Porosity/%	Permeability/mD
859-1	8.666	2.506	28.99	365.170
859-5	8.561	2.499	32.15	350.885

Table 2. Mixed wetting index and initial oil saturation before core experiment.

Core Number	Wettability	Mixed Wetting Index Wettability		Initial Oil Saturation	
		CO_2 Displacement	WAG	CO_2 Displacement	WAG
859-5	OW-Oil wet	−0.728	−0.689	95.54%	94.86%

The ISCO-260D high-precision displacement pump (Teledyne ISCO, Lincoln, NE, USA), the SPEC-PMR nuclear magnetic resonance core analyzer (Beijing Spike Technology Development Co., Ltd., Beijing, China), and the OCA20 video optical contact angle measuring instrument (Dataphysics, Filderstadt, Germany) were used

2.2. Experimental Methods

2.2.1. Mechanism Experiment of Organic Scale Plugging after CO_2 Flooding

The experimental displacement process was carried out according to the industry standard SY/T 6315-2017: *Determination method of high-temperature relative permeability and oil displacement efficiency of heavy oil reservoirs* [10]. Through CO_2 flooding with different injection methods at a constant flow rate under the formation temperature and formation pressure on the cores obtained from field sampling, the influence of organic scale deposition on the reservoir was judged by combining the changes in the core physical properties before and after displacement, and the mechanism of organic scale blockage was analyzed. The core was installed on the core gripper to test the sealing of the pipeline, and then the core was vacuumed. After the formation water was saturated at the experimental temperature of 61 °C, the core was scanned by nuclear magnetic resonance.

The core was loaded into the core holder, vacuumized, and pressurized to saturate the formation water, and the amount of pump entering was recorded. After saturation, the core was taken out and weighed, and the pore volume of the core was calculated. The formation water flooding was carried out at a certain flow rate, and the initial water phase permeability of the core was measured after the differential pressure flow was stable. The sand-filled pipe model of crude oil displacement taken from the oil field site after dehydration and degassing was used to record the amount of water discharged and calculate the irreducible water saturation until no water was discharged. Under the condition of formation temperature and pressure, the dead oil-saturated formation crude oil was displaced by live oil until the gas–oil ratio at the outlet end was consistent with the gas–oil ratio of the compound fluid. Under the conditions of the formation temperature and pressure, continuous CO_2 flooding was carried out at a certain flow rate, the pressure changed under different injection amounts, and the oil output at the outlet end was recorded until the displacement multiple reached more than 20 times the pore volume. The core after displacement was cleaned with n-heptane, and the pore volume and water phase permeability were measured after re-saturation after drying. The experimental results are the results of porosity and permeability under the influence of organic precipitation and inorganic precipitation. Subsequently, it was washed with toluene + alcohol, dried again, and re-saturated to measure its pore volume and water phase permeability, that is, the porosity and permeability results under the influence of inorganic precipitation. By comparing the physical properties after two cleanings, the influence of organic scale on reservoir porosity and permeability after continuous CO_2 flooding could be obtained. Then we changed the injection method to CO_2–water alternating flooding, a core washing oil, and repeated the above steps.

2.2.2. Evaluation Experiment of Rock Corrosion by CO_2–Aqueous Solution

Taking the cuttings and formation water taken from the target reservoir block as the research object, the dissolution experiment of the CO_2–water solution on the rock was carried out by using the high-temperature and high-pressure reactor, and the XRD and CT scanning analysis devices were assisted to simulate the formation temperature and formation pressure. The change in core physical properties was caused by the interaction of CO_2–water–rock, the dissolution evaluation of CO_2–water solution on rock, and the dissolution mechanism of CO_2–water solution on rock. The XRD diffraction experiment was carried out according to the industry standard SY/T 5163-2018: *X-ray diffraction analysis method of clay minerals and common clay minerals in sedimentary rocks* [11].

2.2.3. CO_2 Flooding Characterization of Reservoir Wettability Experiment

Yang et al. [12] proposed an experiment to determine the wettability of the core by using the fluid distribution in pores less than the T_2 cutoff value. The experiment is based on GB/T 28912-2012: *Method for the determination of the relative permeability of two-phase fluid in rock* [13].

