

Original Paper

Unlocking shale oil: Synergistic mechanisms of CO₂ extraction enhanced by fractures and surfactants

Huan Zhang^{a,b,c}, Ming-Wei Zhao^{a,b,c,**}, Hou-Jian Gong^{b,c}, Cai-Li Dai^{a,b,c,*},
Ming-Zhe Dong^d, Xin Li^{a,b,c}, Zhen-Feng Ma^{a,b,c}, Zhi-Hao Zhang^{a,b,c},
Zhong-Zheng Xu^{a,b,c}, Xin-Jie Xu^{a,b,c}

^a State Key Laboratory of Deep Oil and Gas, China University of Petroleum (East China), Qingdao, 266580, Shandong, China

^b Key Laboratory of Unconventional Oil & Gas Development (China University of Petroleum (East China)), Ministry of Education, Qingdao, 266580, Shandong, China

^c Shandong Key Laboratory of Oil and Gas Field Chemistry, China University of Petroleum (East China), Qingdao, 266580, Shandong, China

^d Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta T2N 1N4, Canada

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ABSTRACT

The development of unconventional oil and gas resources is currently the primary focus of the petroleum industry. Shale oil has attracted significant attention due to its vast reserves. However, shale oil reservoirs are characterized by low porosity and low permeability, combined with rich organic matter, resulting in low oil recovery. The extraction efficiency of CO₂ is one of the key mechanisms for enhancing oil recovery. In this study, a comprehensive analysis was conducted on the factors influencing the extraction efficiency of CO₂, including CO₂ development parameters, core properties, and fractures. Additionally, the effect of C₄EO₃PO₆ (a polyether surfactant) on enhancing extraction efficiency of CO₂ was evaluated. The results show that the developed micropore and nanopore structure in shale makes oil in micropores, as well as absorbed and adsorbed oil, particularly difficult to mobilize. Under comparable permeability and porosity conditions, the CO₂ extraction recovery for tight sandstone is 2.2 times higher than that for shale, and the mobilization efficiency of free oil is 3.87 times higher than that of absorbed and adsorbed oil. The presence of fractures facilitates the dissolution and diffusion of CO₂ within the rock matrix. After three CO₂ extraction cycles, the extraction recoveries reach 81.6% for the naturally fractured shale core (containing natural fractures) and nearly 100% for both shale block samples and tight sandstone block samples. C₄EO₃PO₆ effectively reduces the interfacial tension and minimum miscibility pressure between CO₂ and shale oil, significantly enhancing the extraction efficiency of CO₂. With the addition of C₄EO₃PO₆, the extraction recovery of the shale core increases by 29.43%, with improvements of 27.25% for oil in micropores and 27.31% for absorbed and adsorbed oil. This work aims to provide an innovative development strategy for enhancing shale oil recovery through CO₂ injection.

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1. Introduction

With advances in exploration and development technologies, shale oil has attracted significant attention due to its vast reserves and considerable development potential (Feng et al., 2020; Jiang et al., 2016; Zhang et al., 2024b). The successful development of

shale oil resources in North America has provided valuable reference experience for shale oil development worldwide (Soeder, 2018; Tovar et al., 2021). Low permeability and low porosity are distinct characteristics of shale reservoirs, with tiny flow paths that make it difficult for fluids in the pores to move through the rock (Xu et al., 2022; Zhang et al., 2024c). Shale reservoirs exhibit a high degree of heterogeneity; the natural and induced fractures are necessary to enable the flow of shale oil (Jin et al., 2016; Yu et al., 2023).

In the process of shale oil development, there is a challenge of rapid production decline. North American shale oil wells typically experience approximately 70% production decline within the first year after fracturing, with recovery usually below 10% (Eltahan

* Corresponding author.

** Corresponding author.

E-mail addresses: zhaomingwei@upc.edu.cn (M.-W. Zhao), daicl@upc.edu.cn (C.-L. Dai).

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et al., 2024; Lei et al., 2022, 2023a). Therefore, replenishing formation energy after hydraulic fracturing is crucial for maintaining stable shale oil production (Fakher and Imqam, 2020; Liu et al., 2022a; Ozowe et al., 2020). Water and gas injection are viable methods for replenishing reservoir energy. However, in shale formations, the low permeability and porosity lead to significant capillary effects during water flooding, while the presence of clay minerals results in pronounced water sensitivity effects (Hu et al., 2022; Zhang et al., 2019). Compared with water flooding, gas injection for shale oil development can effectively avoid the aforementioned issues. Conventional gas injection methods include N_2 flooding, light hydrocarbon flooding, and CO_2 flooding. Among these, CO_2 flooding achieves higher oil recovery and enables underground sequestration (Fakher and Imqam, 2020; Sheng, 2015; Wang et al., 2023). Injecting CO_2 into the reservoir can effectively reduce crude oil viscosity and enhance its mobility. CO_2 exhibits strong extraction and expansion effects on crude oil, along with low interfacial tension with oil (Kumar et al., 2022; Li et al., 2022; Liu et al., 2022a). The occurrence state of shale oil is diverse, encompassing free oil, adsorbed oil, and absorbed oil (Dong et al., 2022; Xu et al., 2022). Studies indicate that the interaction between CO_2 and kerogen is stronger than that between kerogen and hydrocarbons, allowing for effective mobilization of adsorbed and absorbed oil (Zhao et al., 2021). Unfortunately, even under similar development conditions, the recovery in shale reservoirs remains notably lower than that in tight sandstone reservoirs (Li et al., 2019; Zhu et al., 2021). Therefore, it is necessary to appropriately adjust CO_2 flooding strategies.

Due to the strong heterogeneity of shale reservoirs, the CO_2 huff-and-puff method is commonly adopted to avoid rapid gas channeling (Alfarge et al., 2018). The process of CO_2 huff-and-puff includes CO_2 injection, shut-in for soaking, and initiating production after soak. After entering the reservoir, CO_2 gradually diffuses into the rock matrix and displaces the crude oil through extraction and expansion effects (Jia et al., 2019; Yang et al., 2024). Even after CO_2 channeling occurs, extraction effect continues to contribute to the increase in oil recovery (Liu et al., 2025b). Yu et al. (2021) investigated the extraction effect of CO_2 on shale cores. The results demonstrated that both increasing extraction pressure and the number of fractures enhance the extraction efficiency of CO_2 . Expanding the contact area between CO_2 and the matrix crude oil will contribute to improving shale oil recovery. Amer et al. (2025) conducted a study of the extraction of oil from oil shale using supercritical CO_2 and water as a modifier and also revealed the application potential of CO_2 extraction to enhance oil recovery. Gamadi et al. (2014) conducted CO_2 soaking experiments on cores from Mancos and Eagle Ford, and the results showed that the recovery could be increased from 33% to 85%. Meanwhile, the field production practice shows that enhanced CO_2 production can improve the oil recovery by nearly 10% (Cao et al., 2023). These previous studies show that CO_2 extraction is a feasible method to improve oil recovery in shale reservoirs.

CO_2 has significant potential for applications in shale oil development. However, it is important to note that evidence suggests a significant discrepancy between laboratory studies and field application results concerning CO_2 -enhanced shale oil recovery (Lang et al., 2021; Taheri-Shakib and Kantzas, 2021; Wang et al., 2020, 2022; Yang and Jin, 2019). Incorporating surfactants into CO_2 to enhance its overall performance for improved oil recovery has proven to be an effective gas injection strategy. Numerous studies have shown that surfactants can enhance the extraction and expansion effects of CO_2 , reduce the interfacial tension and minimum miscibility pressure (MMP) between CO_2

and crude oil, and promote mutual dissolution and diffusion, thereby improving the oil recovery (Ding et al., 2019; Kharazi et al., 2023; Lv et al., 2023, 2024). Developing shale oil by CO_2 injection still faces the following challenges: (1) The recovery of shale oil from micropores and small pores is extremely low and the contribution of crude oil in different pores to the recovery remains unclear (Liu et al., 2022b). (2) Cyclic recovery exhibits significant fluctuations with rapid production decline, resulting in short effective stimulation periods. (3) It is difficult for CO_2 and shale oil to achieve complete miscibility under reservoir conditions (Chen and Gu, 2017; Mahzari et al., 2021). Additionally, for the low porosity and permeability of shale formations, it is imperative to further enhance the diffusion effect of CO_2 within the matrix. In CO_2 flooding and CO_2 huff-and-puff technology, the diffusion of CO_2 within the rock matrix and the extraction effect on crude oil are key mechanisms for enhanced oil recovery. Moreover, the contributions of crude oil in different pore size ranges to the recovery are different (Chen et al., 2022; Liu et al., 2025b). However, most existing research discusses the extraction effect based on interfacial tension measurements, PVT experiments, and the microfluidic experiments of CO_2 -shale oil. A systematic evaluation of the extraction effect of CO_2 on shale oil residing in core matrix remains limited.

In this study, considering the impact of organic matter on shale oil development, tight sandstone and shale cores were selected for comparative analysis. To simulate the extraction effect of CO_2 on shale oil at different reservoir locations after hydraulic fracturing, cores with varying degrees of fracture development were selected. In addition, an innovative approach was adopted by processing cylindrical cores into block samples (3–5 mm) to investigate the enhanced extraction effect of CO_2 . Furthermore, the impact of the CO_2 -polyether surfactant composite system on enhancing shale oil recovery was investigated. Our previous work (Zhang et al., 2024a, 2025) demonstrated that the polyether surfactant significantly reduces the interfacial tension and the MMP of CO_2 -shale oil system, thereby enhancing the extraction efficiency of CO_2 . This study aims to provide an innovative development strategy for enhancing shale oil recovery through CO_2 injection.

2. Experimental methods

2.1. Materials

The cores used in the experiments were obtained from the X block of the Ordos Basin, China. Porosity was measured using helium saturation tests, and permeability was determined by the helium pressure-pulse-decay method (Huang et al., 2023; Yang et al., 2016). To emphasize the effect of organic matter (kerogen) on CO_2 extraction from shale oil, a tight sandstone core with the comparable permeability was selected for comparison. The presence of fractures in the reservoir facilitates the diffusion of CO_2 into the matrix, thereby enhancing shale oil recovery. To simulate the effect of CO_2 on the mobilization of shale oil in rock matrices with varying degrees of fracture development after hydraulic fracturing, we compared intact shale core and naturally fractured shale core (core with natural fractures), and also prepared core block samples (3–5 mm) to represent highly developed fractures.

The physical parameters of the shale and tight sandstone are presented in Table 1. All cores used in the experiment are classified as tight cores, characterized by extremely low permeability and porosity. Fig. 1(a) shows a tight sandstone core, Fig. 1(b) a shale core, Fig. 1(c) a naturally fractured shale core, Fig. 1(d) the shale block samples, and Fig. 1(e) the tight sandstone block samples.

The naturally fractured shale core was scanned by CT to characterize its internal structure in detail. Fig. 1(g) shows the 2D CT scan slices of the naturally fractured shale core, in which several through-going fractures can be observed within the core. Based on the Z-direction layer-by-layer porosity analysis, as shown in Fig. 1(h), the slice porosity exhibits relatively small fluctuations

Table 1
Properties of shale and tight sandstone cores.

