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Invited review

Recovery mechanisms and formation influencing factors of miscible CO_2 huff-n-puff processes in shale oil reservoirs: A systematic review

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Abstract:
Shale oil production is vital for meeting the rising global energy demand, while primary recovery rates are poor due to the ultralow permeability. CO_2 huff-n-puff can boost yields by enabling key enhanced oil recovery mechanisms. This review examines the recent research on mechanisms and formation factors influencing CO_2 huff-n-puff performance in shale liquid reservoirs. During the soaking period, oil swelling, viscosity reduction and CO_2-oil miscibility occur through molecular diffusion into shale nanopores. The main recovery mechanism during the puff period is depressurization with oil desorption and elastic energy release. The interplay between matrix permeability and fracture network directly determines the CO_2 huff-n-puff performance. Nanopore confinement, wettability alterations, and heterogeneity also significantly impact the huff-n-puff processes, with controversial effects under certain conditions. This work provides an integrated discussion on the mechanistic insights and formation considerations essential for the advancement of CO_2 huff-n-puff application in shale reservoirs. By synthesizing the recent research findings, we aim to spotlight the key challenges and opportunities in considering reservoirs for this process, thereby contributing to the advancement of CO_2 huff-n-puff applications for enhanced oil recovery.

1. Introduction

The future of global energy is of critical concern due to the expected 47% rise in global energy demand over the upcoming 30 years, driven mainly by both urbanization and economic expansion in rapidly developing nations (Soliman et al., 2021). To meet this demand, a substantial need has arisen for ever-growing fossil production (IEA, 2022). Hydrocarbon resources are projected to make up 28% of the international energy expenditure before the midpoint of the 21st century, with sustainable energy sources accounting for 27%, marking a 36% rise in the requirement for liquid fuels and a remarkable 165% elevation in renewable energy compared to the 2020 levels. Despite the ongoing shift toward renewable energy, the growing demand for fossil fuels necessitates exploring alternative sources, such as shale reservoirs. Hydrocarbon recovery from these reservoirs needs cutting-edge methods such as horizontal borehole drilling, hydraulic fracturing, and enhanced oil recovery (EOR) strategies (Sheng, 2017; Jiang et al., 2022; Sambo et al., 2023). As such, shale oil reservoirs require advanced drilling techniques for optimal hydrocarbon production. Horizontal wells or maximum reservoir contact wells, created through extended reach drilling, enhance reservoir exposure (Wang et al., 2017b; Meng et al., 2020; Deng et al., 2022). When combined with hydraulic fracturing, maximum reservoir contact wells boost hydrocarbon flow

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Table 1. Comparison of the attributes of conventional and unconventional EOR techniques.

Conventional EOR	Unconventional EOR
Prolonged enhancement in estimated ultimate recovery	Only short-term production restoration
Considerable recovery enhancement	Rapid oil production acceleration
Sustained injection of external fluids	Unable to sustain injection/limited external fluid injectivity
Observable mechanics of fluid movement in the matrix	Intricate movement of fluids through natural fractures and nanopores
Targets in-place reservoir volume	Exclusively in the vicinity of the wellbore or in areas with localized fracturing Stimulated reservoir volume is the goal
Development plans based on multiple productions & injection wells	In general, individual well (huff-n-puff) development plans work more efficiently
Mid to late full lifespan utilization	Early life-cycle application
Minimal to moderate levels of risk	High-risk factors present

from the matrix to fractures, increasing the production rates (Zhao et al., 2021; Syed et al., 2022b). Despite technological advancements, the impact of these methods is frequently short-lived owing to the tiny pore space and ultra-low permeability of shale oil reservoirs (Cao et al., 2017; Wanyan et al., 2023), resulting in a low primary depletion recovery rate.

In order to improve the recovery rates, further research and development of EOR techniques are essential both in academia and the petroleum industry. To our knowledge, a 1% increase in estimated ultimate recovery (EUR) can yield significant additional oil (Syed et al., 2022a). Conventional EOR relies on the sustained injection of external fluids, while unconventional methods focus on local areas, posing higher risks due to the incomplete understanding of fluid flow physics and chemical processes. Fluid flow through natural fractures and nanopores presents challenges in unconventional EOR (Sheng, 2017). A comparison of conventional and unconventional EOR techniques is illustrated by Table 1. Gas injection, particularly CO_2, has been distinguished as a potent EOR technique for shale oil reservoirs due to various mechanisms (Saini, 2018; Kumar et al., 2022; Yuan et al., 2023). CO_2, with its lower minimum miscibility pressure (MMP) and other advantages, is preferred for miscible gas EOR (Habibi et al., 2017; Li et al., 2019a). Secondly, CO_2 exhibits higher injectivity (Thakur, 2019) and larger sweep efficiency (Li et al., 2019a). Additionally, CO_2 EOR can mitigate climate change through carbon capture, utilization and storage (Hill et al., 2020; Jiang et al., 2022; Wei et al., 2023).

Continuous CO_2 injection (Hu et al., 2019; Lan et al., 2019; Wang et al., 2020; Awag et al., 2023) and CO_2 huff-n-puff (Pu et al., 2016; Alfarge et al., 2017; Li et al., 2019a; Zhou et al., 2022) are common injection methods for shale oil reservoirs, with the latter being more efficient for low-permeability formations (Zuloaga et al., 2017; Tang and Sheng, 2022). This review aims to provide an integrated analysis of recent research on CO_2 huff-n-puff mechanisms and formation influencing factors in shale oil reservoirs and give insights into future areas of study. For clarity, a broad definition of shale oil is adopted in this paper, encompassing both tight or shale oils, given the shared low-permeability characteristics. The interchangeable use of these terms reflects the lack of a universally agreed-upon differentiation (Sambo et al., 2023).

2. The CO_2 huff-n-puff process

The CO_2 huff-n-puff process is commonly used for EOR following hydraulic fracturing in the target oil reservoir. It comprises three main stages: Injection, soaking and production, as illustrated in Fig. 1. During the injection or “huff” stage (Fig. 1(a)), CO_2 is injected into the reservoir via the wellbore, initially flowing through fractures and infiltrating the matrix due to pressure gradients. This can either displace oil into fractures, aiding recovery, or carry oil deeper into the formation, hindering EOR goals (Lee et al., 2019a). During this “huff” stage, the formation is repressurized until the formation pressure is increased to the target value, while convective flow remains the dominant flow regime in the rock porosities. The soaking phase (Fig. 1(b)) suspends production to allow CO_2 diffusion and oil displacement from tight pores and low-permeability zones with the whole pressure field in the near-borehole fracture-matrix system being equalized. In fact, equilibrium reservoir pressure enables CO_2 diffusion into the matrix pores where interactions between CO_2 and in-situ oil molecules result in secondary mechanisms like oil swelling, viscosity reduction, wettability alteration, and light component extraction (bottom of Fig. 1(b)). This diffusion process further vaporizes the trapped remaining oil, enhancing the recovery factor (Chen et al., 2022). In the production phase (Fig. 1(c)), CO_2 and oil migrate to the wellbore, facilitated by depressurization and the fracture network, while a certain amount of CO_2 remains in the rock porosities for geological storage.