2.2.4. Evaluation Experiment of the Oil–Water Relative Permeability Curve after CO_2 Flooding

The unsteady state method is based on the principle of one-dimensional two-phase water flooding, and describes the relationship between the distribution law of oil–water saturation with time and distance during the displacement process [14]. Based on the unsteady state method, the oil–water two-phase relative permeability curve was measured, and the oil–water two-phase seepage law before and after CO_2 flooding in the target reservoir and the mechanism of CO_2 flooding were clarified. The water flooding experiment was carried out by using the core at a constant speed. By recording the changes in pressure, oil production, and water production at both ends of the core with time under the conditions of the formation temperature (50 °C) and 8 MPa pressure, the relationship between water saturation and the relative permeability of oil and water phases was calculated. The determination method of oil–water two-phase permeability curve refers to the industry standard GB/T 28912-2012: *Determination method of relative permeability of two fluids in rock*.

3. Experimental Results and Discussion

3.1. The Law of Organic Fouling Blockage under Different CO_2 Injection Modes

In the process of CO_2 flooding, the dissolution of CO_2 in crude oil or the extraction of light components of crude oil leads to the change in fluid composition and thermodynamic conditions in the reservoir, destroying the fluid phase equilibrium in the original system, precipitating the heavy components such as asphaltene and resin in crude oil, and causing blockage or adsorption on the rock at the pore throat, resulting in an increase in flow resistance of crude oil in the reservoir, formation damage, a wellbore, and wellbore blockage. In order to clarify the law of organic scale plugging under different CO_2 injection methods and effectively reduce the damage of organic scale to reservoir seepage capacity, continuous CO_2 flooding and CO_2–water alternate flooding were carried out on the cores obtained from the field sampling at constant flow rate under formation temperature and formation pressure, respectively. Combined with the changes in core physical properties before and after flooding, the influence of organic scale precipitation on the reservoir was judged, the advantages of CO_2–water alternate flooding were analyzed, and the recovery rate of water injection wells was improved.

3.1.1. Continuous CO_2 Flooding

Under the experimental conditions of 50 °C and 8 MPa, the target core was injected with 20.2 times pore volume by continuous CO_2 flooding. The experimental results are shown in Table 3.

Table 3. Comparison of changes of porosity and permeability before and after continuous carbon dioxide flooding experiment.

Core Number	Displacement Method	Time	Porosity/%	Permeability/mD
859-1	Continuous CO_2 flooding	Before displacement	27.398	102.089
		After washing with n-heptane	26.911	31.014
		Toluene + anhydrous ethanol after washing	27.227	44.103

After continuous CO_2 flooding, n-heptane was used to clean and blow dry the core, and then the saturated water was re-evacuated. The measured core porosity decreased from 27.398% to 26.911%, with a loss of about 1.78%, and the permeability decreased from 102.089 mD to 31.014 mD, with a loss of about 69.6%. Because n-heptane can be fully mixed with other components in crude oil, the remaining fluid in the core can be removed. At this time, the decrease in porosity and permeability is mainly caused by inorganic precipitation and asphaltene deposition, and the blockage of the two is very serious. Using toluene and anhydrous ethanol to clean the core, the measured porosity increased from 26.911% to 27.227%, which was about 1.17% higher than that before cleaning, and the permeability increased from 31.014 mD to 44.103 mD, which was about 42.2%. Because the asphaltene can be washed out after toluene and anhydrous ethanol cleaning, the recovery of core porosity and permeability is caused by the removal of asphaltene. By comparing the damage degree of permeability before and after cleaning, it was found that the final permeability decreased from 102.089 mD to 44.103 mD, with a loss of about 56.80%. At this time, the decrease in porosity and permeability was caused by the residual inorganic scale. It can be seen that the organic scale blockage caused by continuous CO_2 flooding is strong, and the final permeability loss rate of the core is large, which affects the fluid seepage capacity.

3.1.2. CO_2-Alternating-Water Flooding

Under the experimental conditions of 50 °C and 8 MPa, the target core was injected with 20.2 times of pore volume by CO_2–water alternate flooding. The experimental results are shown in Table 4.