Core type	Permeability, mD	Porosity, %	TOC, %	Length, mm	Diameter, mm
Shale core	0.052	5.20	9.66	66.70	25.02
Naturally fractured shale core*	–	5.27	8.96	66.84	25.76
Tight sandstone core	0.049	5.14	–	49.88	24.70

Note: * The naturally fractured shale core contains several through fractures, so it is impossible to measure its permeability by the helium pressure-pulse-decay method.

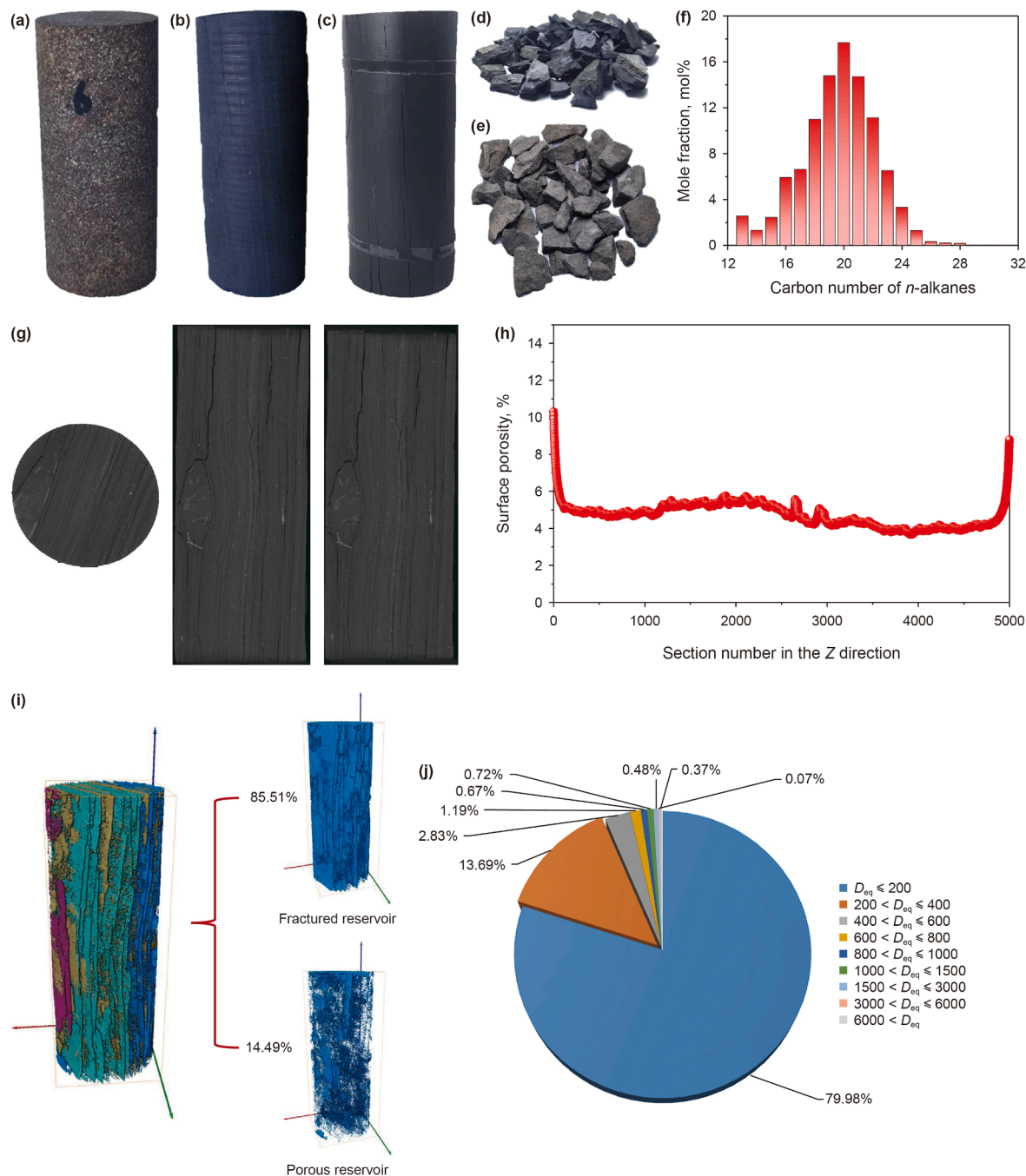


Fig. 1. Experimental materials. (a) Tight sandstone core; (b) shale core; (c) naturally fractured shale core; (d) shale block samples; (e) tight sandstone block samples; (f) components of 7# white oil; (g) 2D CT scan slices of the naturally fractured shale core; (h) layer-by-layer porosity analysis of the naturally fractured shale core along the Z direction; (i) reservoir analysis of the naturally fractured shale core; (j) equivalent diameter screening of pores in the naturally fractured shale core.

overall and shows a gradually decreasing trend. The average slice porosity is 4.2%, with the maximum value of 10.1% and the minimum value of 3.6%. Fig. 1(i) shows the reservoir analysis of the naturally fractured shale core. Reservoir types were classified based on morphological differences, showing that the contribution of fractured reservoirs was 85.51%, whereas that of porous reservoirs was 14.49%. Fig. 1(j) shows the equivalent diameter screening of pores in the naturally fractured shale core. It can be seen that pores with an equivalent diameter (D_{eq}) of $\leq 200 \mu\text{m}$ account for a relatively large proportion of the pore volume, approximately 79.98%.

For the reproducibility of the experiments, 7# white oil (the mixture of multi-component hydrocarbons) provided by Sino-pharm Chemical Reagent Co., Ltd. was used to simulate the crude oil. At 25 °C, the density of oil is 0.840 g/cm³ and the viscosity is 5.8 mPa·s. These values are comparable to the reported properties of Chang 7 shale oil in the Ordos Basin, for which the density of crude oil was 0.830 g/cm³ and the viscosity was 5.8 mPa·s (Guo et al., 2023). The distribution of *n*-alkanes in white oil is shown in Fig. 1(f). It can be seen that the main components range from C₁₃ to C₂₈, with C₁₆–C₂₃ alkanes accounting for the major proportion. This distribution broadly overlaps with that of Chang 7 crude oil in the Ordos Basin, where the carbon numbers of *n*-alkanes are mainly distributed from C₁₀ to C₃₅, with the main peak carbon numbers of C₁₉–C₂₁ (Ma et al., 2026). The CO₂ used in the experiment is provided by Qingdao Tianyuan Industrial Gas Co., Ltd. (purity 99.8%).

2.2. Experimental setup and procedure

The experimental setup consisted of a core saturator (a device used to saturate core samples with oil), an NMR instrument, and a CO₂ pressurization unit, as shown in Fig. 2(a). The low-field NMR instrument with a magnetic field strength of 0.28 T and a hydrogen proton resonance frequency of 12 MHz (Shanghai Niumag Analytical Instrument Corporation) was used, equipped with a 60 mm probe coil (Huang et al., 2023). A fluorocarbon oil bath

maintained the temperature of the CO₂ extraction tank, while a thermostat controlled the gas temperature. The experimental temperature was set to 50 °C to simulate the shale reservoir conditions in the X block of Changqing, China.

The specific experimental procedure is as follows.

- (1) The cores were first ultrasonically cleaned for 4 h to completely remove impurities from their surfaces. They were then extracted with ethanol-toluene mixtures and dichloromethane for 10 d, followed by drying at 100 °C until their weight did not change (Gong et al., 2019).
- (2) The T_2 spectra of the cores were measured using the NMR apparatus to obtain the intrinsic ¹H signal of the cores.
- (3) The cores were placed in the intermediate container and vacuumed at 5 Pa for 12 h to remove air from the apparatus and core pores. The cores were then saturated with oil using the hand pump at a saturation pressure of 24 MPa for 120 h.
- (4) The T_2 spectra of the cores were measured again using the NMR apparatus after saturation. The T_2 spectra of oil saturated in the core were obtained by subtracting the baseline peaks of the core from the combined NMR spectra of the oil and core.
- (5) The core saturated with oil was placed in the CO₂ extraction tank and the experimental equipment was connected according to the experimental flow chart shown in Fig. 2. The CO₂ extraction tank was evacuated and pretreated using the vacuum pump.
- (6) The CO₂ or CO₂–surfactant composite system was introduced into the CO₂ extraction tank, and the gas pressure in the tank was adjusted using the ISCO pump. The T_2 spectra of the core, obtained at different extraction times, pressures, and cycles were measured using the NMR apparatus.

Fig. 2(b) shows the schematic diagram of CO₂-enhanced extraction method for improved shale oil recovery. In this study, the oil-saturated core was placed in the CO₂ extraction tank, allowing CO₂ to enter the core from all directions and more

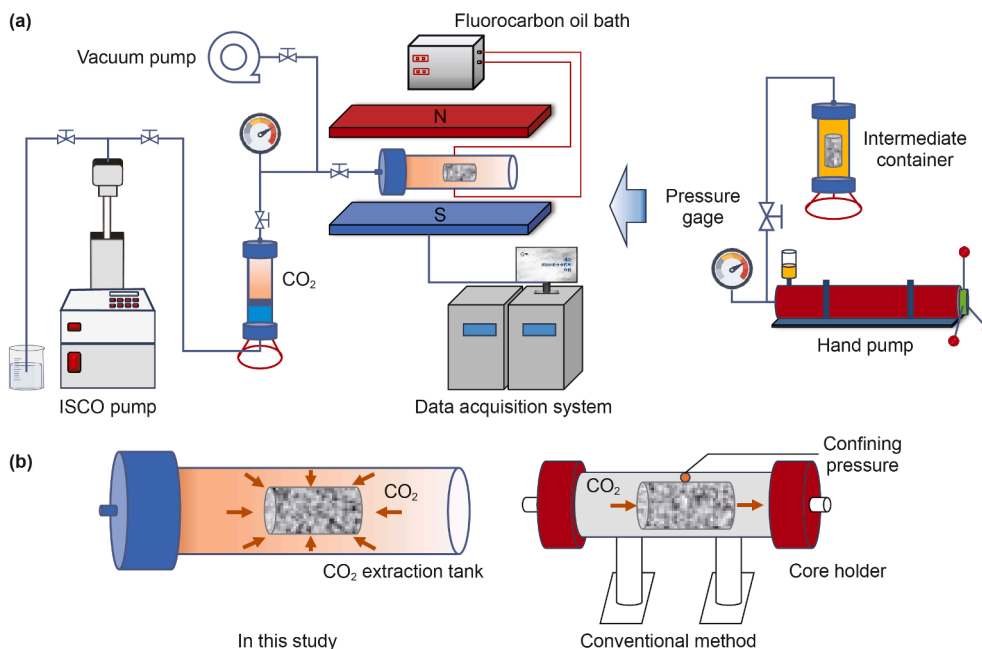


Fig. 2. Schematic diagrams of the experimental apparatus. (a) CO₂ extraction system for cores; (b) schematic diagram of CO₂-enhanced extraction method for improved shale oil recovery.

effectively diffuse into the matrix, thereby enhancing shale oil recovery.