3. Mechanism of CO_2 huff-n-puff processes

3.1 Miscibility

In immiscible multiphase fluid flow, similar to water flooding, the interface between phases is essential and depends on interfacial tension and rock wettability, impacting residual oil saturation. For immiscible CO_2 EOR, crucial properties inclu-

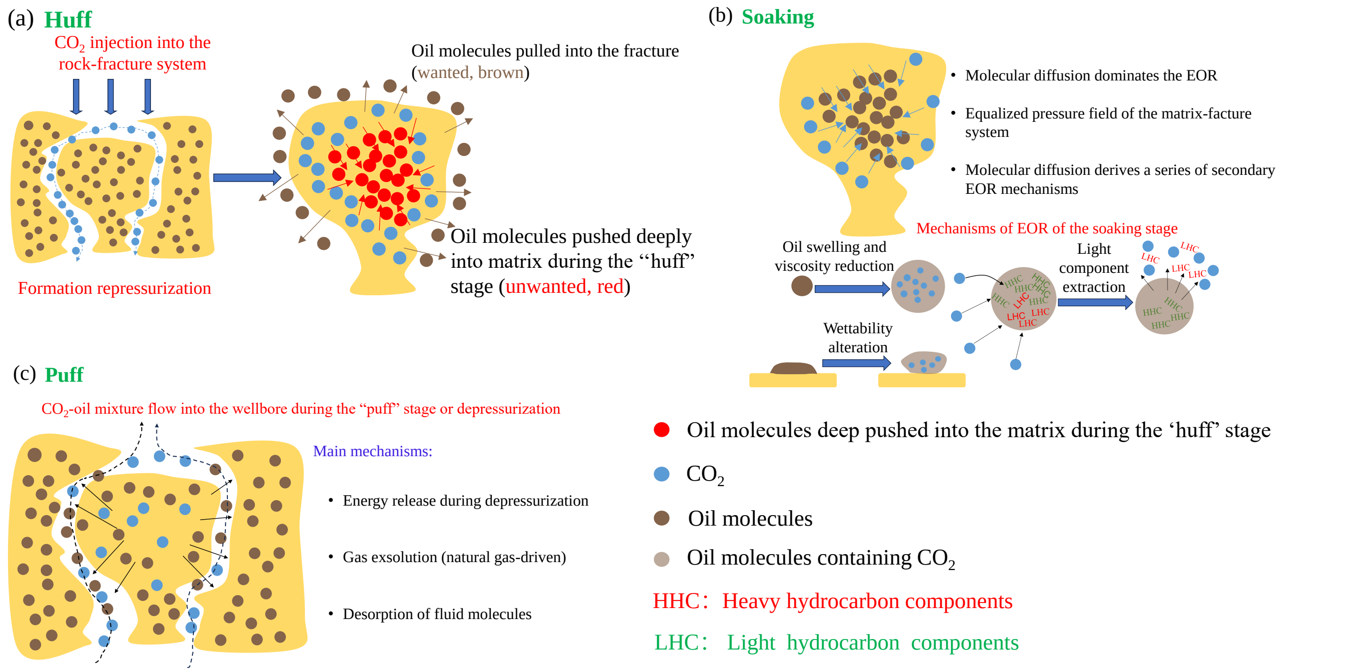

Fig. 1. Schematic diagram of the three stages of CO_2 huff-n-puff in shale oil reservoirs.

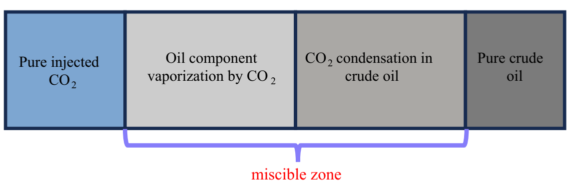

Fig. 2. Schematic diagram of Vaporization/Condensation Gas Drive or VCGD, where the miscible zone is generated between pure oil (dark gray) and pure injected CO_2 (blue) by the simultaneous CO_2 vaporization of oil components (light gray) and condensation into oil (medium gray).

de CO_2 displacement efficiency, sweep volume, and CO_2 solubility in the crude oil, which are subject to factors like gravity segregation, rock wettability, reservoir heterogeneity, phase behavior, and viscous fingering (Iwasaki et al., 2023). Removing the interfaces between CO_2 and oil appears as a direct and effective way to enhance recovery. Miscibility refers to the ability of substances to form a homogeneous mixture. CO_2 EOR means the dissolution of CO_2 into oil, requiring reservoir pressure exceeding the MMP (Elturki and Imqam, 2023). Achieving miscibility involves multiple contacts due to factors like reservoir conditions and oil composition, rather than first contact. Dynamic miscible processes encompass three mass transfer mechanisms, such as:

1) Vaporization gas drive (VGD): In VGD, CO_2 vaporizes the intermediate hydrocarbon components from crude oil as it passes through reservoir rocks, enabling more effective crude oil displacement by the solvent.
2) Condensing gas drive (CGD): CGD achieves miscibility by transferring lighter hydrocarbon components from CO_2 into the crude oil, which leads to changes in oil composition, emphasizing oil swelling and viscosity reduction.
3) Vaporization/condensation gas drive (VCGD) (Fig. 2): VCGD combines VGD and CGD, where intermediate components from crude oil vaporize into the gas phase, while CO_2 condenses into crude oil, along with lighter hydrocarbon components. This establishes a miscible zone of a certain scale.

In shale oil reservoirs, miscible CO_2 EOR outperforms immiscible methods by eliminating interfaces, reducing capillary entrapment, and extracting lighter components. While the applicability of heavy oil is limited, the dominance of light and intermediate hydrocarbons in shale oils favors miscible CO_2 EOR (Li et al., 2020; Taheri-Shakib and Kantzas, 2021; Cui et al., 2022).

3.2 Molecular diffusion

Molecular diffusion, which follows Fick's Law, involves random molecular movement from regions of higher to lower concentration (Paul et al., 2014; Hashim et al., 2023). In reservoirs with low permeability, like shales where convective flow and gravity drainage are insignificant, molecular diffusion plays a crucial role in CO_2 huff-n-puff processes (Yu et al., 2019; Wang et al., 2022; Peng and Sheng, 2023), which also leads to secondary mechanisms like swelling, viscosity reduction, and component extraction, vital for shale oil recovery. Moreover, CO_2 diffusivity during soaking determines the sweep volume (Moh et al., 2022; Wei et al., 2022; Xu et al., 2022).