Table 4. Comparative results of changes in porosity and permeability before and after CO_2 water alternate flooding experiment.

Core Number	Displacement Method	Time	Porosity/%	Permeability/mD
859-1	CO_2–water alternate flooding	Before displacement	30.665	103.826
		After washing with n-heptane	30.214	58.310
		Toluene + anhydrous ethanol after washing	30.362	72.475

After CO_2–water alternating flooding, n-heptane was used to clean and blow dry the core and re-evacuate the saturated water. The measured core porosity decreased from 30.665% to 30.214%, with a loss of about 1.47%, and the permeability decreased from 103.826 mD to 58.310 mD, with a loss of about 43.83%. Because n-heptane can be fully mixed with other components in crude oil, the remaining fluid in the core can be removed. At this time, the decrease in porosity and permeability is mainly caused by inorganic precipitation and asphaltene deposition, and the blockage of both is very serious. Using toluene and anhydrous ethanol to clean the core, the measured porosity increased from 30.214% to 30.362%, which was about 0.49% higher than that before cleaning, and the permeability increased from 58.310 mD to 72.475 mD, which was about 24.29% higher than that before cleaning. Because the asphaltene can be washed out after toluene and anhydrous ethanol cleaning, the recovery of core porosity and permeability is caused by the removal of asphaltene. By comparing the damage degree of permeability before and after cleaning, it is found that the final permeability decreases from 103.826 mD to 72.475 mD, with a loss of about 30.20%. At this time, the decrease in porosity and permeability is caused by the residue of inorganic scale. Compared with the experimental results of continuous CO_2 flooding, it can be seen that the organic scale blockage caused by CO_2–water alternating flooding is weaker than that caused by continuous CO_2 flooding, and that the permeability is higher and the final permeability loss rate of the core is also larger. At the same time, it shows that the asphaltene produced by CO_2 flooding causes serious blockage, which aggravates the decline of fluid seepage capacity.

3.2. The Experimental Results and Analysis of CO_2–Water Solution Dissolution

It can be seen from the experiment of organic scale blockage caused by the CO_2 flooding process that the organic scale produced after CO_2 injection into the formation will cause serious blockage to the reservoir. However, at the same time, when CO_2 enters the reservoir, it dissolves in the formation water and forms carbonic acid, and gradually dissociates H^+. As the concentration of H^+ increases, the acidity in the solution gradually increases, and the rock minerals in the reservoir come into contact with it and dissolve, forming non-precipitates that can be dissolved in water, thereby deblocking the reservoir or increasing porosity and permeability.

In order to observe the effect of dissolution on the reservoir under different injection modes of rock minerals and CO_2 in the reservoir, and further analyze the influence of organic scale on the reservoir, the dissolution experiment under the action of CO_2–aqueous solution was carried out by assisting XRD and CT devices.

3.2.1. XRD Experiments before and after Corrosion

In order to observe the effect of CO_2–water solution on rock dissolution after CO_2 displacement under different injection methods, the dried core powder was put into the reactor, CO_2 was injected to 8 MPa, and the temperature was raised to 50 °C. The dissolution experiment was carried out and the XRD was used to carry out the scanning electron microscope experiment before and after the dissolution of the cleaned core powder. The XRD results before and after the dissolution experiment of the CO_2–water solution and core powder are shown in Table 5.

Table 5. XRD experimental results of whole rock analysis before and after CO_2–aqueous solution dissolution of rock under different injection modes.

Displacement Method	Time	Component Content/%											
		Quartz	Potash Feldspar	Plagioclase	Calcite	Dolomite	Pyrite	Hematite	Siderite	Gypsum	Anhydrite	Ankerite	Chlorite
Continuous CO_2 flooding	Before dissolution	31	16	45	5	1	0	1	0	0	7	4	52
	After dissolution	26	14	42	3	1	0	1	0	0	5	3	45
CO_2–water alternate flooding	Before dissolution	31	16	45	5	1	0	1	0	0	7	4	52
	After dissolution	24	14	42	3	0	0	1	0	0	4	2	40