2.3. The method for determining the pore size limits of movable shale oil

The T_2 cutoff value is a critical parameter in NMR measurements used to assess fluid mobility within core samples, reflecting the degree of fluid mobility under specific conditions. This method estimates a conversion method between core pore diameter and T_2 relaxation time to determine the T_2 cutoff pore diameter for shale oil, which can be used to evaluate the extraction efficiency of CO_2 . This work utilized a 3A molecular sieve with standard pore sizes as a reference to develop an evaluation method for the T_2 cutoff pore diameter of shale oil.

Fig. 3(a) presents the N_2 adsorption and desorption isotherms of the 3A molecular sieve, while Fig. 3(b) shows its pore size distribution. The average pore diameter of the molecular sieve was determined through N_2 adsorption and desorption tests. Fig. 3(c) displays the T_2 NMR spectrum of the oil-saturated 3A molecular sieve. The relationship between the T_2 relaxation time and pore diameter is given by Eq. (1). Based on the average pore diameter of the 3A molecular sieve and the T_2 relaxation time corresponding to

the peak in the T_2 NMR spectrum of the saturated oil, the pore size conversion coefficient, C , was calculated to be 0.1341 ms/nm.

$$T_2 = CD \quad (1)$$

where T_2 is the relaxation time, ms; C is the pore size conversion factor, ms/nm; D is the pore diameter, nm.

Fig. 3(d) illustrates the method for determining the T_2 cutoff pore size. The curve showing signal intensity changing with pore diameter was integrated to obtain the cumulative signal intensity curve. A horizontal line drawn from the peak of the cumulative intensity curve after CO_2 extraction intersects the cumulative intensity curve of the oil-saturated core. The pore diameter corresponding to this intersection point is defined as the T_2 cutoff pore diameter, which represents the pore size range responsible for the majority of oil production from the core.

Compared to the traditional mercury intrusion method, this method has several advantages and broader applicability: (1) it avoids damaging the internal pore structure of core samples, thereby preserving sample integrity; (2) the experimental procedure is highly repeatable, cost-effective, and time-efficient; (3) the method is highly scalable, enabling the establishment of conversion coefficients between T_2 relaxation time and pore size for different samples, saturating fluids, and nuclear magnetic resonance detection equipment. Lang et al. (2021) and Huang et al.

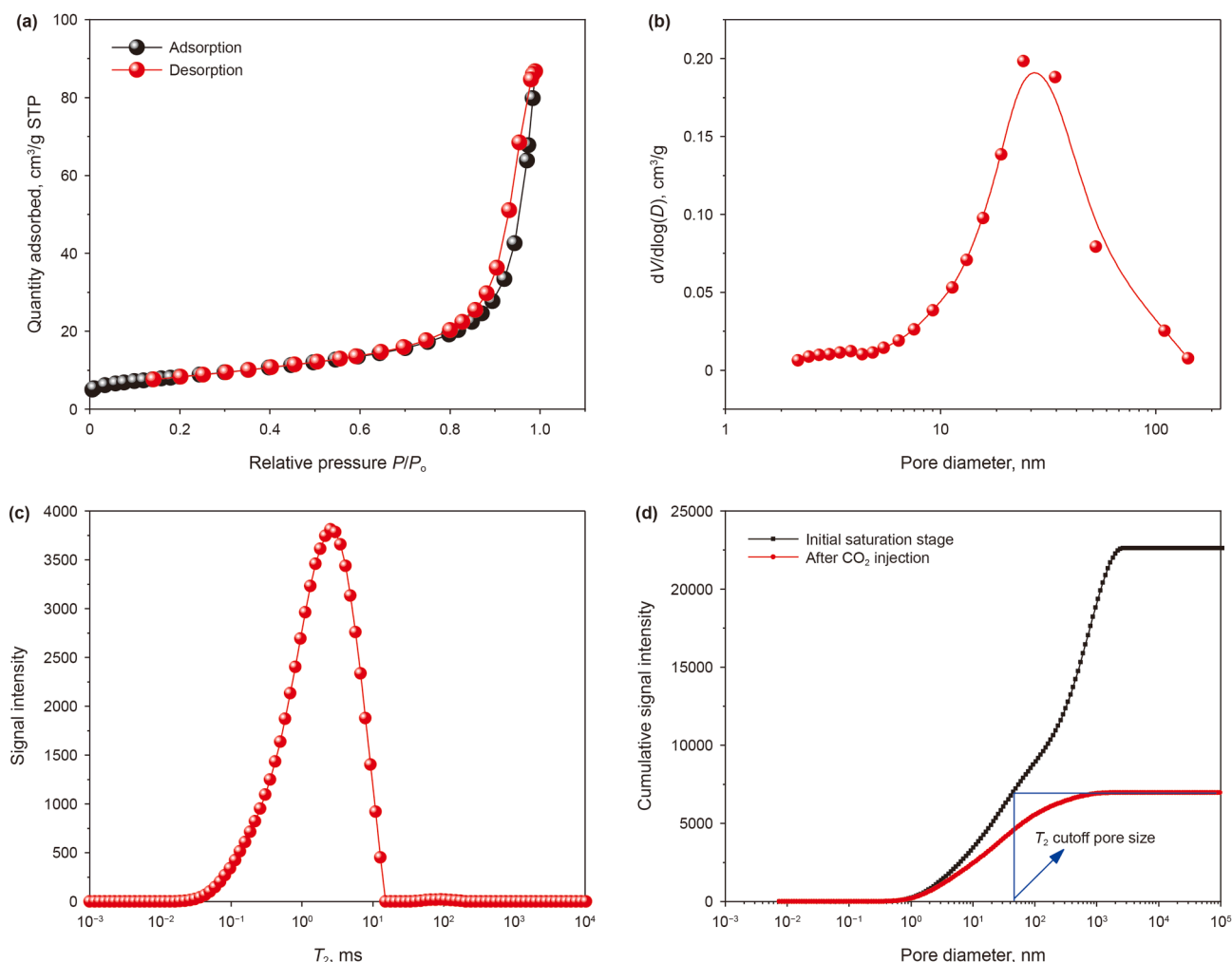


Fig. 3. Determination of the conversion coefficient between pore diameter and T_2 relaxation time. (a) N_2 adsorption and desorption isotherms of 3A molecular sieve; (b) pore size distribution of 3A molecular sieve; (c) T_2 spectra of 3A molecular sieve saturated with crude oil; (d) determination of T_2 cutoff pore size.

(2022) applied the similar methodology to calculate the conversion coefficient between pore diameter and T_2 relaxation time for shale cores, confirming the applicability of this method.

3. Results and discussion

3.1. Effects of injection parameters on CO₂ extraction efficiency

The extraction efficiency of CO₂ for shale oil is influenced by multiple factors. During the interaction between CO₂ and oil within porous media, CO₂ gradually diffuses into and dissolves within the shale oil. Key development parameters such as extraction pressure, time, and cycle significantly affect the extraction efficiency of CO₂. When the extraction pressure of CO₂ reaches the minimum miscibility pressure (MMP) between CO₂ and oil, miscible flooding can theoretically be achieved (Kumar et al., 2022). In previous research, the MMP of CO₂ and oil was determined to be 17.5 MPa, and various experimental pressures were applied to study their influence on extraction efficiency (Zhang et al., 2025).

The extraction recovery of CO₂ and the mass of extracted oil at different pressures are shown in Fig. 4(a), with the extraction time fixed at 12 h. With increasing extraction pressure, both the extraction recovery and the mass of extracted oil increased rapidly, followed by a slow rate of increase. At an extraction pressure of 8.0 MPa, the CO₂ extraction recovery was only 19.0%. At lower

extraction pressures, the solubility of CO₂ in oil is low, resulting in weaker diffusion and mass transfer between CO₂ and the oil.

When CO₂ reaches its supercritical state, its properties change significantly. At the extraction pressure of 20.0 MPa, the core extraction recovery was 46.82%. When the pressure increased to 24.0 MPa, the extraction recovery reached 47.50%, representing a mere increase of 0.68%. This indicates that the extraction recovery does not increase indefinitely with rising pressure but instead approaches a plateau. Even when the pressure exceeds the MMP between CO₂ and oil, it remains difficult to completely extract all the oil from the core matrix. Therefore, extending the extraction time is necessary to further enhance the CO₂ extraction efficiency.

When the CO₂ extraction pressure was fixed at 24.0 MPa, the effect of extraction time on the CO₂ extraction efficiency was further studied. Fig. 4(b) shows the CO₂ extraction recovery and the mass of extracted oil at different times. With the increase in CO₂ extraction time, the extraction recovery gradually increased, although the rate of increase gradually slowed down. Despite the extraction pressure of CO₂ being higher than the MMP, the maximum extraction recovery of CO₂ reached 60.94%. Beyond this point, further increases in extraction time resulted in minimal improvement in extraction efficiency.

During the interaction between CO₂ and oil, CO₂ continuously extracts light and medium components from crude oil, while heavy components are more difficult to extract (Li et al., 2021). As the extraction time increases, CO₂ gradually diffuses into the core matrix, and the oil in different pores progressively dissolves in CO₂.