The diffusion coefficient expresses the phase rate of diffu-

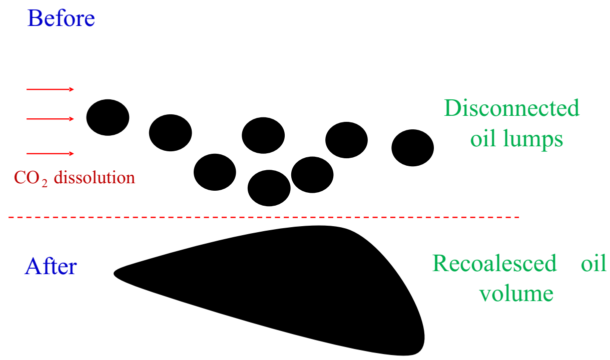

Fig. 3. Schematic showing the coalescence of disconnected oil lumps into a new big volume due to CO_2 dissolution that favors oil recovery.

sion, which is determined experimentally or through empirical correlations (Farajzadeh et al., 2007; Paul et al., 2014; Li et al., 2022). Various experimental methods exist for diffusion coefficient measurement, including nuclear magnetic resonance (NMR) (Wen et al., 2005a, 2005b; Marica et al., 2011; Muir et al., 2011), X-ray computer-assisted tomography (Wen and Kantzas, 2005b; Eide et al., 2016), and sampling analysis (Tick et al., 2007; Zheng et al., 2016). On the other hand, indirect methods observe variations in oil properties due to gas diffusion (Yang and Gu, 2006), which include the pressure-decay method (Li and Yang, 2016; Li et al., 2018), dynamic pendant drop shape analysis (Yang and Gu, 2006), and dynamic volume analysis (Hall et al., 1992; Pei et al., 2012; Zheng and Yang, 2017). Nevertheless, these methods have intrinsic limitations. In terms of the direct methods, firstly, they often require specialized equipment and techniques, making them complex, time-consuming and costly; secondly, they may require a significant volume of crude oil, which could be impractical in some situations. Lastly, direct measurements can disturb the natural state of the system, potentially affecting the diffusion process. Regarding indirect methods, they may have lower precision and accuracy compared to direct methods. At the same time, they rely on models and assumptions, which can introduce errors if the models are not perfectly representative of the system. Indirect methods may provide information on bulk properties but lack the ability to capture localized variations, especially when applied in porous media. Such methods, however, require a complicated adjustment procedure to transform experimental data into precise diffusion coefficients. In addition to experimental methods, various mathematical models exist for estimating diffusion coefficients based on factors like density, temperature, critical properties, and mole fraction, including the Sigmund method (Sigmund, 1976a, 1976b), the Wilke-Chang method (Wilke and Chang, 1955), Leahy-Dios and Firoozabadi method (Leahy-Dios and Firoozabadi, 2007), and Maxwell Stephan equations (Palancz, 1976; Rouzineau et al., 2000), among which the Sigmund and Wilke-Chang methods are the two most widely used ones.

Despite the above achievements, a significant research gap still remains in effectively measuring diffusion coefficients in oil-saturated rock samples with permeability below 0.1 mD. Therefore, the urgent development of applicable laboratory methods under in-situ reservoir conditions is required for validating some of the empirical models proposed in the literature. In the meantime, shale oil reservoirs, featured by strong heterogeneity and multiscale porosities, pose challenges regarding the prediction of CO_2 diffusion within crude oil while considering varying levels of pore confinement and pore-wall sorption effects. As a result, understanding nanoscale diffusion mechanisms in different-sized shale nanopores and their pore wall compositions necessitates thermodynamic theoretical analysis (Page et al., 2009; Alharthy et al., 2016; Hu et al., 2020), the use of numerical methods like molecular dynamics (Islam et al., 2015; Mamoudou et al., 2020; Zhu et al., 2020; Wang et al., 2022), and experimental approaches such as nanofluidics (Mehmani et al., 2019; Quintero et al., 2019). Consequently, the effective diffusion coefficient derived from this scale can inform further pore-scale investigations that involve fluid dynamics simulations such as the lattice Boltzmann method (Kohanpur et al., 2020; Nemer et al., 2020; Santos et al., 2021; An et al., 2022; Liu et al., 2023b), based on real pore structures reconstructed from X-ray CT scanned digital rocks.

3.3 Oil swelling

When CO_2 is introduced into shale oil structures, a fraction of it becomes soluble in the crude oil, leading to an expansion of its volume (Jha, 1986; Do and Pinczewski, 1991; Bijeljic et al., 2003; Marica et al., 2011). This phenomenon, wherein oil absorption of CO_2 from injections results in increased volume, is termed as oil swelling. For example, Li et al. (2019a) conducted an oil swelling test with CO_2 injection at a pressure of 18.62 MPa and temperature of 69.9 °C to simulate the reservoir conditions, and suggested that the swelling factor of oil increases exponentially and reaches 1.5 when the CO_2 mole fraction reaches 0.7. There are two main reasons for swelling being a main mechanism: firstly, the residual oil content after EOR is conversely related to the extent of oil swelling, which means that the greater swelling extent of oil with the dissolved gas, the larger the EOR potential and the lower residual oil left behind in the reservoir; secondly, the oil swelling mechanism can coalesce the disconnected oil lumps into a large volume (See Fig. 3), which can drive water out of the pore space and enhance the relative permeability of the oil phase. As a matter of fact, many of experimental and numerical studies have shown that oil swelling has a significant positive impact on oil recovery in shale formations, especially for the cyclic injection or huff-n-huff mode (Kar et al., 2015; Hoffman and Reichhardt, 2020; Zuo et al., 2023). Using a reservoir simulation technique, Hoffman and Reichhardt (2020) highlighted the relative greater importance of oil swelling compared to other mechanisms, such as light component extraction, pressure maintenance and viscosity reduction in the CO_2 huff-n-puff performance for black and volatile oils and gas condensates cases. In Fig. 4, it is not hard to see that oil swelling contributes 50% to 70% of the total oil recovery when it involves black and volatile oils.

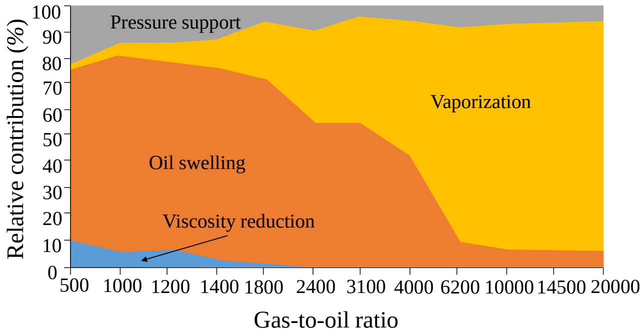

Fig. 4. Contributions of different recovery mechanisms to oil recovery in CO_2 huff-n-puff simulations for various oil types (the data are percentages; black means volatile oils and gas condensate) (Hoffman and Reichhardt, 2020).

