The role of supercritical carbon dioxide for recovery of shale gas and sequestration in gas shale reservoirs†

Qiao Lyu,†a Jingqiang Tan,⁎a,b Lei Li,†a Yiwen Ju,*b Andreas Busch,†c David A. Wood,†d Pathegama Gamage Ranjith,†e Richard Middleton,† Biao Shu,a Changher Hu,a Zhanghu Wang† and Ruining Hu†

The development of hydraulic fracturing and horizontal drilling techniques has promoted the exploitation of shale gas resources. However, using water has several potential drawbacks including environmental issues; e.g., the contamination of groundwater, surface water, and soil. Supercritical carbon dioxide (SC-CO2), with its special physical properties, has shown potential to enhance shale gas recovery replacing water as the stimulation fluid. This review summarizes the current status of shale gas recovery, the potential role of SC-CO2 as a working fluid for shale gas recovery, and CO2 geological sequestration in shale reservoirs. SC-CO2 has a better rock-breaking capability than water, which is useful when drilling through shale formations. SC-CO2 fracturing creates rougher and more complex fracture networks than hydraulic fracturing, leading to higher permeabilities. Some of the injected CO2 for shale gas recovery could also be safely sequestered in shale reservoirs, whereby lowering carbon emissions and accessing CO2 tax credits. However, shale–CO2 or shale–water/brine–CO2 interactions during & after shale gas recovery and sequestration can affect reservoir properties. The implied shale–CO2 imbibition process from available data generally persists for several years, far more than the several days assumed for most laboratory tests. A more detailed understanding is required for SC-CO2 injection on the efficiency of shale gas recovery and the cost and environmental concerns of this technology. This will support the development of safe sequestration methods, supported by suitable laboratory and field tests, especially those focusing on geochemical, petrophysical, geomechanical and hydraulic properties.

Broader context
The production of shale gas has been drastically increased because of the development of hydraulic fracturing. Though shale gas is a much cleaner energy resource compared to coal and oil, hydraulic fracturing has potential environmental impacts, e.g., the large consumption of water and the contamination of groundwater and earth surface. Supercritical carbon dioxide (SC-CO2), with its special physical properties, has shown potential to enhance shale gas recovery replacing water as the stimulation fluid. This article summarizes the current status of shale gas development, the potential role of SC-CO2 as a working fluid for shale gas recovery, and CO2 geological sequestration in shale reservoirs. Meanwhile, the challenges of SC-CO2 fracturing in shale reservoirs are discussed in detail. Particularly, the concerns of SC-CO2 enhanced shale gas recovery are addressed which includes diffusion and adsorption of CO2 in shale gas reservoirs, the CO2–shale or CO2–water/shale interactions and related changes in shale properties, and further concerns such as the costs, environmental impacts, and life cycle assessments of using SC-CO2 for shale gas extraction. This review provides an overall understanding of the application of SC-CO2 in shale gas development and the feasibility of CO2 sequestration in shale reservoirs.

1 Introduction
The United States Energy Information Administration (EIA) world energy outlook (2019) predicted that world energy demand will rise nearly 50% between 2018 and 2050, and fossil fuel will still be the dominant energy source.1 As stated in the 2015 Paris Agreement as well as the Intergovernmental Panel on Climate Change (IPCC), the transition to consuming more environmentally friendly energy is being pursued as a matter of...
urgency by many counties to meet the 1.5 °C target.2 Compared to oil and coal, natural gas is a much cleaner energy source, producing only 45% of the carbon dioxide (CO2) of coal.3 Unconventional gas (e.g. shale gas or tight gas), which is known to be present in large resource quantities around the world, shows potential as a bridging fuel to transition to renewable energy sources. Natural gas from shale could adequately supply the continued growth in energy demand for developing economies in the next few decades and contribute significantly to the demand for decreasing CO2 emissions.4

The development of hydraulic fracturing and horizontal drilling techniques has promoted the rapid exploitation of shale gas resources, particularly in North America.5,5 In the US, shale gas production increased from 1990 billion cubic feet in 2007 to 23 550 billion cubic feet in 2018.6 In addition to the US and Canada, other countries like China and Argentina are making progress in commercial shale gas production. However, drilling, and hydraulic fracturing require large amounts of water. In the US, the amount of injected water per well is 10 000 to 50 000 cubic meters, only 9–34% of which returns to the surface after hydraulic fracturing.7–11

Based on the research from the World Resources Institute (WRI), eight of the top 20 countries with the largest shale gas resources face arid conditions or high to extremely high baseline water stress where the shale resources are located. China and India, which account for one-third of the world’s population, are included in the eight countries. The widespread use of hydraulic fracturing will put more people at risk of water shortages and more pressure on existing water resources.12