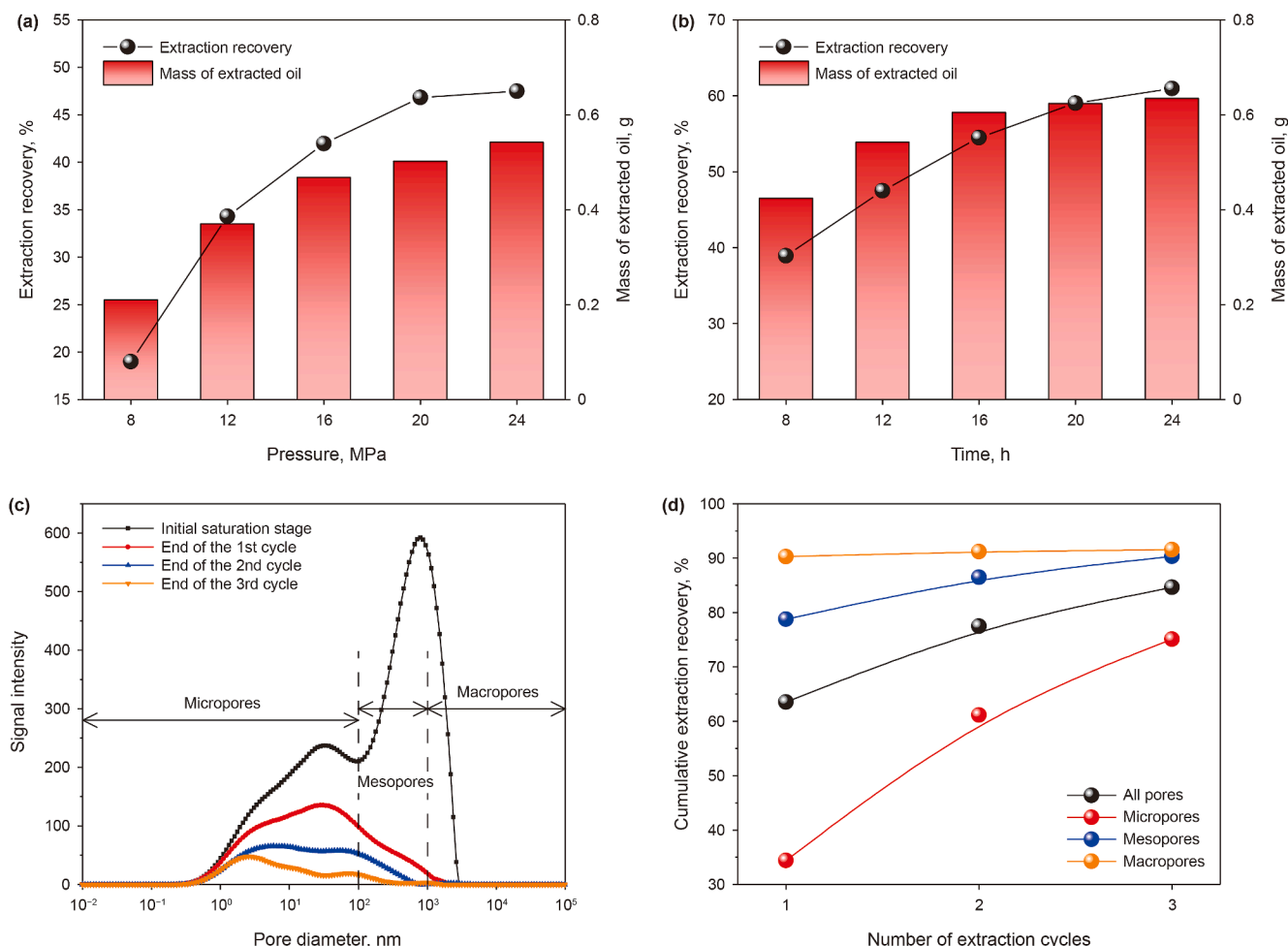


Fig. 4. Factors influencing CO₂ extraction efficiency. (a) Extraction pressure; (b) extraction time; (c, d) extraction cycles.

Shale exhibits a well-developed micropore and nanopore structure, which imposes significant migration resistance on shale oil during movement. Coupled with the strong interactions between organic matter and shale oil, it is difficult for CO₂ to fully extract the oil. Therefore, multiple extraction cycles are required to further enhance recovery.

The oil-saturated core was extracted over several cycles to investigate the effect of multiple CO₂ extraction cycles on the extraction efficiency. The CO₂ extraction time was fixed at 24 h, and the extraction pressure was maintained at 24.0 MPa. Using the method for determining the pore size limits of movable shale oil, the relationship between the T_2 spectrum and pore diameter was established, as shown in Fig. 4(c). This study adopts the pore classification method proposed by Lu et al. (2018) and Zhang et al. (2017), which is applicable to both shale and tight reservoirs, categorizing pores into micropores (<100 nm), mesopores (100–1000 nm), and macropores (>1000 nm).

As shown in Fig. 4(c), the T_2 spectrum of the core exhibits a typical bimodal distribution, indicating a broad pore size distribution comprising well-developed nanopores and micropores. Based on the pore classification standard, the oil content within pores of different diameters was calculated. As shown in Table 2, the oil in micropores, mesopores, and macropores accounts for 38.72%, 44.45%, and 16.83%, respectively. This indicates that the saturated oil primarily resides in the micropores and mesopores of the core. With an increasing number of extraction cycles, the signal intensity of oil in all types of pores gradually declined. After three cycles of CO₂ extraction, the signal intensity from mesopores and macropores nearly dropped to zero, indicating that the oil within these pores was almost completely extracted. In contrast, some oil in micropores remained difficult to mobilize. After three CO₂ extraction cycles, the overall extraction recovery of the core reached 84.63%. Macropores and mesopores contributed significantly, with cumulative extraction recoveries of 91.54% and 90.33%, respectively, while the cumulative extraction recovery for micropores was 75.09%.

By investigating the influence of CO₂ injection parameters on extraction efficiency, it was determined that the optimal CO₂ extraction pressure is 24 MPa, the extraction time is 24 h, and the extraction cycle is 3. A longer interaction time is necessary for CO₂ to dissolve into the residual oil within micropores and to overcome the migration resistance during oil displacement. Therefore, enhancing the mobilization of oil from micropores is crucial for improving recovery.

3.2. Effects of core properties on CO₂ extraction efficiency

Shale oil exists in the forms of adsorbed oil, absorbed oil, and free oil. Understanding the interactions between CO₂ and shale oil in these different states is crucial for optimizing CO₂ flooding strategies and enhancing shale oil recovery.

For shale cores saturated with oil, the occurrence states of shale oil can be distinguished based on T_2 relaxation times. Existing research indicates that the T_2 cutoff values between adsorbed oil, absorbed oil, and free oil in one-dimensional NMR T_2 spectra typically range between 1 and 10 ms (Gong et al., 2020; Liu et al., 2018; Zhu et al., 2019). In this study, shale cores were processed into 3–5 mm shale block samples. After thoroughly cleaning to remove the residual oil, the remaining ¹H signals of the shale block samples were measured to distinguish the T_2 relaxation times corresponding to adsorbed oil, absorbed oil, and free oil. Fig. 5 shows the T_2 spectrum of the shale block samples after oil

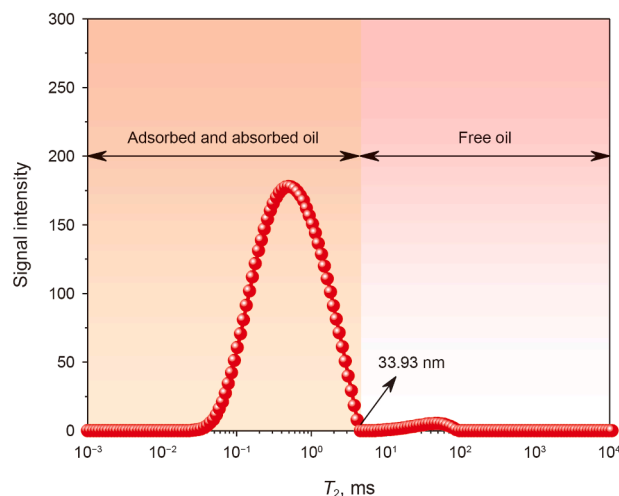


Fig. 5. T_2 spectrum of shale block samples after oil washing.

washing. A distinct signal peak was observed in the region where the T_2 relaxation time is less than 4.55 ms. The critical pore diameter was calculated to be 33.93 nm according to the conversion equation between T_2 relaxation time and pore size. These ¹H signals primarily originate from kerogen, as well as adsorbed and absorbed oil that was not completely removed after oil washing. Therefore, pores smaller than 33.93 nm were considered dominated by adsorbed and absorbed oil, whereas pores larger than 33.93 nm were considered dominated by free oil.

Shale reservoirs are rich in organic matter. In this study, the shale and tight sandstone cores were compared. The variations in T_2 spectra of tight sandstone and shale cores after multiple cycles of CO₂ extraction are shown in Fig. 6(a) and (b). The T_2 spectra of both core types exhibit a characteristic bimodal distribution, indicating the presence of well-developed micropores and nanopores. A higher proportion of oil is retained within the micropores of the shale core. After the first cycle of CO₂ extraction, the oil content in the mesopores and macropores of the shale core decreased rapidly. With increasing extraction cycles, the oil within the micropores was gradually extracted into the CO₂ phase as well.

Table 2 presents the oil content in pores of different sizes in tight sandstone and shale cores. Fig. 6(c) and (d) shows the extraction recoveries from micropores, mesopores, and macropores in tight sandstone and shale cores. The data indicate that in the oil-saturated shale core, micropores account for 80.04% of the total oil, mesopores for 13.66%, and macropores for 6.29%. After three cycles of CO₂ extraction, the oil extraction recoveries were 24.99% from micropores, 80.97% from mesopores, and 97.70% from macropores. However, the overall extraction recovery for the shale core was only 37.21%. During diffusion within the shale core, CO₂ preferentially accessed macropores and mesopores. Consequently, the oil in these larger pores was mobilized first. Additionally, compared with the oil in micropores, the migration resistance in macropores and mesopores was lower. For the tight sandstone core, which had permeability comparable to that of the shale core, the extraction recovery from micropores reached 75.01% after three CO₂ extraction cycles—three times higher than that of the shale core. It should be noted that with increasing extraction cycles, the extraction recovery from macropores and mesopores in shale decreases. When the oil in micropores migrates outward under the extraction of CO₂, some oil remains trapped in macropores and mesopores due to migration resistance. Within the shale