It can be seen from the XRD results that after continuous CO_2 flooding, the content of potassium feldspar decreased from 16% to 14%, the content of plagioclase decreased from 45% to 42%, the content of ankerite decreased from 4% to 3%, and the content of calcite decreased from 5% to 3%. The content of quartz decreased from 31% to 26%, and the content of chlorite decreased from 52% to 45%. The decrease was the most significant, indicating that the rock minerals in the formation were in contact with the CO_2–aqueous solution and had dissolution. The reaction minerals were mainly chlorite and quartz. The dissolution plays a role in deblocking the reservoir or increasing the porosity and permeability, and the dissolution effect is significant. When CO_2 enters the reservoir, it dissolves and forms carbonic acid in the formation water and gradually dissociates H^+. With the increase in the concentration of H^+, the acidity in the solution also gradually increased, and the rocks and minerals in the reservoir came into contact with it and dissolved, forming non-precipitates that can be dissolved in the water, thus improving the reservoir permeability and achieving the effect of enhanced oil recovery. After the reaction of CO_2–water alternating flooding, the content of quartz decreased from 31% to 24%, which was 2% more dissolved than that of continuous CO_2 flooding, and the content of chlorite decreased from 52% to 40%, which was 5% more dissolved than that of continuous CO_2 flooding. It shows that the dissolution of CO_2–water alternating flooding is more obvious and can improve the seepage capacity of the reservoir.

3.2.2. CT Scanning Experiment before and after Corrosion

In order to further explore the influence of dissolution on reservoir seepage capacity after CO_2 flooding and analyze the best injection method for CO_2 flooding, CT scanning technology was used to analyze the change in pore throat radius of the target core after CO_2 injection by different injection methods, as shown in Figures 1 and 2.

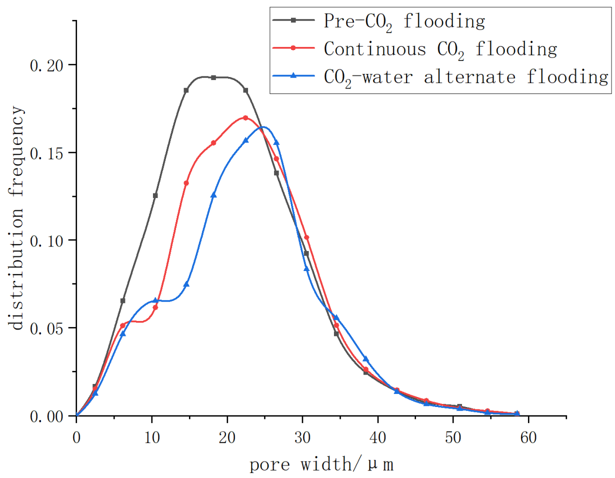

Figure 1. Distribution characteristics of pore radius before and after core reaction of No.859-5.

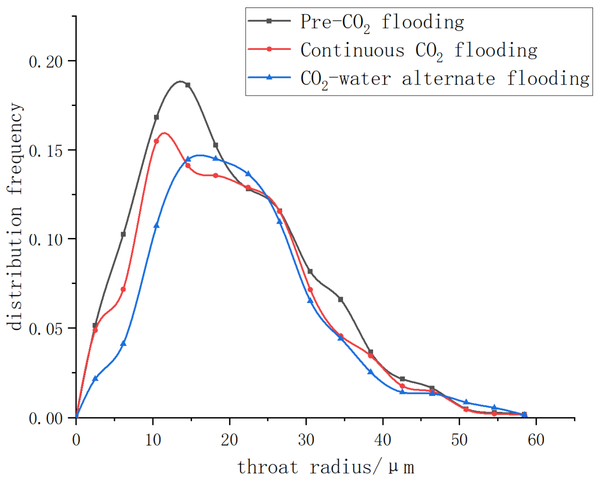

Figure 2. The comparison results of porosity and permeability changes before and after the experiment.