The fracturing fluids are usually composed of water plus proppant (≥98%) and chemical additives (<2%).13 It has been estimated that about 14 types of chemicals are used in each well, such as gelling agents to improve the carrying ability of proppant, hydrochloric acid to open the fractures and dissolve carbonate minerals, friction reducers (slick water) to aid the penetration of the injected fluids and other substances.14–16 Some chemical additives are toxic and some toxic substances are produced during fracturing,13 although, over time, the toxic components historically used in fracturing fluids have been significantly reduced by most operators under pressure to reduce their environmental impacts. The residual fracturing fluids in the shale reservoirs and the disposal of flowback water potentially leads to the contamination of groundwater, surface water, and soil if not handled carefully.17–20 In addition, hydraulic fracturing can induce microseismic events.21 Based on the above drawbacks, Western Australia, New Brunswick, and California, as well as France, Ireland, and South Africa have banned hydraulic fracturing. Therefore, it is essential to explore new approaches for shale gas recovery which could reduce or even eliminate water consumption in fracture stimulation.22,23

With its attractive physical properties (e.g., liquid-like density, gas-like viscosity, no capillary force and good miscibility with hydrocarbons), supercritical carbon dioxide (SC-CO2) is now under consideration as a fracture stimulation fluid or component of energized fluids injected into unconventional shale or tight gas reservoirs to enhance gas recovery.24–27 Similar to slick water, the low viscosity of SC-CO2 can create complex, multi-orthogonal fracture networks allowing high flow rates.28 SC-CO2 has a lower value of chemical potential than methane,29 which offers a significant advantage over water in that methane can be easily desorbed by SC-CO2 as the adsorptive capacity of SC-CO2 in shale is about 2–3 times higher than methane.30 In addition, shale gas reservoirs have the potential to become targets for CO2 sequestration when using SC-CO2 as the fracturing fluid.31–33 The development of techniques for capturing CO2 from fossil-based power plants and the atmosphere will make it possible to offer sufficient CO2 for shale gas recovery.34–36 Meanwhile, obstacles like the current high costs of capturing, pressurizing, and transporting of CO2, the efficiency of shale gas recovery affected by CO2–shale interactions, and the reliability of long-term entrapment and safety of CO2 sequestration in shale reservoirs, remain uncertain. The IPCC report states that CO2 emission reduction targets can only be met if carbon capture and storage significantly contribute to the mitigation strategies. If implemented, CO2 will become available in significant amount, ultimately reducing costs for capturing.

This paper systematically summarizes the current status of shale gas exploitation, the geological utilization and sequestration of CO2, and the role of SC-CO2 in shale gas recovery including SC-CO2 used as a drilling fluid, SC-CO2-based fracturing, and CO2 storage in shale gas reservoirs. The advantages and drawbacks of these (SC-)CO2-related studies and applications in literature are discussed. Further, the concerns of SC-CO2 enhanced shale gas recovery are addressed which includes diffusion and adsorption of CO2 in shale gas reservoirs, the CO2–shale or CO2–water–shale interactions and related changes in shale properties, and further concerns such as the costs and the environmental impacts of SC-CO2 injection for shale gas recovery. Challenges and perspectives are presented to expand our understanding and verify the feasibility of SC-CO2 enhanced shale gas recovery and CO2 sequestration in shale gas reservoirs.

2 Shale gas and exploitation

2.1 Global shale gas resources and exploitation status

Based on the EIA findings in 2016, the world’s technically recoverable shale gas resources are over 200 trillion cubic meters (TCM), which could support global natural gas consumption for more than six decades based on current gas consumption.37 Fig. 1 shows the distribution of the global shale gas resources: China has the largest gas reserves of 36.1 TCM. However, in 2019, China’s foreign dependence on oil and natural gas amounted to 72% and 43%, respectively.38 The US and Argentina have the second and third highest resources with 24.4 and 21.9 TCM, respectively. However, it should be noted that many countries and regions have yet to fully evaluate and quantify their shale gas resources; especially in the Middle East, Australia, North Africa, and Russia where large resources are expected. Though such evaluations could change over time as more data...
becomes available, the reserves of unconventional natural gas, e.g., shale gas, are widely considered to be significantly greater than conventional natural gas.