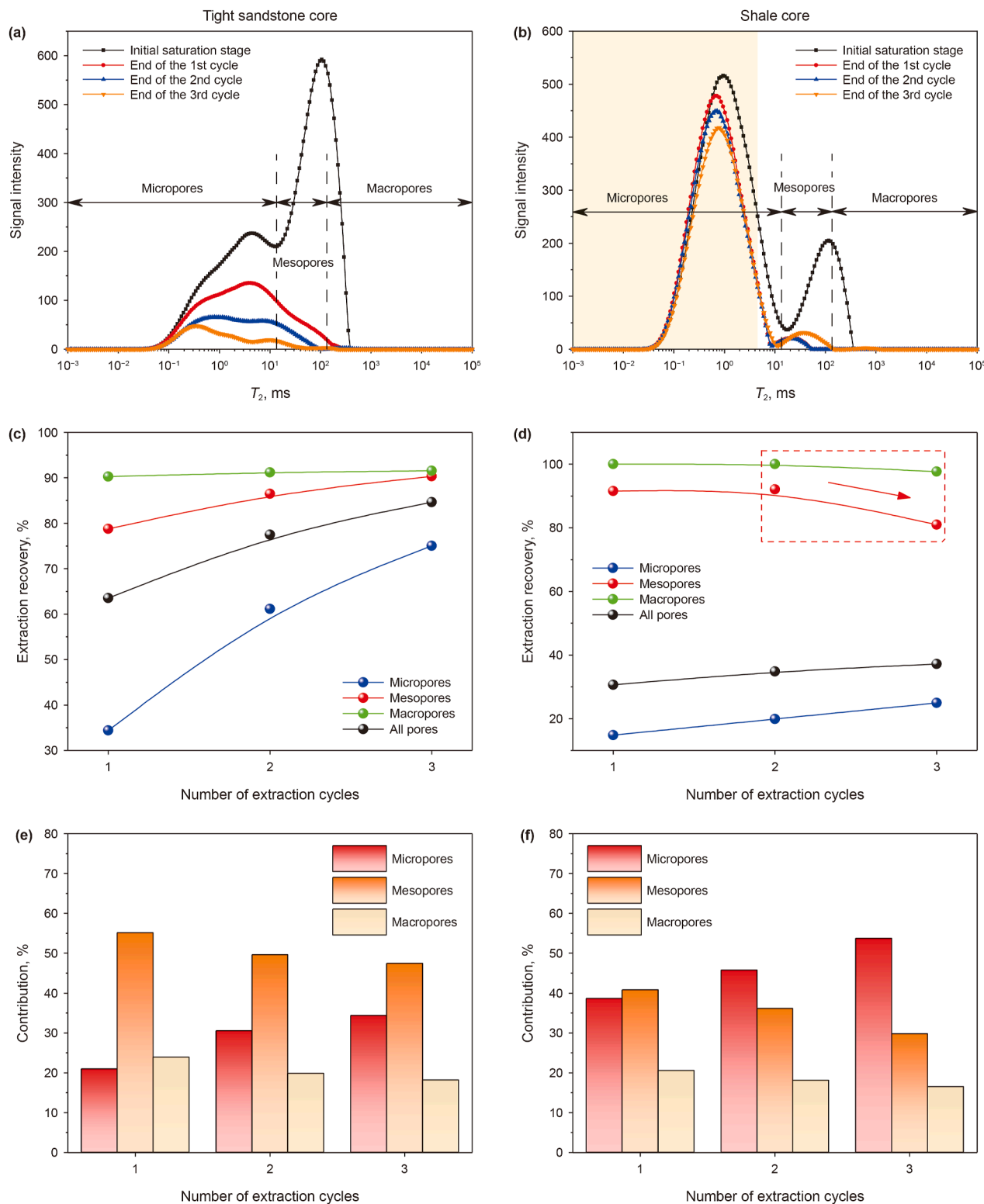


Fig. 6. Extraction efficiencies of CO₂ from tight sandstone and shale cores under different extraction cycles. (a, b) T₂ spectra of tight sandstone and shale cores; (c, d) extraction recoveries from micropores, mesopores, and macropores in tight sandstone and shale cores; (e, f) contributions of different types of pores to extraction recovery.

matrix, shale oil migrates from micropores to mesopores and subsequently into macropores. Therefore, cyclic CO₂ injection is of great significance for enhancing shale oil recovery (Gamadi et al., 2014).

Furthermore, the contribution of the oil extracted from different types of pores to the overall extraction recovery was calculated. Fig. 6(e) and (f) shows the contribution of different types of pores in tight sandstone and shale cores to extraction recovery under

Table 2
Oil content in different types of pores in tight sandstone and shale cores.

Core type	Initial oil content in different types of pores, %			Initial oil content in all pores, %
	Micropores	Mesopores	Macropores	
Tight sandstone core	38.72	44.45	16.83	100.00
Shale core	80.04	13.67	6.29	100.00

different extraction cycles. For both core types, as the number of extraction cycles increased, the contribution of micropores to the extraction recovery gradually increased, while the contributions of mesopores and macropores gradually decreased. After three CO₂ extraction cycles, the contributions of micropores, mesopores, and macropores to the total extraction recovery were 34.36%, 47.45%, and 18.20% for the tight sandstone core, and 53.74%, 29.74%, and 16.52% for the shale core, respectively. The increasing contributions from micropores and mesopores indicate a further enhancement in oil production capacity.

The mobilization capacity of CO₂ towards absorbed oil, adsorbed oil, and free oil in the shale core was quantitatively evaluated. Based on the method illustrated in Fig. 5, the absorbed and adsorbed oil together accounted for 73.41%, while the free oil constituted 26.59%, meaning that the combined content of absorbed and adsorbed oil was 2.76 times that of the free oil. After three CO₂ extraction cycles, the recovery for absorbed and adsorbed oil was 21.09%, whereas that for free oil reached 81.73%. The mobilization efficiency of free oil was 3.87 times higher than that of absorbed and adsorbed oil. As indicated in Fig. 6(b), the absorbed and adsorbed oil are predominantly located within the micropores of the shale. Absorbed and adsorbed oil have strong interactions with organic kerogen. Competitive adsorption among CO₂, shale oil, and kerogen is the primary reason for the low recovery of absorbed and adsorbed oil (Dong et al., 2022). Therefore, effectively mobilizing the oil within shale micropores, particularly absorbed and adsorbed oil, is key to enhancing shale oil recovery.

The T_2 cutoff pore diameters of the tight sandstone and shale cores were further determined to identify the pore size ranges that predominantly contribute to the major oil production. Fig. 7 shows the T_2 cutoff pore sizes of tight sandstone and shale cores under different extraction cycles. With increasing CO₂ extraction cycles, the T_2 cutoff pore diameter shows a gradual decreasing trend for both core types. After three extraction cycles, the T_2 cutoff pore diameters for the tight sandstone core were 45.85, 10.99, and 3.96 nm, respectively. For the shale core, the corresponding T_2 cutoff pore diameters were 26.00, 20.21, and 17.63 nm. The mobilization capacity of CO₂ for

oil in smaller pores is progressively enhanced, which is closely related to the deep diffusion of CO₂ within the core matrix. Therefore, enhancing the deep penetration of CO₂ within shale reservoirs is of great significance for improving oil recovery.

3.3. Effects of fractures on CO₂ extraction efficiency

For shale reservoirs characterized by low porosity and low permeability, large-scale hydraulic fracturing is essential. The created fracture networks facilitate the diffusion of CO₂ within the reservoir, thereby enhancing oil recovery from the matrix. This section investigates the influence of fractures on the effectiveness of CO₂ extraction. Samples, including a naturally fractured shale core, shale block samples, and tight sandstone block samples, were selected to simulate the enhanced CO₂ extraction process in reservoirs with highly developed fractures. The naturally fractured shale core contains multiple through-going fractures and complex natural fractures, serving as a comparison to the shale core used in Section 3.2. Shale block samples and tight sandstone block samples are compared with the naturally fractured shale core to highlight the influence of higher development degree of fractures for CO₂ extraction efficiency.

The T_2 spectra of the naturally fractured shale core, shale block samples, and tight sandstone block samples under different extraction cycles are shown in Fig. 8(a)–(c). In the naturally fractured shale core, saturated oil is predominantly stored in mesopores and macropores, with relatively lower oil content present in micropores. The naturally fractured shale core contains several throughgoing fractures that effectively connect to natural microfractures, significantly altering the internal pore structure of the core. Saturated oil in the shale block samples also predominantly resides in mesopores and macropores, showing a distribution pattern similar to that of the naturally fractured shale core. In contrast, saturated oil in the tight sandstone block samples is primarily located within micropores, aligning with the distribution observed in the tight sandstone core (Lei et al., 2023b).

As the number of extraction cycles increased, the oil content in the macropores and mesopores of the naturally fractured shale core significantly decreased, as CO₂ diffused more readily into these pores,

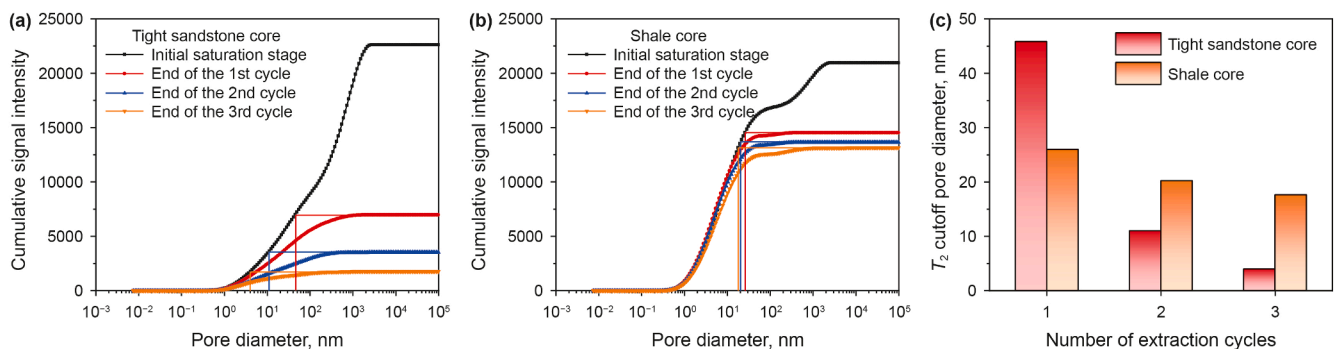


Fig. 7. T_2 cutoff pore sizes of tight sandstone and shale cores under different extraction cycles. (a, b) Cumulative signals of tight sandstone and shale cores under different extraction cycles; (c) T_2 cutoff pore sizes of tight sandstone and shale cores under different extraction cycles.

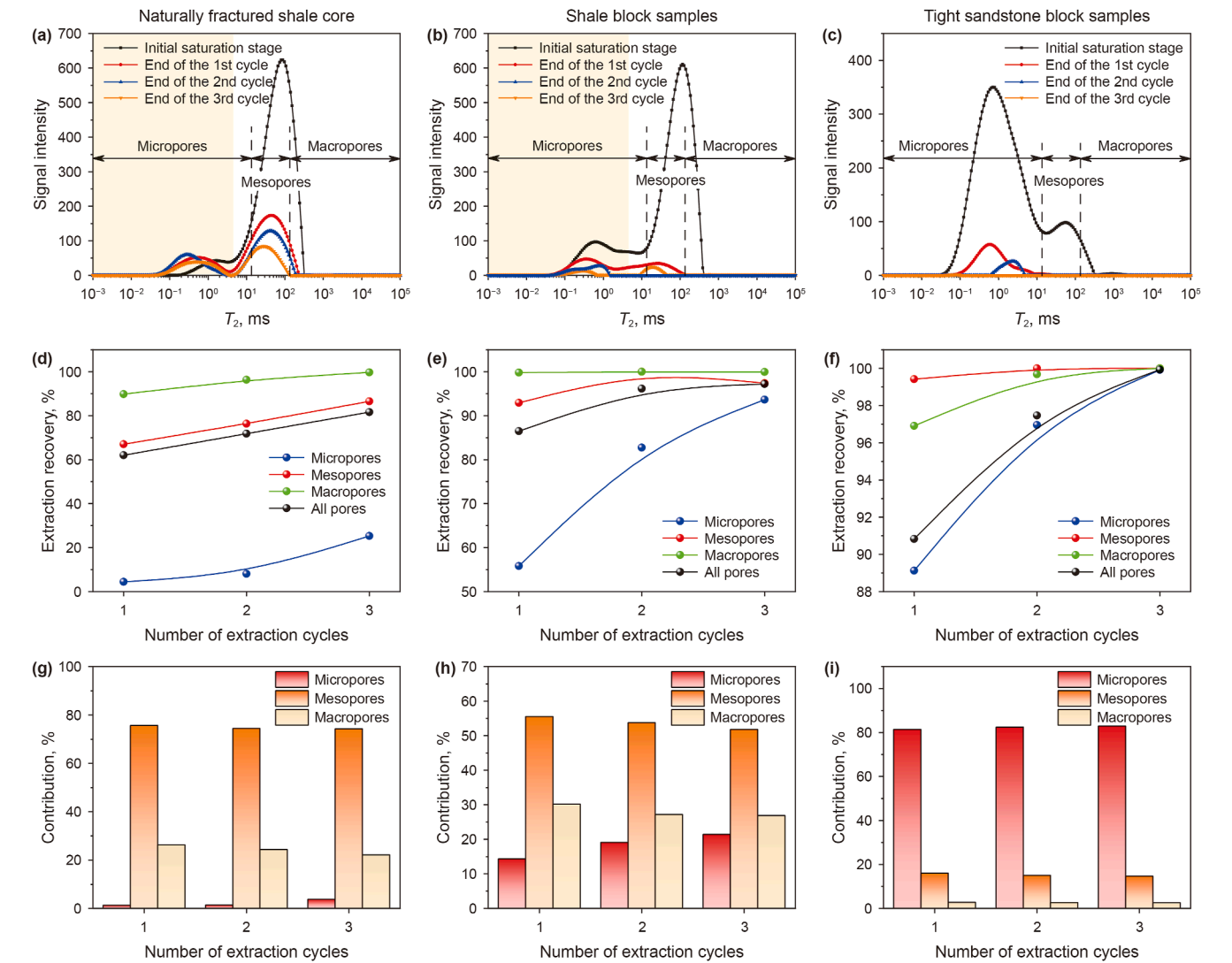


Fig. 8. Extraction recoveries of CO₂ from naturally fractured shale core (left), shale block samples (center), and tight sandstone samples (right). (a–c) T_2 spectra; (d–f) extraction recovery; (g–i) contributions of different pore types.