It can be seen from the results that the dissolution of pores after CO_2 flooding caused the average pore radius distribution to shift to the right, the frequency of pore distribution in 10–25 μm to decrease, and the frequency of pore distribution in 25–50 μm to increase slightly, indicating that the CO_2–aqueous solution has a dissolution effect on rocks, and the fluid mainly enters the pores with a space of 10–50 μm to contact the pore rocks in this part, and then dissolution occurs. The pore space increased slightly, the average pore radius increased, and the seepage capacity was enhanced. Compared with continuous CO_2 flooding, CO_2–water alternate flooding can increase the pore throat radius of rock more effectively. The decrease in the pore distribution frequency in 5–15 μm increased, the increase in the pore distribution frequency in 15–30 μm increased, the pore space increased, and the seepage capacity increased, which further indicates that CO_2–water alternate flooding has a more significant effect on reservoir dissolution, larger pore space, larger average pore radius, and stronger seepage capacity.

3.3. The Effect of Different CO_2 Injection Methods on Reservoir Wettability

The wettability of reservoirs is related to the mineral composition and physical and chemical properties of reservoir rocks. The influence of reservoir wettability on water flooding has been fully studied [15], and water flooding can obtain higher recovery under neutral wetting conditions [16].

NMR techniques can be used to evaluate pore structures quantitatively and non-destructively, and NMR tests performed on plunger cores in the laboratory can further provide guidance for NMR logging. In the T_2 spectrum measured after core saturation, the relaxation time is proportional to the pore size to some extent, and the signal amplitude is directly related to the porosity. The NMR relaxation time of low-permeability and dense cores is small due to the narrow pore throat. NMR measurements are more sensitive to pore size, and given that most pore volume is composed of pores, NMR can more fully characterize pore distribution at different pore sizes [17–20].

In order to further explore the influence of CO_2 flooding on reservoir seepage capacity, the best injection method was selected, and the microscopic residual oil distribution of the core after CO_2 flooding under different injection methods was analyzed by nuclear magnetic resonance technology. The residual oil distribution can fully explain the influence of different injection methods on reservoir seepage capacity.

3.3.1. Continuous CO_2 Flooding

According to the relaxation time, the core was divided into micropores (less than 1 ms), small pores (1~10 ms), medium pores (10~100 ms), and large pores (more than 100 ms). The injected CO_2 preferentially entered the large pores and gradually diffused into the small pores, and the utilization degree of crude oil in the small pores was low [21]. The remaining oil distribution of the target core after CO_2 flooding was analyzed by nuclear magnetic resonance technology, as shown in Figure 3 and Table 6.

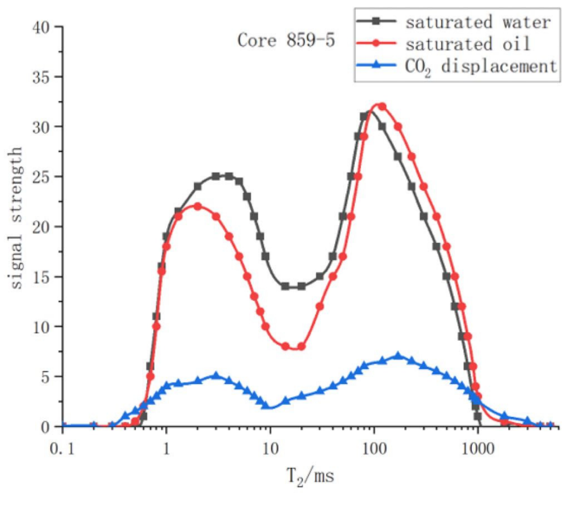

Figure 3. T_2 spectrum of core 859-5 after CO_2 flooding.

Table 6. Residual oil distribution in different pore distribution ranges after CO_2 flooding.

Core Number	<0.1 ms	0.1~10 ms	10~100 ms	>100 ms	Percentage Recovery/%
859-5	29.54	32.85	35.12	26.95	62.54

The irreducible water of core 859-5 was mainly distributed in small pores and medium pores, and the oil saturation reached 95.54%. The crude oil in the pores was distributed in a continuous phase, and CO_2 gradually diffused from the large pores into the small pores. The crude oil at the end of the pores can be driven out by CO_2 through the expansion effect and the extraction effect. The residual oil saturation in different pore ranges of the core was less than 36%. From the perspective of recovery, the recovery rate of CO_2 flooding was 62.54%, and the recovery effect was good.