North America was the first region of the world to achieve commercial shale gas production. From 2007 to 2018, shale gas production increased by 702% to 0.6072 TCM per year,\textsuperscript{40} which is expected to increase until 2050. Texas' Barnett shale was the first formation to commercially produce large quantities of shale gas and was the beginning or rapid technology development.\textsuperscript{41} The large-scale recovery of shale gas has helped the US to transform from an importer of natural gas into an exporter.\textsuperscript{3,42} Shale gas recovery has also rapidly developed in Canada. Although hydraulic fracturing is suspended or prohibited in the east of the country, shale gas production is expected to grow to annual values of 0.1926 TCM in 2050, mainly from western Canada.\textsuperscript{43} Commercial shale gas production in China commenced in 2010 and has grown continuously reaching annual volumes of 0.0154 TCM in 2019, making it the world’s second-largest shale gas producer.

2.2 Overview of current gas recovery methods and fracturing fluids

Unconventional tight reservoirs, such as shale oil/gas, tight gas or coalbed methane, are characterized by their low permeability which is typically $<1$ mD.\textsuperscript{44,45} Therefore, advanced technologies such as horizontal drilling and multi-stage fracturing are required to commercially recover gas from such reservoirs.\textsuperscript{46–49}

Shale formations are often characterized by laminated morphologies made up of multiple thin layers. Regionally, in broad basins the formations tend to be dominated by shallow dips, particularly in the deeply buried, thermally mature basin centers. In such conditions, horizontal wells can access much larger volumes of shale gas than vertical wells.\textsuperscript{50} When the vertical well reaches the shale formation, the drilling trajectories are adjusted by nearly 90 degree to a near-horizontal direction. One vertical well is likely to be branched into several lateral horizontal wells extending into the shale formation in different directions, like a radial net. The length of the horizontal well is commonly about 1 to 2 km.\textsuperscript{51} Horizontal drilling cannot on its own offer sufficient flow paths for gas moving from the adjacent shale formations into the wellbores. Therefore, hydraulic fracturing is needed to extract shale gas economically. Hydraulic fracturing is now widely used to enhance the production of unconventional oil and gas which are stored in tight reservoirs. During a hydraulic fracturing operation, high-pressure water is injected into a well and flows through the perforated zones. Fractures are created around and beyond the well. The hydraulic conductivity increases substantially following fracture stimulation, allowing more gas to be drained and flow into the wellbore.\textsuperscript{52} In order to maximize the fracturing efficiency, multi-stage hydraulic fracturing has become the standard stimulation technique applied to horizontal wellbores.\textsuperscript{53,54}

There are various types of fracturing fluids employed for unconventional oil and gas recovery, which can be categorized as liquid-based fluids, foam-based fluids, and gas-based fluids, as shown in Table 1.

Water-based fluids were first used for hydraulic fracturing in Kansas in 1947.\textsuperscript{63} Slickwater, which is comprised of water-based fluids by 90 vol\%, has the benefit of producing multi-fracture networks with high penetration depths, resulting in significantly enhanced permeabilities. Although such fluids are commonly the first choice for developing shale gas reservoirs, they have substantial drawbacks in certain locations and formations. Injecting large amounts of water typically results in a range of water–rock interactions, potentially causing formation damage.\textsuperscript{64}
process of foam generation at the surface.\textsuperscript{75} As with water-based fracturing fluids, the potential environmental impacts of these additives raise concerns about foam-based fracture stimulation fluid applications on a large scale.

Among the gas-based fracturing fluids, N\textsubscript{2} has received more attention in research studies.\textsuperscript{76–80} Fracturing with N\textsubscript{2}-based foams consumes relatively little water and low quantities of chemical additives. Despite the easy accessibility, the large consumption of N\textsubscript{2} in the stimulation of each well makes the fracturing process expensive. The low viscosity of N\textsubscript{2} further limits its proppant suspension and transportation capability. N\textsubscript{2}-based fracturing can also induce self-propping fractures which contribute to fracture opening.\textsuperscript{81} However, this phenomenon is typically only induced on a meaningful scale in shallow wells. For shale reservoirs in China for example, most of which are deeper than 3000 m, self-propping typically only makes a minor contribution.

2.3 Drawbacks of hydraulic fracturing

2.3.1 Environmental concerns. In general, environmental concerns associated with unconventional oil and gas development can be categorized into four main groups, including community issues (e.g., industrial noise and induced seismicity), water issues (e.g., groundwater and surface water contamination), land issues (e.g., ecosystem impacts), and atmospheric issues (e.g., air pollution).\textsuperscript{82–84} Recently, there is extensive research and debate in academia, industry, and society in general about the environmental impacts of unconventional reservoir development. In 2016, the US Environmental Protection Agency (EPA) reported the impacts of hydraulic fracturing water cycle on drinking water resources.\textsuperscript{85} It is widely recognized that the injection of water at high-pressure into subsurface formations can lead to pollution of the hydrosphere, biosphere, and atmosphere with serious consequences for flora and fauna and the quality of drinking waters. Another consequence is induced seismicity which may cause damage to surface structures, associated risks of personal injury, and potentially compromise the integrity of wellbores and other subsurface infrastructure (e.g., flowlines and pipelines).\textsuperscript{7,84,86–90} Among all above mentioned environmental risks, water issues, including water use and reuse, water contamination, and wastewater disposal, are the most direct and perhaps have the greatest negative impacts.