resulting in higher extraction efficiency. After three CO₂ extraction cycles, the oil content in both the shale block samples and the tight sandstone block samples was very low, indicating a significant improvement in extraction effectiveness. Table 3 presents the oil content in micropores, mesopores, and macropores of the naturally fractured shale core, shale block samples, and tight sandstone samples. Simultaneously, the extraction recovery of CO₂ for oil in different pore types was quantitatively calculated, as shown in Fig. 8(d)–(f). In the naturally fractured shale core, the oil content in mesopores is the highest, accounting for 69.97%, followed by macropores at 18.09%, and micropores at 11.93%. After three CO₂ extraction cycles, the extraction recovery of CO₂ to the naturally fractured shale core reaches 81.60%, which is 2.19 times that of the shale core discussed in

Section 3.2. These results indicate that the presence of fractures greatly enhances CO₂ extraction efficiency. For the shale block samples, oil distribution was 22.19% in micropores, 51.68% in mesopores, and 26.13% in macropores. After three CO₂ extraction cycles, the oil extraction recovery exceeded 90% across all pores, achieving a total extraction recovery of 97.23%. For the tight sandstone block samples, the total extraction recovery reached 99.93%, indicating that nearly all the saturated oil was extracted. In reservoirs with highly developed fractures, the contact area between CO₂ and the matrix increases substantially, enabling CO₂ to rapidly diffuse into the matrix (Yu et al., 2021). These results demonstrate that CO₂ enhanced extraction is highly significant for shale and tight reservoirs with well-developed fracture networks. Increasing the contact area

Table 3
Oil content in different types of pores in naturally fractured shale core, shale block samples, and tight sandstone samples.

Core type	Initial oil content in different types of pores, %			Initial oil content in all pores, %
	Micropores	Mesopores	Macropores	
Naturally fractured shale core	11.93	69.97	18.10	100.00
Shale block samples	22.19	51.68	26.13	100.00
Tight sandstone block samples	82.88	14.61	2.51	100.00

between CO₂ and the rock matrix facilitates CO₂ diffusion into different types of pores, thereby improving the overall oil recovery.

The contributions of different pore types to the extraction recovery across various samples were analyzed in depth to elucidate the impact of pore size on oil recovery. Fig. 8(g)–(i) shows the contributions of different pore types in the fractured shale core, shale block samples, and tight sandstone block samples to extraction recovery under different extraction cycles. The contributions of different pore types to the extraction recovery are consistent with the conclusions presented in Section 3.2. It is noteworthy that for both the naturally fractured shale core and the shale block samples, mesopores contribute the most to the total extraction recovery. In contrast, micropores make the greatest contribution in tight sandstone block samples. Therefore, it is concluded that the contribution of different pore types to the extraction recovery depends primarily on the

two factors: the initial oil saturation within each pore type and the extent of deep diffusion of CO₂ into the rock matrix.

The extraction mechanisms of CO₂ on absorbed oil, adsorbed oil, and free oil under conditions of highly developed fractures in the reservoir are further analyzed. Table 4 shows the extraction recovery of different types of oil in naturally fractured shale core and shale block samples. Compared to the shale core, the initial content of absorbed and adsorbed oil in the naturally fractured shale core and shale block samples was less than 20%, while the free oil content accounted for 93.81% and 82.16%, respectively. The extraction recovery of CO₂ for absorbed and adsorbed oil in the shale block samples reached as high as 93.60%. This result strongly demonstrates that enhancing the diffusion capacity of CO₂ can significantly improve its ability to mobilize shale oil. However, the absorbed and adsorbed oil content in the naturally fractured shale core increased. This is attributed to the fact that

Table 4
Extraction recoveries of different types of oil in naturally fractured shale core and shale block samples.

Sample type	Absorbed and adsorbed oil		Free oil	
	Initial content, %	Extraction recovery, %	Initial content, %	Extraction recovery, %
Naturally fractured shale core	6.19	–14.57	93.81	87.94
Shale block samples	17.84	93.60	82.16	98.03

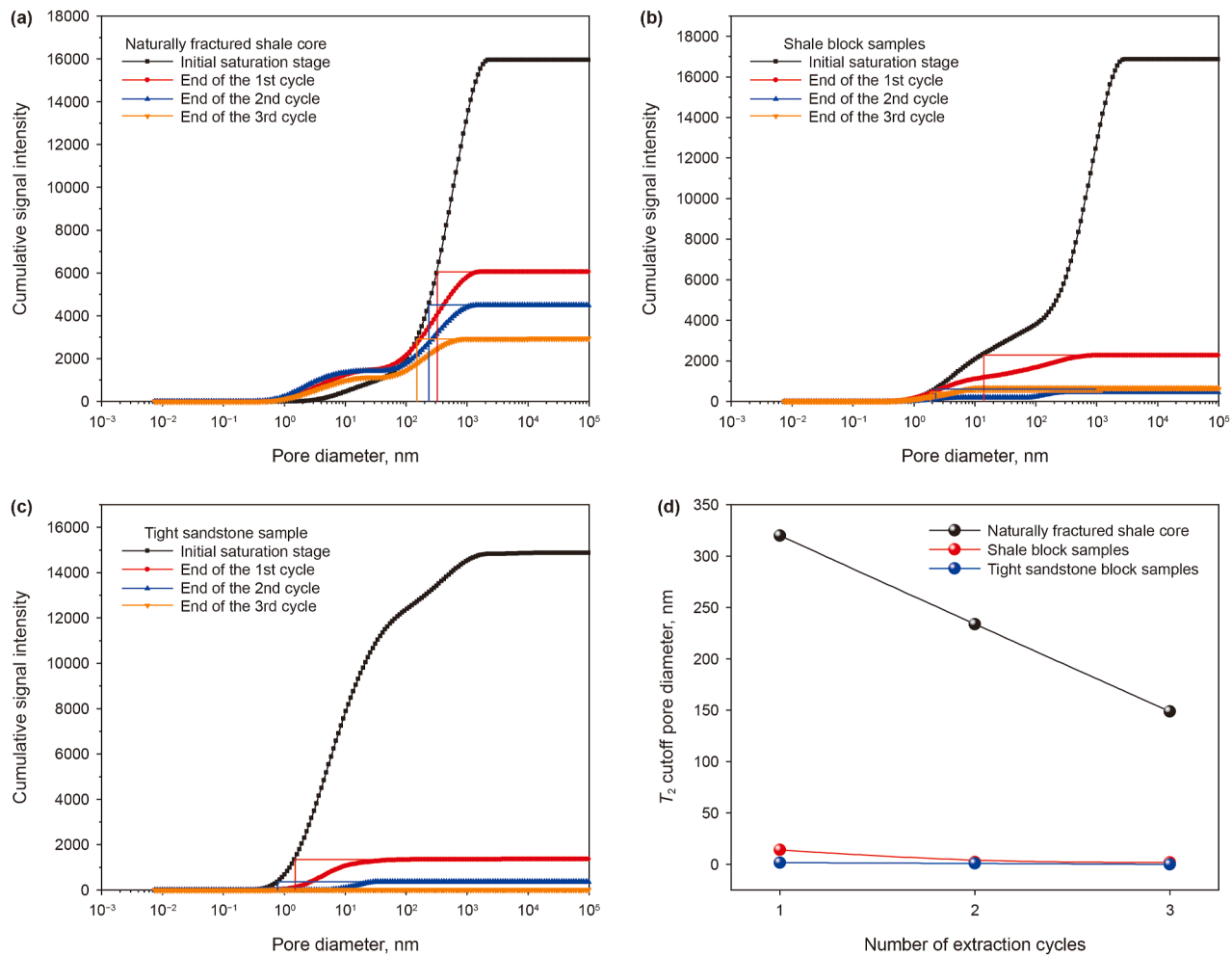


Fig. 9. T₂ cutoff pore sizes of naturally fractured shale core, shale block samples, and tight sandstone samples under different extraction cycles. (a–c) Cumulative signals; (d) T₂ cutoff pore sizes.

during the diffusion of CO₂ into the core matrix, part of the oil dissolved in CO₂ encountered strong interactions with organic matter and significant migration resistance, resulting in some oil being retained within the micropores.

Fig. 9 shows the T_2 cutoff pore sizes of naturally fractured shale core, shale block samples, and tight sandstone block samples under different extraction cycles. The results indicate that as the number of extraction cycles increased, the oil production capacity from smaller pores is progressively enhanced. The T_2 cutoff pore diameters for the naturally fractured shale core, shale block samples, and tight sandstone block samples are 148.65, 1.84, and 0.07 nm, respectively. For both the shale block samples and the tight sandstone block samples, the T_2 cutoff pore diameters were very small after the first CO₂ extraction cycle. This indicates that increasing the contact area between the injected fluid and the rock matrix facilitates the mobilization of oil from micropores. Therefore, it can be concluded that the T_2 cutoff pore size correlates with the pore size of the primary oil-bearing pores and the enhanced extraction efficiency of CO₂.

3.4. Effect of polyether surfactant on CO₂ extraction efficiency

In previous study, surfactant C₄EO₃PO₆ has demonstrated effective performance in reducing the interfacial tensions between CO₂ and shale oil as well as between CO₂ and water, while also enhancing the extraction and expansion effects of CO₂ on the oil. In this section, C₄EO₃PO₆ was dissolved in CO₂ to construct the CO₂–surfactant composite system, and the extraction effect on cores with different properties was further studied. Our previous study investigated the effects of surfactant concentration on the CO₂–shale oil interfacial tension and the MMP. The research results show that when the mass fraction of C₄EO₃PO₆ is 1%, its dissolution pressure in CO₂ is 15.65 MPa, and the MMP of CO₂ and shale oil can be reduced by 21.20% (Zhang et al., 2024a). In this study, the mass fraction of C₄EO₃PO₆ is set to 1%. In this section, shale core, naturally fractured shale core, and tight sandstone core were selected as the study subjects for comparison with the results in Sections 3.2 and 3.3, in order to highlight the effect of the surfactant on CO₂ extraction effect.