3.3.2. CO_2–Water Alternate Flooding

The remaining oil distribution of the target core after CO_2–water alternating flooding was analyzed by nuclear magnetic resonance technology, as shown in Figure 4 and Table 7.

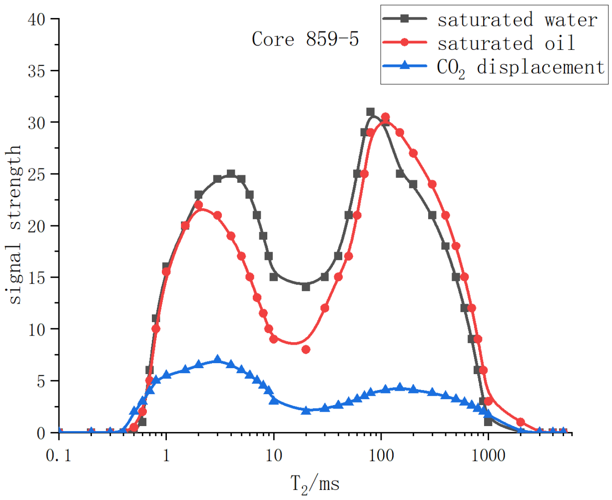

Figure 4. T_2 spectrum of No.859-5 core after CO_2-water alternating flooding.

Table 7. Remaining oil distribution in different pore distribution ranges after CO_2–water alternating flooding.

Core Number	<0.1 ms	0.1~10 ms	10~100 ms	>100 ms	Percentage Recovery/%
859-5	32.62	35.84	27.36	20.93	78.54

After the water slug in the 859-5 core displaced the crude oil in the large pores, the pore wall and the small pores were still occupied by the oil phase, and the remaining oil had good continuity. The CO_2 slug had a high probability of contact with the remaining oil and could diffuse into the crude oil in the small pores, so the crude oil in different pore ranges in the core could be basically used passively. The recovery rate of the core after CO_2–water alternating flooding reached 78.54%, which was 16% higher than that of CO_2 flooding (62.54%). Since the continuity of crude oil distribution in pores is an important factor affecting the effect of CO_2 flooding, the distribution of the remaining oil after CO_2–water alternating flooding is better, resulting in CO_2 effectively improving oil recovery. The formation water injected in the process of CO_2–water alternating flooding was distributed in the center of medium and large pores. The Jamin effect is beneficial to the dissolution and diffusion of CO_2 into crude oil with small pores, which makes it obtain higher recovery [8,21,22].

3.4. Evaluation Experiment of Oil–Water Relative Permeability Curve after CO_2 Flooding

In order to further study the damage degree of CO_2 flooding to the reservoir and the influence of different displacement methods on the seepage capacity of the core, the relative permeability curve of the target core under different CO_2 injection methods was tested after the target core was washed with toluene + anhydrous ethanol, and the characteristic parameters of the relative permeability curve after flooding were statistically sorted out. The summary results are shown in Table 8.

Table 8. Summary table of comparison results of characteristic parameters of oil–water two-phase relative permeability curves before and after CO_2 flooding.

Injection Mode	K_w	S_{wi}	S_{or}	K_{rw} (S_{or})	K_w (S_{or})	E/%	$S_{co\text{-}permeation\ zone}$/%
Pre-CO_2 flooding	38.308	38.14	30.45	0.1485	5.35	50.45	30.48
Continuous CO_2 flooding	42.568	40.16	27.88	0.1322	5.63	53.57	32.16
CO_2-alternating-water flooding	48.815	43.92	23.05	0.1202	5.87	58.90	33.03

K_w—water phase permeability; S_{wi}—bound water saturation; S_{or}—irreducible oil saturation; $K_{rw}(S_{or})$—the relative permeability of water phase under residual oil saturation; $K_w(S_{or})$—water phase permeability under residual oil saturation; e-clogging ratio; E—blockage ratio; $S_{co\text{-}permeation\ zone}$—saturation of co-permeation zone.