The hydraulic fracturing fluid generally consists of three components: (i) the base fluid, which is the largest constituent (usually 98% or more) by volume and is typically water, (ii) the additives, which are generally a mixture of chemicals (as listed in Table 2), and (iii) the proppant, which is solid material designed to keep hydraulic fractures open. The chemical additives in the fracturing fluid and the products of their interaction with the organic matter and radioactive elements in the formation are initially released into the subsurface shale formation, some of which eventually flows back to the surface.\textsuperscript{82} The flow-back water may contaminate underground drinking water sources and the surface environment if not carefully handled.\textsuperscript{93,94} Of course, there has been a continuous effort to develop safer additives, and more
importantly, there are no documented cases of propagation and contamination of fracturing fluid to shallow aquifers, though the potential for hydraulic fractures to propagate to the near-surface deserves special concern.\(^{85}\) Water contamination may occur especially in scenarios of shallow fracturing in the vicinity to aquifers and/or the regional groundwater levels, poorly cemented casing in the wellbores, and surface spills due to equipment failures or improper fluid-handling operations.\(^{46,95,96}\) In addition to the leakage of fracturing fluids, flow-back fluids and wastewater may perturbate the groundwater equilibrium and the stability of geochemical and hydrodynamic processes in the subsurface.\(^{88}\)

The development of shale gas plays can also lead to air pollution. Greenhouse gases, such as methane from fugitive emissions and carbon dioxide, and toxic gases like ozone and aromatic-rich vapors released from aromatic hydrocarbon liquids such as benzene, are produced regularly during fracture stimulation activities. The released greenhouse gases can degrade air quality and contribute to climate change. The toxic components can have negative health impacts and cause eco-system damage.\(^{97,98}\)

### 2.3.2 Poor hydrocarbon recovery.

Shale is mostly water-wet and the initial water saturation is less than 100\%.\(^{99,100}\) During the shale gas recovery process via hydraulic fracturing, water will imbibite into microfractures and shale pore system. Because of the capillary force, water will stay in the fractures or pores which narrows or even block the gas flow pathways.\(^{101}\) Therefore, the permeability of shale will decrease after water imbibition.\(^{102–104}\) The reduction of shale permeability will increase with the increase of water saturation.\(^{47,105}\)

Injecting large amounts of water into shale reservoirs may cause specific water–shale interactions, potentially leading to reduced hydrocarbon recovery. Swelling clays, such as smectite, have the ability to take up water, leading to a volumetric expansion. If present in the shale reservoir, this can result in a reduction in pore and pore throat sizes.\(^{106}\) The swelling potential can be classified by the activity value which is a ratio of plasticity index and clay fraction.\(^{107}\) Fig. 2 summarizes the swelling potential of several shales with different clay fractions.\(^{108–111}\) It can be seen that shales present appreciable swelling potential which increases with increased clay content. Even with clay content as low as 7\%,\(^{112}\) the maximum free swelling percentage was about 1.6\%. The swelling of shale can decrease the accessible specific surface area, ultimately reducing gas that could desorb and produced from the shale matrix.\(^{113}\) As water filtrates into cracks and pores, it tends to block the pore throats and trap hydrocarbons. The water-blocking effect leads to a decrease in permeability.\(^{102,114}\)

### 3 CO₂ emissions and CO₂ utilization, and storage

#### 3.1 Anthropogenic CO₂ emissions and global impacts

Present and future worldwide economic growth relies on the consumption of fossil fuels. Coal, oil and natural gas are responsible for a large amount of the global energy supply and similarly contribute to overall CO₂ emission.\(^{115}\) In 2019, a total of 33.3 gigatons (Gt) of CO₂ were emitted to the atmosphere globally, which is \(~60\%\) higher than in 1990.\(^{116}\) In the US, more than 60\% of the total stationary CO₂ emissions are contributed by large stationary sources, like power plants, cement production plants, iron and steel manufacturing facilities, etc.\(^{117}\) It is important to note that different stationary sources have different CO₂ quantities in their flue gases. Coal
3.2 CO₂ utilization and sequestration in geoenery exploitation

CO₂ capture, utilization, and storage (CCUS) is considered a key requirement to limit CO₂ emissions to the atmosphere, contributing at least one-sixth of global CO₂ emission reductions by 2050. It is further estimated that CCUS will lead to a 14% reduction in cumulative emissions between 2015 and 2050 to achieve the targeted 2°C scenario by 2050, and thereby reduce the overall costs required to mitigate the negative global impacts of climate change. The utilization and sequestration of CO₂ in energy exploitation have shown promising potential to decrease the total CO₂ emission.