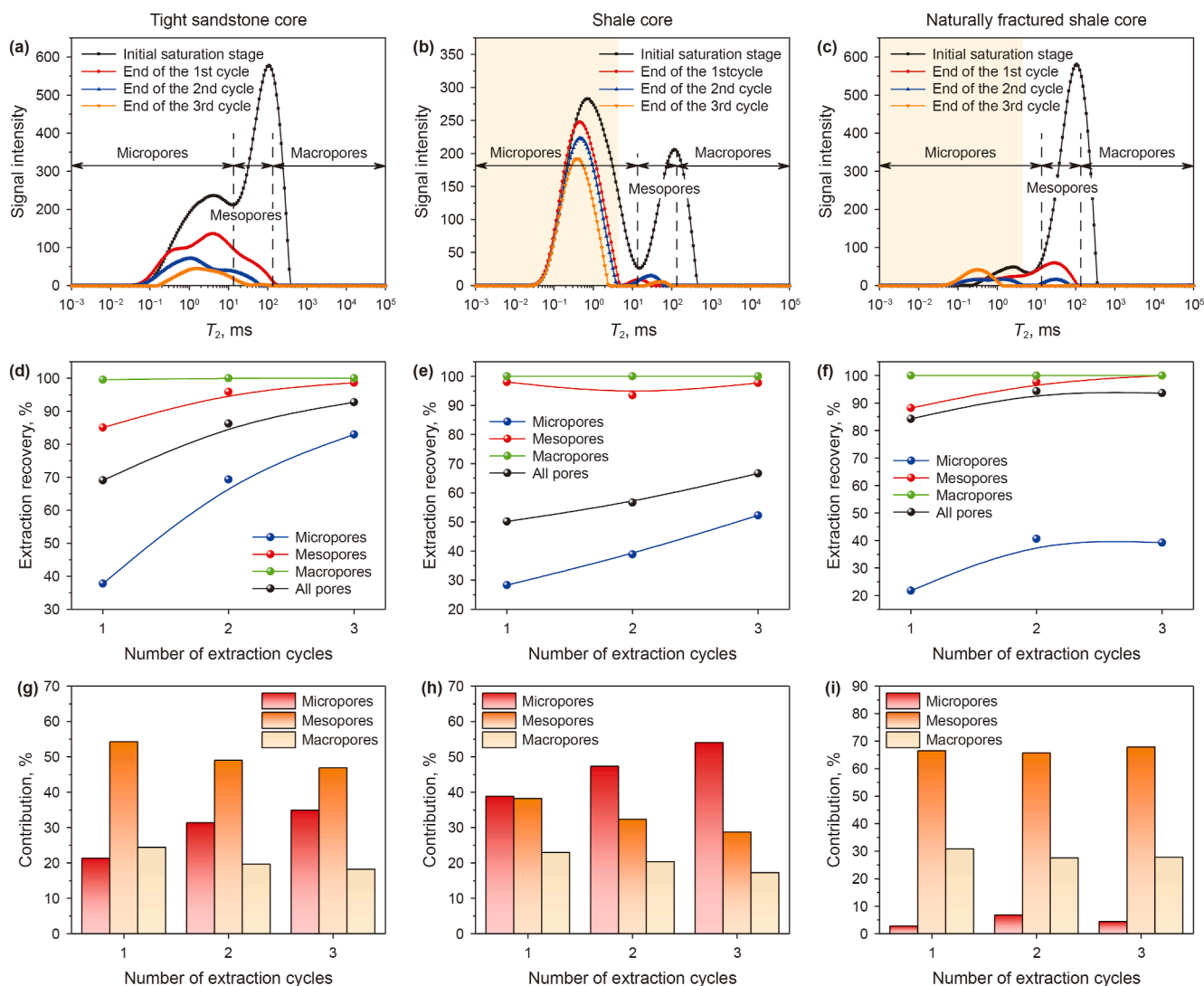


Fig. 10. Extraction recoveries of CO₂ from tight sandstone core, shale core, and naturally fractured shale core: (a–c) T_2 spectra; (d–f) extraction recoveries; (g–i) contributions of different pore diameters.

Fig. 10(a)–(c) shows the T_2 spectra of tight sandstone core, shale core, and naturally fractured shale core under different extraction cycles. As the number of extraction cycles using CO_2 –surfactant composite system increased, oil was more readily extracted from the macropores and mesopores of all three core types. Subsequently, oil in the micropores was gradually mobilized as well. The extraction recovery of oil from different cores with varying pore diameters after adding surfactant to CO_2 was quantitatively analyzed.

Table 5 lists the oil content in different pore types within tight sandstone core, shale core, and naturally fractured shale core. The extraction recoveries of the CO_2 –surfactant composite system from all three core types are shown in Fig. 10(d)–(f). After three extraction cycles using CO_2 –surfactant composite system, the extraction recoveries for tight sandstone core, shale core, and naturally fractured shale core reached 92.75%, 66.64%, and

93.61%, respectively. Compared to the pure CO_2 without surfactant (the results presented in Sections 3.2 and 3.3), the extraction recoveries increased by 8.12%, 29.43%, and 12.01%, respectively. Following the three extraction cycles, the oil extraction recoveries from the micropores in the three core types were 82.96%, 52.24%, and 39.27% and increased by 7.87%, 27.25%, and 14.00%, respectively. The addition of surfactant resulted in the greatest increase in oil production from shale micropores, further improving the recovery of shale core. Notably, while the surfactant significantly enhanced extraction recovery from micropores, it also achieved near-complete extraction of oil from the macropores and mesopores across all three core types. These results provide strong evidence that the surfactant enhances CO_2 diffusion into the matrix and accelerates interactions between CO_2 and shale oil.

Oil production from different pore size ranges within the core was quantitatively analyzed, and the contributions of different pore

Table 5

Oil content in different pore sizes of tight sandstone core, shale core, and naturally fractured shale core.

Core type	Initial oil content in different types of pores, %			Initial oil content in all pores, %
	Micropores	Mesopores	Macropores	
Tight sandstone core	39.02	44.06	16.92	100.00
Shale core	68.92	19.58	11.50	100.00
Naturally fractured shale core	10.49	63.53	25.97	100.00

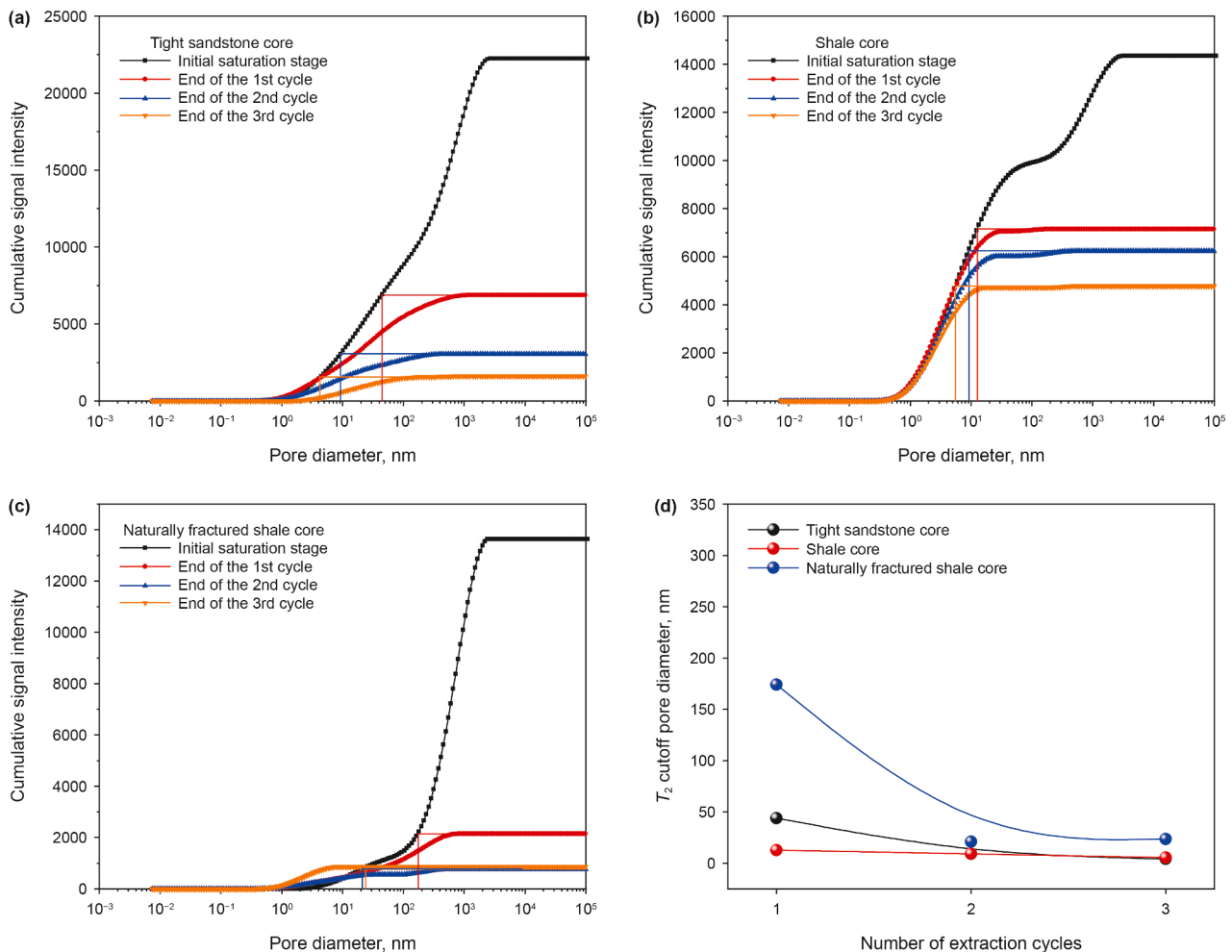


Fig. 11. T_2 cutoff pore sizes of tight sandstone core, shale core, and naturally fractured core under different extraction cycles. (a–c) Cumulative signals; (d) T_2 cutoff pore sizes.

types in tight sandstone core, shale core, and naturally fractured shale core to extraction recovery under different extraction cycles are presented in Fig. 10(g)–(i). In tight sandstone and naturally fractured shale cores, mesopores contribute more significantly to oil production, whereas in the shale core, micropores contribute the most. After three extraction cycles using the CO₂–surfactant composite system, the contribution of shale micropores to the total extraction recovery is 54.02%, while mesopores and macropores contribute 28.71% and 17.27%, respectively. With increasing extraction cycles, CO₂ enhances the ability to mobilize oil from smaller pores within the core. The addition of surfactants to CO₂ further improves the extraction efficiency, thereby increasing shale oil recovery.