It can be seen from the results that compared with before CO_2 flooding, the irreducible water saturation increased after CO_2 flooding, the residual oil saturation decreased, and the relative permeability of the water phase endpoint under the condition of residual oil saturation increased slightly, indicating that the hydrophilicity of the rock increased after CO_2 flooding, and the seepage capacity of the water phase increased after CO_2 flooding, which was helpful to the water injection capacity of the later water flooding. It is further explained that although the organic scale blocked the pore throat of the rock and affected the seepage capacity of the reservoir, the CO_2 flooding improved the seepage capacity of the fluid as a whole, and the dominant seepage channel became larger, which improved the existence condition of the particle migration blockage. At the same time, it also increased the movable space volume of the fluid and improved the water wettability of the rock, which is conducive to improving the efficiency of water flooding. Compared with continuous CO_2 flooding, the physical parameters of CO_2–water alternate flooding increased more significantly, so it can be seen that CO_2–water alternate flooding is more helpful in improving reservoir seepage capacity and increasing oil recovery.

4. Conclusions

Based on the full investigation, combined with the characteristics of the target reservoir and the analysis of the development characteristics, this study carried out the mechanism experiment of continuous CO_2 flooding and CO_2–water alternating flooding, the evaluation experiment of CO_2–aqueous solution on rock dissolution, and the reservoir wettability experiment, and evaluated the variation characteristics of the relative permeability curve parameters. The following understandings and conclusions were obtained:

1. In the process of CO_2 flooding, the blockage caused by asphaltene is serious, which aggravates the decline in fluid seepage capacity. Compared with the experimental results of continuous CO_2 flooding, it can be seen that the organic scale blockage caused by CO_2–water alternate flooding was weaker than that caused by continuous CO_2 flooding, the permeability was higher, and the final permeability loss rate of the core was also larger, indicating that CO_2–water alternate flooding had less damage to the reservoir.
2. The CO_2–aqueous solution has a certain dissolution effect on rocks. The fluid mainly entered the pores with a space of 10–50 μm and contacted the pore rocks in this

part. The occurrence of dissolution improved the seepage capacity of the fluid, and the dominant seepage channel became larger, which can improve the water injection capacity and water injection effect of CO_2 flooding to subsequent water flooding to a certain extent. Compared with continuous CO_2 flooding, CO_2–water alternating flooding can increase the pore throat radius of rock and its dissolution is more significant.

3. CO_2 flooding can use crude oil in different pore ranges, and the remaining oil distribution is relatively uniform. By comparing the remaining oil distribution after continuous CO_2 flooding and CO_2–water alternate flooding in the target core, it was found that CO_2–water alternate flooding can achieve a better oil displacement effect in pores with pore size greater than 0.2 μm.
4. The characteristic parameters of the relative permeability curve before and after CO_2 flooding showed that the irreducible water saturation increased, the residual oil saturation decreased, the two-phase co-permeability zone increased, and the oil displacement efficiency increased, which further indicated that although the CO_2–water–rock reaction occurred in CO_2 flooding caused the blockage of organic scale, the dissolution effect increased the pore space and seepage channel as a whole, and improved the injection capacity of injected water. Compared with continuous CO_2 flooding, the physical parameters of CO_2–water alternating flooding increased more significantly, so it can be seen that CO_2–water alternating flooding is more helpful in improving reservoir seepage capacity.