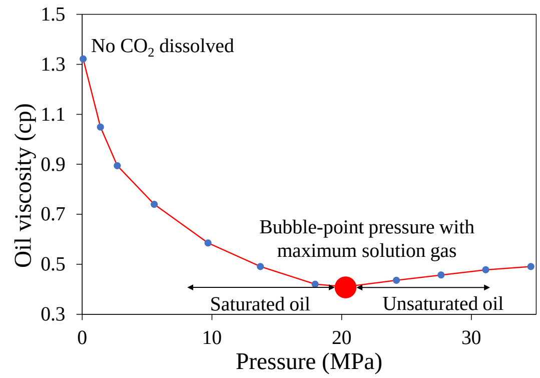

Fig. 5. Viscosity changes of oil with soluble CO_2 versus pressure. Oil viscosity reduces with pressure before reaching bubble point at the saturated state and increases slightly with pressure at the unsaturated state where no solution gas is present (revised from Hemmati-Sarapardeh et al., 2013).

3.4 Viscosity reduction

Except for oil swelling, another critical mechanism is viscosity reduction, the result of CO_2 dissolution into crude oil (Li et al., 2013; Barclay and Mishra, 2016; Or et al., 2016). For example, the application of CO_2 huff-n-puff technique in the Fuyu oil reservoir could lead to a substantial reduction in the viscosity of crude oil, that is, up to 50.7% (Shabib-Asl et al., 2022). In fact, almost all injected gas during EOR can cause the reduction of in-situ crude oil viscosity to various extents. However, CO_2 has been well recognized as the most effective viscosity reducer amongst all, given that it requires lower pressure to achieve miscibility with liquid hydrocarbons in the subsurface (Li et al., 2013; Barclay and Mishra, 2016; Or et al., 2016; Syed et al., 2022b). Importantly, the magnitude of viscosity reduction by CO_2 is more significant in heavy oil samples than gas condensates and volatile oil samples that are mainly dominated by light and intermediate components. Many of studies in the literature have underscored the significance of viscosity reduction in CO_2 huff-n-puff in shale oil reservoirs. For instance, Zhu et al. (2021) conducted a numerical study on the performance of CO_2 huff-n-puff in shale oil reservoirs, and the results showed that CO_2 injection can indeed reduce the oil viscosity by almost 35 times, enhancing the oil mobility and flow to wellbores. A similar study (Li et al., 2019b) demonstrated that the viscosity of crude oil reduced by around 75% from 2 to 0.5 cp after cyclic CO_2 gas injection into the shale oil reservoir. In general, the primary mechanisms that govern viscosity reduction through the dissolution of CO_2 into oil can be classed into four key categories: (a) selective flushing of certain components in the oil-CO_2 mixture by CO_2; (b) removal of viscous deposits facilitated by CO_2; (c) further dilution of crude oil by the solvent properties of CO_2; and (d) ultimate demulsification of the injected CO_2 into crude oil. It is worth noting that, when the oil composition is certain, the main factors contributing to the magnitude of oil viscosity reduction are pressure and temperature. An increase in the injection pressure of CO_2 can improve the effect of viscosity reduction of crude oils, particularly when its value is higher than the MMP. This enables the CO_2 and oil to mix more easily, significantly reducing the density and viscosity of crude oil, thereby mitigating the resistance to its flow. However, a monotonic rise of injection pressure does not necessarily imply sustainable viscosity reduction; instead, the viscosity of crude oil may increase reversely to some extent as pressures exceed the bubble point pressure, above which no more gas phases will exist, thus restricting hydrocarbon movement out of the pores (Hemmati-Sarapardeh et al., 2013) (refer to Fig. 5).

There is a negative physical correlation between oil viscosity and temperature. Meanwhile, the greater extent of viscosity reduction of crude oil during CO_2 injection is attributed to two main reasons: (a) an increase in temperature enhances the CO_2 solubility in the oil phase under constant pressure, and (b) this temperature rise reduces the viscosity of oil itself. Chung et al. (1988) illustrated the trend of variation in oil viscosity with increasing pressure under three temperatures for both cases with and without CO_2 injection. It was revealed that the impact of temperature on oil viscosity reduction is weakened but still noticeable under CO_2 injection compared with scenarios without this practice, while oil viscosity seems insensitive to pressure without CO_2 injection. In summary, although many studies have underscored the essence of this mechanism during CO_2 huff-n-puff in shale oil reservoirs, it has been acknowledged that the effect may not be pronounced in several shale environments where most of the residing oil is light oil with low inherent viscosity.

3.5 Depressurization during the 'puff' stage

During the CO_2 huff-n-puff process, repressurization in the "huff" stage and depressurization in the "puff" stage play important roles in maximizing oil recovery in shale oil reservoirs. Repressurization involves injecting CO_2 into the reservoir to increase the formation pressure beyond the MMP, in order to improve the displacement efficiency by replenishing the formation energy and reduce CO_2 consumption (Kar et al., 2015; Huang et al., 2020). On the other hand, depressurization involves decreasing the reservoir pressure below the hydrate stability pressure to induce CO_2 exsolution and mobi-

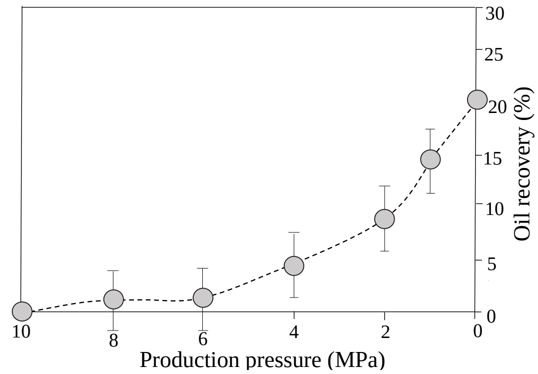

Fig. 6. Oil recovery of CO_2 huff-n-puff experiment at a multi-depressurization stage with different production pressures of 10, 8, 6, 4, 2, 1, and 0 MPa (Liu et al., 2022).