Table 6 presents the extraction recovery of different types of oil from shale core and naturally fractured shale core. After three extraction cycles using a CO₂–surfactant composite system, the extraction recoveries for absorbed/adsorbed oil and free oil in the shale core reached 48.41% and 98.78%,

respectively, representing increases of 27.31% and 17.04% compared to extraction without surfactant. In the naturally fractured shale core, the extraction recoveries of absorbed/adsorbed oil and free oil increased by 27.33% and 12.04%, respectively, relative to those without surfactant. These results demonstrate that adding surfactant to CO₂ significantly enhances the extraction efficiency of CO₂, and the extraction recoveries of absorbed/adsorbed oil and free oil are improved. The presence of surfactant facilitates the dissolution of CO₂ into kerogen, strengthens competitive adsorption, and weakens the interactions between absorbed oil, adsorbed oil and kerogen (Zhao et al., 2021).

Fig. 11 shows the T₂ cutoff pore sizes of tight sandstone core, shale core, and naturally fractured shale core under different extraction cycles using the CO₂–surfactant composite system. After adding surfactant to CO₂, the T₂ cutoff pore size decreased by 1.80–1.89 nm for tight sandstone, 11.02–13.41 nm for the shale

Table 6
Extraction recoveries of different types of oil in shale core, and naturally fractured shale core.

Sample type	Absorbed and adsorbed oil		Free oil	
	Initial content, %	Extraction recovery, %	Initial content, %	Extraction recovery, %
Shale core	63.79	48.41	36.21	98.78
Naturally fractured shale core	7.31	12.76	92.69	99.98

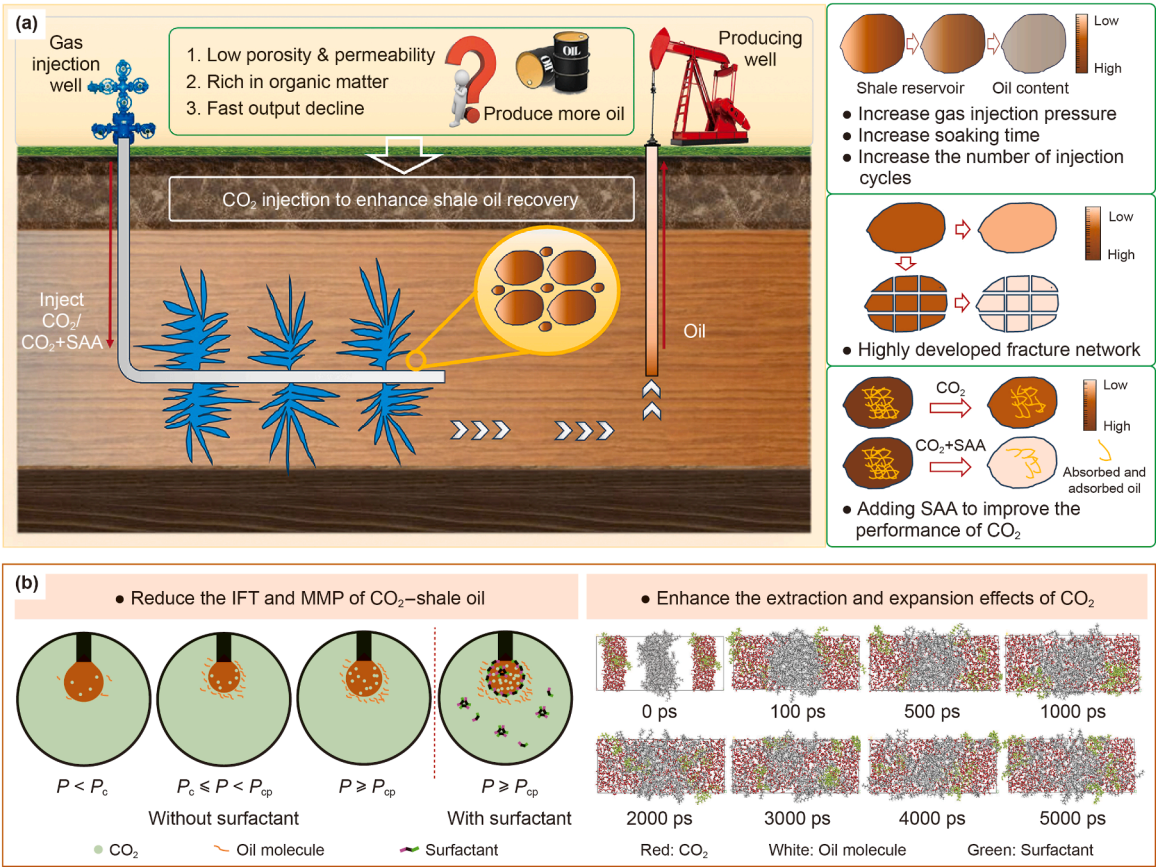


Fig. 12. Schematic diagram of CO₂-enhanced shale oil recovery. (a) Synergistic mechanisms of CO₂ extraction enhanced by fractures and surfactants; (b) effect of the polyether surfactant C₄EO₃PO₆ (Zhang et al., 2024a, 2025).

core, and 125.00–212.65 nm for naturally fractured shale core. These results indicate the reductions in the T_2 cutoff pore sizes for all core types, indicating that CO_2 can extract more oil from smaller pores. This effectively enhances the mobilization of shale oil, thereby improving shale oil recovery. Dissolving $\text{C}_4\text{EO}_3\text{PO}_6$ in CO_2 and utilizing hydraulic and natural fractures to increase the contact area between the CO_2 composite system and the matrix will unlock substantial potential for shale oil development.

3.5. Mechanisms of CO_2 -enhanced shale oil recovery

Addressing the challenges of low porosity and permeability, high organic content, and rapid production decline in shale reservoirs, CO_2 injection has emerged as one of the most promising technologies for shale oil development. This section discusses the mechanisms responsible for CO_2 -enhanced shale oil recovery, with a particular focus on the extraction mechanism of CO_2 . Fig. 12 shows a schematic diagram illustrating the CO_2 -enhanced extraction effect for improved shale oil recovery, as well as the effect of the polyether surfactant $\text{C}_4\text{EO}_3\text{PO}_6$.

This study and previous research have demonstrated that increasing soaking time, injection pressure, and the number of injection cycles during CO_2 flooding and the CO_2 huff-and-puff process enhances oil recovery (Gamadi et al., 2014; Li et al., 2021; Wang et al., 2024). A longer injection time allows CO_2 to diffuse deeper into the matrix, contacting more oil stored in nanopores. Higher injection pressure increases CO_2 density, its solubility in crude oil, and the extraction efficiency, thereby improving the mass transfer and diffusion of CO_2 in shale oil (Yu et al., 2021; Zhu et al., 2021). In addition, multiple injection cycles enable CO_2 to diffuse deeper into the matrix and contact more oil stored in nanopores. Therefore, these injection parameters collectively improve the sweep efficiency and oil mobilization capability of CO_2 in shale reservoirs.

Shale reservoirs are rich in organic matter, resulting in the coexistence of shale oil in the forms of absorbed oil, adsorbed oil, and free oil. However, the absorbed oil and adsorbed oil exhibit strong interactions with kerogen, making them difficult to mobilize, this is one of the primary reasons for low recovery (Liu et al., 2025a). The synergistic effect of fractures and surfactants can effectively “unlock” shale oil trapped within the micro- and nano-scale pore throats of the matrix. On the one hand, large-scale hydraulic fracturing creates artificial fractures that connect with natural fractures in the reservoir. This complex fracture network facilitates the diffusion of CO_2 into the rock matrix and its dissolution in shale oil. Studies indicate that CO_2 exhibits a more pronounced extraction efficiency in the naturally fractured shale, with a greater amount of oil extracted from micropores. On the other hand, the polyether surfactant $\text{C}_4\text{EO}_3\text{PO}_6$ can significantly reduce the interfacial tension between CO_2 and shale oil, lower the MMP, and enhance extraction and expansion effects (Zhang et al., 2024a, 2025). Meanwhile, surfactants can enhance the competitive adsorption of CO_2 and kerogen, thereby mobilizing both absorbed and adsorbed shale oil more effectively. Further reductions in application costs and improvements in technological maturity will help accelerate the progress of the shale oil revolution.

Incomplete flowback of fracturing fluid results in a large amount of water being retained in the near-wellbore region. The impact of water barrier on CO_2 flooding for shale oil development warrants further investigation. Furthermore, given the presence of hydrophilic groups in the $\text{C}_4\text{EO}_3\text{PO}_6$ molecular structure, the performance of the CO_2 - $\text{C}_4\text{EO}_3\text{PO}_6$ composite system in water-bearing shale reservoirs will be investigated in the future.

4. Conclusions

This study revealed the mechanisms of CO_2 -enhanced shale oil recovery and conducted a comprehensive analysis of the factors influencing the CO_2 extraction efficiency, including CO_2 injection parameters, core properties, and fractures. Concurrently, the effectiveness of surfactants in enhancing shale oil recovery was evaluated. Based on this study, the major findings and conclusions are presented below.

- (1) Using a 3A molecular sieve with a standard pore size as a reference, a method for determining the pore size limits of movable shale oil was established. The calculated conversion coefficient between the T_2 relaxation time and core pore diameter is 0.1341 ms/nm. This method is nondestructive to the experimental samples, highly repeatable, easy to operate, and of significant practical value.
- (2) The effects of CO_2 injection parameters on shale oil recovery were comprehensively analyzed. Increasing injection time, injection pressure, and the number of injection cycles allows CO_2 to diffuse deeper into the matrix and contact more oil stored in nanopores. Meanwhile, the solubility of CO_2 in shale oil further increases, thereby enhancing mass transfer and diffusion of CO_2 in shale oil and improving CO_2 sweep efficiency.
- (3) Under comparable core permeability and porosity conditions, the CO_2 extraction recovery from tight sandstone is 2.2 times higher than that from shale. The oil contained within shale micropores and nanopores is more difficult to mobilize because the absorbed and adsorbed oil strongly interacts with organic matter. The mobilization efficiency of free oil is 3.87 times higher than that of absorbed and adsorbed oil. Therefore, further improving the mobilization of bound oil is essential to enhance shale oil recovery.
- (4) The synergistic effect of fractures and surfactants can effectively “unlock” shale oil trapped within the micro- and nano-scale pore throats of the matrix. A complex fracture network facilitates the diffusion of CO_2 into the rock matrix and its dissolution in the shale oil. Studies indicate that CO_2 exhibits a more pronounced extraction efficiency in naturally fractured shale and a greater amount of oil is extracted from micropores. Meanwhile, surfactants enhance the competitive adsorption between CO_2 and kerogen, thereby mobilizing both absorbed and adsorbed shale oil more effectively.

CRedit authorship contribution statement

Huan Zhang: Writing – original draft, Methodology, Investigation, Formal analysis. **Ming-Wei Zhao:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Hou-Jian Gong:** Writing – review & editing, Investigation, Funding acquisition, Formal analysis. **Cai-Li Dai:** Resources, Project administration, Methodology, Funding acquisition. **Ming-Zhe Dong:** Resources, Investigation. **Xin Li:** Methodology, Investigation. **Zhen-Feng Ma:** Methodology, Investigation. **Zhi-Hao Zhang:** Methodology, Investigation. **Zhong-Zheng Xu:** Methodology, Investigation. **Xin-Jie Xu:** Methodology, Investigation.

Declaration of competing interest

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.

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