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References

1. Lei, S. Damage characteristics of CO_2 huff and spit asphaltene deposition on tight sandstone reservoir. *Oilfield Chem.* **2022**, *39*, 343–348.
2. Zheng, W. Experimental study on solid phase deposition law of CO_2 flooding in low permeability reservoir. *Pet. Geol. Recovery Effic.* **2021**, *28*, 131–136.
3. Liu, L.; Ma, Y.; Pi, Y.; Liu, J.; Bai, M. Effect of CO_2 flooding on rock properties under different formation water salinity. *Oilfield Chem.* **2020**, *37*, 665–668.
4. Ding, S.; Xi, Y.; Liu, G.; Liu, Q.; Yu, H. Adaptability of different injection methods of CO_2 flooding to enhanced oil recovery and geological storage in low permeability reservoirs. *Pet. Geol. Recovery Effic.* **2023**, *30*, 104–111.
5. Wang, Q.; Yang, S.; Han, H.; Qian, K.; Wang, L.; Li, J. Effects of CO_2 displacement on physical properties of ultra-low permeability sandstone reservoirs. *J. China Univ. Pet. (Ed. Nat. Sci.)* **2020**, *44*, 124–133.
6. Mohammed, I.; Mahmoud, M.; El-Husseiny, A.; Al Shehri, D.; Al-Garadi, K.; Kamal, M.S.; Alade, O.S. Impact of Asphaltene Precipitation and Deposition on Wettability and Permeability. *ACS Omega* **2021**, *6*, 20091–20102. [CrossRef] [PubMed]
7. Sun, Z. Experimental study on asphaltene deposition under CO_2 flooding. *Oilfield Chem.* **2010**, *27*, 374–376.
8. Qian, K.; Yang, S.; Huang, F.; Dou, H.; Wang, Q. Damage of asphaltene precipitation to low permeability reservoir and its influence on wettability during CO_2 injection. *Oilfield Chem.* **2020**, *37*, 536–541.
9. Hosseini, E. Experimental investigation of effect of asphaltene deposition on oil relative permeability, rock wettability alteration, and recovery in WAG process. *Pet. Sci. Technol.* **2019**, *37*, 2150–2159. [CrossRef]
10. *SY/T 6315-2006*; Determination of High Temperature Relative Permeability and Displacement Efficiency of Heavy Oil Reservoirs. National Development and Reform Commission: Beijing, China, 2006.
11. *SY/T 5163-2018*; Methods for Quantitative Analysis of Total Clay Minerals and Common Non-Clay Minerals in Sedimentary Rocks by X-ray Diffraction. National Energy Administration: Beijing, China, 2018.

12. Yang, Z.; Huang, H.; Luo, Y.; Lei, Q.; Li, H. A new method for testing mixed wettability of tight reservoirs and its application. *Acta Pet. Sin.* **2017**, *38*, 318–323.
13. *GB/T 28912-2012*; Method for Determination of Relative Permeability of Two-Phase Fluids in Rocks. National Standards of People's Republic of China: Beijing, China, 2012.
14. Peng, C.; Xue, X.; Wang, F.; Shi, G. Experimental data processing method of oil-water relative permeability by unsteady state method. *Pet. Geol. Oilfield Dev. Daqing* **2018**, *37*, 74–78.
15. Anderson, W. Wettability Literature Survey-Part 6: The Effects of Wettability on Waterflooding. *J. Pet. Technol.* **1987**, *39*, 1605–1622. [CrossRef]
16. Rao, D.; Girard, M.; Sayegh, S. The Influence of Reservoir Wettability On Waterflood And Miscible Flood Performance. *J. Can. Pet. Technol.* **1992**, *31*. [CrossRef]
17. Xiao, P.; Yang, Z.; Wang, X. Study on microscopic oil displacement mechanism of indoor CO_2 injection. *J. Southwest Pet. Univ. (Nat. Sci. Ed.)* **2015**, *37*, 161–165.
18. Zhao, Y.; Liu, K.; Wang, W.; Yao, Z. Prediction method of enhanced oil recovery by CO_2 flooding in low permeability reservoirs. *Energy Environ. Prot.* **2022**, *44*, 95–101.
19. Cerda, C.M. Mobilization of quartz fines in porous media. *Clays Clay Miner.* **1988**, *36*, 491–497. [CrossRef]
20. Li, L.; Ju, B.; Jiang, H.; Di, P. Oil particle migration and its influence on reservoir physical properties. *China Int. Energy Resour.* **2011**, *16*, 50–54.
21. Zhang, D.; Rao, L.; Cai, X. Mechanism of particle migration plugging damage in low permeability reservoir in Changqing Oilfield. *Fault Block Oil Gas Field* **2023**, *30*, 441–447.
22. Yuan, Z.; Liao, X.; Zhao, X.; Chen, Z. Effect of dissolution on reservoir physical properties during CO_2 displacement in sandstone reservoir. *Pet. Geol. Recovery Effic.* **2020**, *27*, 97–104.

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