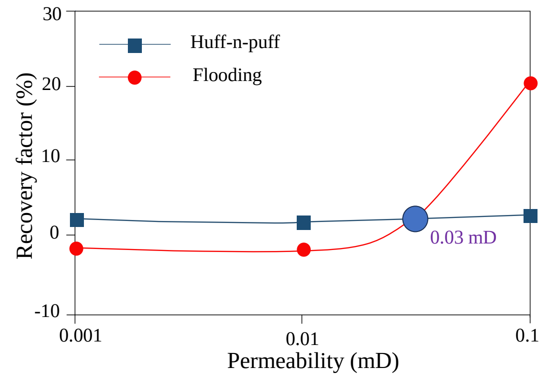

Fig. 7. Comparison of CO_2 huff-n-puff and flooding performance under different matrix permeabilities: A critical value of 0.3 mD separates the superiority of flooding and huff-n-puff (Zuloaga et al., 2017).

lization of the remaining oil. In this chapter, we typically focus on two main accessorial mechanisms during the release of formation elastic energy during depressurization by CO_2 huff-n-puff processes in shale reservoirs: Oil sorption, and CO_2 exsolution or solution gas drive.

In the CO_2 huff-n-puff processes in shale reservoirs, due to the confinement of nanopores, oil desorption and absorption is highly complex and pressure-dependent. These mechanisms are still insufficiently understood; however, some studies have highlighted the important role of depressurization in extracting oil from the formation. For example, Billemont et al. (2013) and Liu et al. (2022) suggested that a larger pressure depletion magnitude in the "puff" stage will increasingly facilitate the cumulative oil recovery, and the corresponding sorption hysteresis of oil on rock surface is an innegligible factor in the EOR process. In addition, Li et al. (2019b) proposed that the increase in CO_2 injection pressure can result into much better recovery efficacy when the soaking time is constant, but the mechanisms behind were not well characterized.

Depressurization in fact can also trigger the separation of dissolved CO_2 from the oil, leading to CO_2 nucleation, growth and coalescence, which drives additional oil recovery. This mechanism is called CO_2 exsolution or solution gas drive. At higher pressures, the injected CO_2 remains in a dense supercritical phase, occupying less pore space; however, the phase separation of CO_2 and oil can occur and the pore volume occupied by gaseous CO_2 can rapidly increase once the pressure declines to a certain low level (Bora et al., 2000). Liu et al. (2022) carried out a CO_2 huff-n-puff experiment on an oil-saturated tight sandstone core at an injection pressure of 10 MPa and soaking time of 2 hours. At the end of the soaking period, the core was depressurized in stages to 10, 8, 6, 4, 2, 1 and 0 MPa while holding each pressure for 20 mins. 1D NMR profiling at each stage was used to track changes in oil saturation to monitor CO_2-driven oil mobilization and production at different pressures. It was suggested that there is a sharp increase in oil production when the pressure drops below 6 MPa, as CO_2 transitions from supercritical to gaseous phase (Fig. 6), greatly increasing CO_2 gaseous volume and releasing elastic energy, thus displacing more oil. Over 98% of the oil was recovered in the low-pressure stage later, demonstrating that oil production depends mainly on the dissolved CO_2 drive mechanism fueled by depressurization. This serves as a reminder that an optimal pressure window is present for maximizing this effect and oil recovery. It was also noted by the authors that the depressurization rate affects CO_2 nucleation/growth kinetics and oil recovery, making optimizing the production pressure decrease rate an important task.

Consequently, understanding the phase behavior dynamics of CO_2/oil systems and sorption hysteresis during depressurization in nanopores remains a significant challenge, which could directly explain the importance of depressurization to the EOR process on the microscopic scale.

4. Formation factors affecting CO_2 huff-n-puff processes

4.1 Effect of matrix permeability

It has been reported in several studies that matrix permeability has a significant positive impact on the CO_2 huff-n-puff performance in shale oil reservoirs. For instance, the dominant mechanism shifts from capillary trapping to molecular diffusion as the matrix permeability decreases (Song and Yang, 2017; Zuloaga et al., 2017; Zhang et al., 2018; Bai et al., 2019; Wei et al., 2020). Zhang et al. (2018) studied the role of matrix permeability in the CO_2 huff-n-puff recovery factor using core experiments. As shown in Fig. 7, it was suggested that the oil recovery factor is increased significantly with the rise in core matrix permeability by each order of magnitude from 0.001 to 0.1 mD. Meanwhile, Bai et al. (2019) conducted CO_2 huff-n-puff experiments on three cores with different matrix permeabilities of 9.35, 5.79, 0.89 mD, with 3 cycles. The corresponding results indicated that the difference in the cyclic oil recovery between cores of 9.35 and 5.79 mD was much smaller than that of cores of 5.79 and 0.89 mD, implying that the rise in matrix permeability within a certain order of magnitude will not linearly enhance its CO_2 huff-n-puff recovery factor when the operational parameters are controlled. As discussed previously, CO_2 huff-n-puff is much superior to CO_2 continuous injection or flooding when it comes to low-permeability reservoir rocks such as tight or

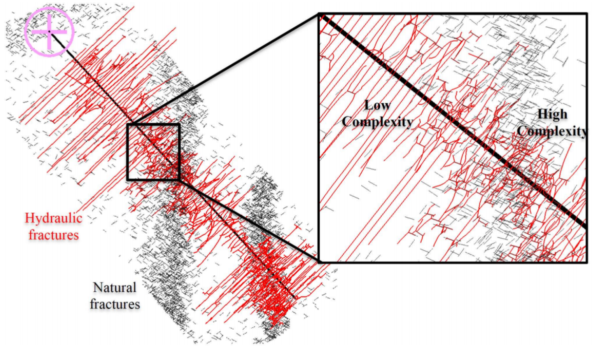

Fig. 8. The complexity of hydraulic and natural fracture system, where higher density of original natural fractures renders higher complexity of the resulting integrated fracture system (Pankaj et al., 2018).

shale oil reservoirs; however, there is a need for a quantitative screening criterion for CO_2 flooding and huff-n-puff for better and more efficient CO_2-EOR outcomes in different reservoir formations based on their matrix permeabilities. Zuloaga et al. (2017) constructed a field-scale compositional reservoir model based on data on the Middle Bakken formation to evaluate the performance of CO_2 flooding and huff-n-puff under a permeability span from 0.001 to 0.1 mD. Therein, a critical permeability value of 0.03 mD was captured and the CO_2 huff-n-puff achieved a better outcome than CO_2 flooding when the matrix permeability was lower than this critical value (See Fig. 7). Furthermore, an additional response surface methodology was utilized to conduct sensitivity analysis of this reservoir model with four parameters: Matrix permeability, number of wells, well pattern, and fracture half-length. It turned out that matrix permeability is of paramount importance compared to other parameters in terms of the incremental recovery factor. Especially, the interaction with the fracture network serves as a critical determinant in the success of CO_2 huff-n-puff processes. While permeability is crucial, permeability impairment may also occur due to mechanisms such as mineral and asphaltene deposition and kerogen swelling that occur with CO_2 absorption and stress sensitivity during depressurization. Although matrix permeability is the primary consideration, future studies should incorporate factors into the evaluation system that are likely to impair the matrix permeability.

4.2 Effect of fracture system

As discussed in the previous part of this paper, shale oil reservoirs necessitate massive hydraulic fracturing in combination with horizontal well technology to maximize the contact area between in-situ oils and wellbores. However, the production capacity from primary depletion is still limited due to the tiny pore sizes and quick decline of formation pressure. In addition, the complex fracture system containing both artificial and natural fractures generated by hydraulic fracturing could also be of great significance to the performance of CO_2 huff-n-puff in shale oil reservoirs. Such fracture system would not only boost greater contact area between CO_2 and shale formation surface, facilitating its penetration into fragmented matrices and interacting with in-situ hydrocarbons, but also provide the flow pathway for oil.

A series of field-scale numerical studies (Mugisha et al., 2021; Wang et al., 2023b) have been performed on the effects of fracture parameters, such as fracture half length, fracturing spacing and fracture effective permeability, on CO_2 huff-n-puff performance. For instance, by using compositional reservoir modeling based on geological information on a typical US shale oil reservoir, Syed et al. (2022c) investigated the effect of fracture properties, including the number of clusters, fracture half length, fracture spacing and fracture conductivity, or effective permeability on the ultimate oil recovery. The results showed that an increase in the number of clusters is helpful to boost the oil recovery, while this effect is limited since it is subjected to the stimulated reservoir volume or SRV. Actually, numerical studies of this kind (Safi et al., 2014; Song and Yang, 2017; Sennaoui et al., 2022) fail to consider the complexity of facture systems induced by the interaction between artificial and natural fractures, which leads to the inaccurate prediction of the fluid flow mechanisms and the oil recovery factor. To this end, another study (Pankaj et al., 2018) coupled the compositional reservoir simulation with the complex fracture simulation model generated from a calibrated geomechanical model based on real petrophysical and geomechanical properties from the Eagle Ford formation. The greatest highlight of this work is utilizing the unconventional fracture model method (Weng et al., 2011), which characterizes fracture propagation and the ultimate complex system. It does so by analytically solving the interaction of artificial and natural fractures based on the crossing criterion. This contrasts with a user-defined fracture system with a set number and density of natural fractures. The complexity of the fracture system may be higher with a higher density of natural fractures (Fig. 8). Based on cutting-edged methodology, this paper concluded that the complexity of the fracture system would render higher ultimate oil recovery, since more surface area was created with the same operation control strategy.

Subsequently, many studies have further demonstrated the importance of the complexity of fracture network for CO_2 huff-n-puff performance evaluation. Wan et al. (2016) indicated that the complexity of fracture network controls the conductivity maintained by proppants regarding EOR in shale oil reservoirs. Burrows et al. (2020) noted that the connection of natural and artificial fractures would improve the oil recovery by 20% compared to models not considering the natural fractures. However, some recent studies obtained opposite findings; for example, Alfarge et al. (2017) suggested that the more extensive and denser natural facture system with higher conductivity would exert a more harmful effect on the CO_2 huff-n-puff recovery efficacy in some cases. Moreover, Sanchez-Rivera et al. (2015) established that the CO_2 huff-n-puff effect would not be consequential when the conductivities of natural and artificial fractures were similar. Thus, there seem to be great controversies in terms of this effect.

In summary, further research is still needed for investigating the characterization of natural fracture systems as a basis for high-efficiency fracturing treatment, to maximize the complexity and surface area of integrated fracture systems.

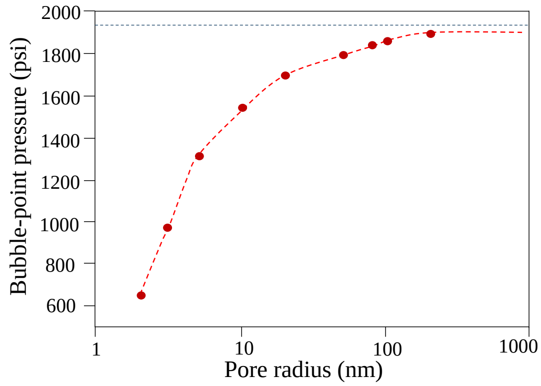

Fig. 9. Effect of nanopore confinement on bubble-point pressure (Zheng et al., 2021).

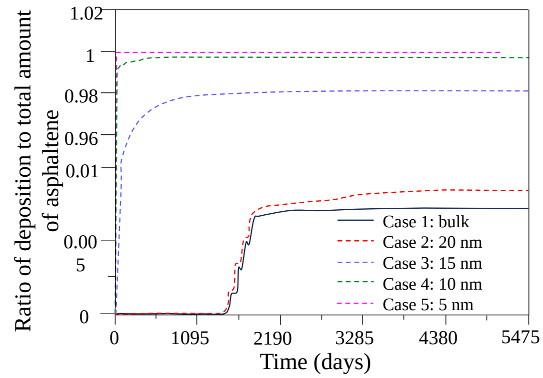

Fig. 10. Nanopore confinement effect on asphaltene deposition during CO_2 huff-n-puff, revised from Lee and Lee (2019b).

Meanwhile, an effective triple-porosity matrix-fracture model should be established that finely captures the fluid transport in the system and considers the stress-sensitivity of the system permeability. With this being embedded into the reservoir models, one will be able to better understand the past production history and therefore improve the accuracy of production forecasts using optimized EOR strategies.

4.3 Effect of nanopore confinement

Shale rocks are known for their fine-grained nature and extremely small pore sizes. The shale rock matrix is composed of micropores to mesopores, with diameters less than 2 and 2-50 nm, respectively (Kuila and Prasad, 2011). Interestingly, the throat connecting adjacent pores could be even tighter than the pores themselves, further limiting fluid transport through the rock. The nanopore confinement effect on fluid transport in shale rocks arises from two primary factors: (1) capillary pressure between liquid and gas phases; (2) fluid-solid interaction, particularly fluid sorption in the near-wall space. Capillary pressure is the more dominant of the two (Lee and Lee, 2019b; Yu et al., 2019; Song et al., 2021; Zheng et al., 2021), which plays a crucial role in the transport of fluids within shale rocks, bearing significant implications for shale oil production. Fig. 9 presents the effect of nanopore confinement on the bubble-point pressure as one of the important thermodynamic properties that affect oil production. It is well known that a reduction in bubble point pressure can improve the oil production efficiency since gas will "evolve" from oil at higher reservoir pressures. Thus, Fig. 9 suggests that a stronger nanopore confinement effect will trigger a bubble point pressure reduction because of the capillary effect. In addition, this effect on other key pressure volume and temperature or thermodynamic properties, such as dew point, formation factor and gas-oil ratio, etc., follows nearly the same trend that is favorable for oil production, with a critical threshold value present, below which the nanopore confinement effect is dramatically enhanced. Because of the favorable thermodynamic shift from the bulk phase under nanopore confinement, MMP between oil and CO_2 is also reduced. For example, Zheng et al. (2021) utilized an improved vapor-liquid equilibrium model to validate the MMP reduction by 650 psi as the pore size diminishes to 2 nm. Nevertheless, a recent study Sun et al. (2023) has garnered significant attention for revealing a non-monotonic relationship between the MMP of CO_2 and oil as a function of pore radius. Specifically, if was found that the MMP within nanopores decreases with increasing slit height up to a certain threshold beyond which it begins to increase due to enhanced wall adsorption.

Importantly, nanopore confinement not only results in positive effects on CO_2 huff-n-puff performance, such as decreasing the bubble point pressure as covered above, but also incurs formation damage to some extent, affecting oil production, such as asphaltene deposition. In this regard, Lee and Lee (2019b) developed an integrated model to simulate CO_2 huff-n-puff in shale oil reservoirs, that couples nanopore confinement effects, asphaltene precipitation/deposition and the resulting formation damage, to investigate how nanopore confinement shifts phase behavior and influences asphaltene deposition during the CO_2 injection process. It was found that nanopore confinement shifts the phase behavior and oil properties, increasing asphaltene precipitation. This in turn causes more asphaltene to deposit in the pore spaces, especially in the shale matrix where most of the oil is stored. Without considering formation damage, oil recovery increases with stronger nanoconfinement during CO_2 huff-n-puff due to shifts in the thermodynamic properties, while the increased asphaltene deposition can counteract this benefit. Fig. 10 shows the ratio of deposition to total asphaltene amounts during oil production under confinement cases with 20, 15, 10 and 5 nm pores. It is observed that stronger nanopore confinement substantially increases asphaltene deposition and almost all asphaltene precipitates in the 15, 10 and 5 nm cases. However, for the bulk and 20 nm cases, asphaltene deposition is under 1% of the total asphaltene amount, and for 5 nm confinement, this value is 98%. Therefore, it is safe to say that although oil recovery increases with nanopore confinement, the associated asphaltene deposition can exert negative effects like permeability reduction and wettability alteration, which should not be neglected during simulations.

4.4 Effect of rock wettability

As is well known, the wettability of rock surfaces is a critical factor controlling the flow of fluids in porous media

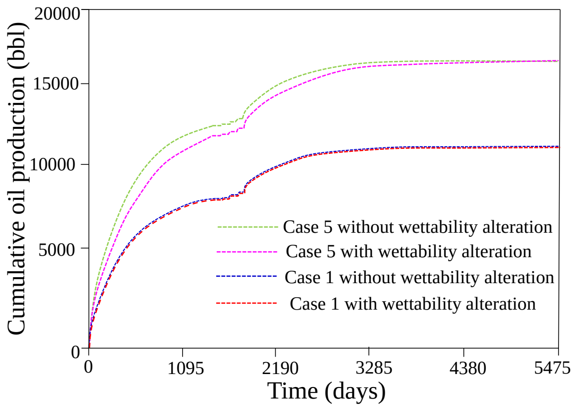

Fig. 11. Cumulative oil recovery in Case 1 (bulk phase) and Case 5 (5 nm) with or without wettability alteration by asphaltene deposition (Lee and Lee, 2019b).

(Sharifigaliuk et al., 2021; Qin et al., 2022; Liu et al., 2023a; Wang et al., 2023a). In fact, the wettability of shale rocks is intricately influenced by a multifaceted interplay of factors, encompassing mineral composition, surface charge, surface roughness, and pore structure. Among them, mineral composition plays a pivotal role, with hydrophilic elements like quartz, feldspar and clay, alongside hydrophobic constituents such as kerogens and calcite demonstrating a strong affinity for oil molecules. Therefore, wettability alteration also has an indispensable role in determining the efficacy of CO_2 huff-n-puff in shale oil reservoirs. During CO_2 injection in shale oil reservoirs, wettability alteration occurs due to the preferential adsorption of CO_2 onto the rock surface, which modifies the surface energy of the rock, changes its wettability further toward CO_2-wet and leads to the mobilization of residual oil and improved displacement efficiency of CO_2 huff-n-puff (Zhou et al., 2018). CO_2 injection also affects the pore-scale fluid distribution and connectivity, greatly enhancing the wettability alteration process. Studies have shown that the extent of wettability alteration during CO_2 huff-n-puff is influenced by a series of operational factors such as CO_2 injection rate and injection pressure (Cao et al., 2017; Chen et al., 2018). Cao et al. (2017) performed numerical reservoir simulations of CO_2 huff-n-puff in a shale oil reservoir considering two cases, namely with and without wettability alteration, which were adjusted by relative permeability curves. The findings showed that considering the CO_2 huff-n-puff process with wettability alteration (toward CO_2-wet) boosted the recovery factor by 3% from the base case of primary depletion, and this was also slightly higher than the CO_2 huff-n-puff case applied without considering wettability alteration.

As mentioned above, most of shale oils are made up of light and intermediate components that are applicable for miscibility during the CO_2 huff-n-puff process. However, some shale formations constitute liquid hydrocarbons with high asphaltenes or C_{30+}, which may precipitate and deposit during the miscible process of light and intermediate components and CO_2, causing the clogging of pore pathways and thus reducing the permeability of the shale matrix. More importantly, the precipitation and deposition of asphaltenes on the rock could also alter the rock wettability toward oil-wetness via creating an absorption film that covers the rock surface, which reduces the surface energy of the rock and makes it more attractive to nonpolar molecules like oils. In addition, the smaller the pore sizes, the greater ratio of asphaltene deposition, which implies that asphaltene deposition is more severe under stronger nanopore confinement effect, making rocks oil-wetter and less mobilized. Here, it is worthwhile to note that in the study by Lee and Lee (2019b), oil recovery after CO_2 huff-n-puff conducted on Case 1 (bulk case) was much weaker than Case 5 (5 nm) when other parameters were controlled because of the nanopore confinement effect on shifts in the thermodynamic properties discussed in the last section. At the same time, the extent of oil recovery ratio reduction in scenarios with and without considering wettability alteration were greater for Case 5 than Case 1, further demonstrating that as a result of the greater scale of asphaltene deposition, wettability alteration toward oil-wetness is more significant under stronger nanopore confinement effect, although this negative effect is far less than the positive impact brought on by phase behavior shift under nanopore confinement.

In conclusion, the role of wettability alteration in CO_2 huff-n-puff processes in shale oil reservoirs should be considered carefully, as it can have both positive and negative effects. On the one hand, CO_2 absorption onto rock surfaces can alter surface energy and reduce oil-wetness, repelling oil and improving its mobility. At the same time, CO_2 injection causes asphaltene deposition in pores and throats, which reduces the surface energy, making the rock more attractive to oil or oil-wet. These mechanisms occur simultaneously and can affect oil recovery in opposing ways. Therefore, future research should be aimed at accounting for this complex interplay between positive and negative wettability impacts, rather than assuming that wettability alteration is universally beneficial or detrimental to EOR. Furthermore, a more in-depth understanding is needed of how CO_2-induced wettability effects create both risks and opportunities in shale reservoirs, which can lead to the better modeling and optimization of CO_2 huff-n-puff performance.

4.5 Effect of reservoir heterogeneity

Shale formations exhibit heterogeneity caused by variations in deposition, diagenesis and tectonics during formation. Fractures at different scales create hierarchical heterogeneity affecting fluid flow and production. Hydrocarbon recovery can be extensively impacted by fractures and geological complexity; however, few studies have examined the effects of these factors on shale oil production through the CO_2 huff-n-puff process. Thus, further research on the heterogeneity impact is crucial to improve recovery efficiency. An early study (Chen et al., 2014) simulated primary and CO_2 huff-n-puff performance in 2D permeable fields using a compositional reservoir simulator. The results showed lower recovery rates in heterogeneous than homogeneous fields during 1,000 days of primary production, indicating convective transport domination. Moreover, the recovery factor with CO_2 huff-n-puff applied was even lower than that without any EOR operations. It was concluded that the sweep volume affected by CO_2 migration is more limited with the stronger formation heterogeneity, under which longer soaking in the huff-n-puff would not only trigger the effectiveness of CO_2 diffusion mechanism but also, conversely, procrastinate the best production timing.

Jia et al. (2018) examined fluid flow in unconventional reservoirs focusing on diffusion and fractures using a dual porosity/permeability model. Under varying natural fracture permeabilities and heterogeneities, they found that effective permeability distribution depended on correlation length. It was also indicated that heterogeneity hampers primary recovery but its huff-n-puff impact depends on factors like correlation length and diffusion; longer correlations and diffusion can lessen the negative effects. Heterogeneity neither favors nor disfavors the ultimate recovery factors. For primary depletion, higher heterogeneity means lower recovery, which is assumed due to hampered convection. In a single-cycle huff-n-puff, longer correlations increase recovery by securing enough time for overcoming injectivity issues, but in multi-cycle cases, longer correlations decrease recovery from early unfavorable injectivity before CO_2 can penetrate. Furthermore, with the aid of sufficient diffusion coefficient, heterogeneity aids recovery by enabling diffusion into lower-permeability zones.

In our view, future studies should examine more complex heterogeneity patterns and mechanisms such as swelling and viscosity reduction alongside diffusion. In other words, heterogeneity hampers primary recovery but the related huff-n-puff impact is nuanced, warranting further research.

In summary, matrix permeability stands as the foremost determinant of CO_2 huff-n-puff feasibility within a specific reservoir scenario. While higher matrix permeability generally enhances CO_2 huff-n-puff performance, it is crucial to note that excessively high matrix permeability (exceeding 0.1 mD, for example) may favor CO_2 flooding over huff-n-puff due to its superior sweep volume and increased hydrocarbon production continuity. After matrix permeability, the fracture system emerges as the second pivotal formation factor significantly impacting CO_2 huff-n-puff performance. It not only extends the contact area between injected CO_2 and the reservoir matrix but also serves as a conduit for hydrocarbon flow. Notably, existing research demonstrates that fracture geometries and complexity exert the greatest influence on fracture quality in EOR processes. Additionally, factors like nanopore confinement, rock wettability and reservoir heterogeneity also play essential roles, whereas their effects on CO_2 huff-n-puff performance remain a subject of debate and context, necessitating further investigations.

5. Summary and conclusion

This work provides an overview of recent advances in understanding CO_2 huff-n-puff enhanced oil recovery mechanisms and the major formation influencing factors in shale oil reservoirs. The key conclusions and implications are presented as follows:

1) The critical soaking period is characterized by CO_2 molecular diffusion into the shale matrix, triggering oil swelling and viscosity reduction that culminate in miscibility under sufficient pressure. The accurate prediction of diffusion coefficients in heterogeneous shale remains challenging and limits pore-scale process simulations.
2) Depressurization during the puff period releases formation elastic energy and desorbs oil molecules, boosting recovery. Conversely, permeability impairment can occur from mineral deposition, kerogen swelling and stress sensitivity.
3) Matrix permeability is the primary screening factor for CO_2 huff-n-puff feasibility. Fracture systems improve the huff-n-puff performance by expanding CO_2-rock contact and sweep. Further work in this area should characterize the complex fracture network interactions.
4) Nanopore confinement impacts fluid transport and thermodynamics, involving lowering the bubble point pressure, but also risks asphaltene precipitation and damage. Consequently, managing this tradeoff is key optimization task.
5) Wettability alteration toward CO_2-wetness aids oil displacement but compromises oil-wetness from asphaltene deposition. Therefore, this effect should be justified weighing both mechanisms under actual reservoir conditions.
6) Reservoir heterogeneity hampers primary recovery but the diffusion and correlation length can lessen its CO_2 huff-n-puff impacts. Validated geological models coupled with nanopore behaviors ought to be developed to better elucidate the effects of heterogeneity.

For future endeavors in this field, the following potential directions are suggested:

1) Quantitative and mechanistic insights into the soaking process at multiple scales and the optimization of soaking time within the rationale of physics.
2) The hydro-mechanical-thermal-chemical coupled modeling of huff-n-puff processes where mechanisms and factors, such as CO_2-water-rock geochemistry, geomechanical effect and fracture activation and propagation, are well established.
3) It is necessary to upscale the experimental or simulation results obtained for a small scale, like pore or core scales to the reservoir scale. Thus, the scaling law of soaking processes have to be worked out, such as diffusion, repressurization and phase behavior at small scales, especially during pore-scale simulations using either molecular dynamic or lattice Boltzmann simulations. Then, the relevant findings can be better utilized for constraining and optimizing reservoir-scale modeling.
4) CO_2 huff-n-puff is a promising technology for boosting oil recovery in unconventional reservoirs, but still faces issues like gas channeling and adsorption (Song et al., 2022; Zhang et al., 2022b; Alahmari et al., 2023). Future studies should focus on optimizing CO_2 blends with foam, nitrogen and produced gases. Foam can reduce gas channeling, nitrogen improves diffusion, and produced gases can alleviate high pressure and adsorption problems. These gas blends could retain the environmental benefits of pure CO_2 while enhancing oil recovery and

cost-efficiency.

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Conflict of interest

The authors declare no competing interest.

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