3.2.1 CO₂ utilization. The utilization of CO₂ can be divided into two types: physical utilization and chemical utilization. The physical utilization involves CO₂ being partially or totally converted to chemicals and fuels. Norhasyima and Mahlia have statistically analyzed the CO₂ utilization methods from 3002 related patents searched from the Derwent Innovation. They found that, more than half of them were related to chemicals and fuel, a quarter to enhanced oil (EOR) and enhanced coalbed methane (ECBM) recovery, 16.3% to biofuels from microalgae, mineral carbonation accounted for 3.4% and enhanced geothermal system (EGS) contributed 1.5%. The patent applications provide insight to the potential utilization of CO₂ in geoenery recovery.

3.2.1.1 CO₂-EOR. The primary oil recovery for conventional and unconventional formation is less than 20% and 10%, respectively. This means that large quantities of oil remain in the reservoir. The injection of CO₂ has the potential to increase oil recovery by 5–15%. A schematic diagram for CO₂ enhanced oil recovery is shown in Fig. 4. The potential additional oil recovery by secondary and tertiary recovery using carbonated (or CO₂-saturated) water injection is 6.2–56.74% and 9–40.54%, respectively. The injection of CO₂ increases the pressure of depleted oil formations and decreases the viscosity of oil, thereby creating high flow rates and mobility for additional recovery of oil. Meanwhile, CO₂ especially under supercritical conditions, is a highly effective solvent that can decrease the viscosity of oil, allowing the oil to flow through the reservoir and into wellbores more easily. CO₂ can penetrate into micropores and nanopores and dissolve the oil, leading to oil expansion. The increase in oil volume makes the oil easier to migrate in the reservoir and to the production well. Intermediate components of oil gradually form the miscible phase with CO₂, reducing the oil and gas interfacial tension. Because of these benefits, CO₂-EOR has been applied in many countries. As of 2019, there are more than 150 individual CO₂-EOR projects around the world.

3.2.1.2 CO₂-ECBM. In 2017, the proven coalbed methane reserves in the US were 11 TCF, with a recovery efficiency of 20–60%. Coalbed methane can be enhanced by CO₂ injection as a secondary recovery mechanism. The injection of CO₂ maintains the pressure of the coal seams and higher sorption ability promotes methane desorption from internal porous surfaces of coal. Then the desorbed methane migrates through the pore space or cleats (fractures in coal) to the production well. Several pilot and micro-pilot projects of CO₂-ECBM have been applied in Australia, Canada, Japan, China, Poland and the US.

Fig. 3 The variations of CO₂ concentration/earth temperature with years.

Fig. 4 A schematic diagram for CO₂-EOR.
3.2.2 CO₂ sequestration. Generally, the approach adopted for CO₂ sequestration is to capture CO₂ emission point sources like coal fired power plants, to transport it to an injection site, and to then sequester it in subsurface formation over long periods of time. 168,169 Considerable amounts of carbon dioxide will dissolve in formation waters, and might become mineralized in the form of carbonates over extended periods of time. 170,171 Potential CO₂ sequestration sites available are saline aquifers, depleted gas and oil reservoirs, unminable coal seams, and actively producing oil fields combined with enhanced recovery processes (see above). 172–177

With more than 100 years of oil and gas exploitation, many oil and gas fields have already been depleted or are approaching the end of their commercially productive lives. 137 Benefits of CO₂ storage in depleted gas and oil reservoirs include: 178 (1) the oil and/or gas already removed offers plenty of original CO₂ storage capacity; (2) CO₂ can be stored at pressures that are close to the original reservoir pressure prior to production which avoids the risk of long-term formation damage and potentially inducing man-made subsidence at the surface; (3) the favorable geological conditions that originally facilitated oil and gas entrapment decrease the risk of CO₂ leakage through the primary caprock; (4) exiting wells and other infrastructure installed originally for oil and gas production purposes can be re-used for CO₂ injection. Meanwhile, the depths of most hydrocarbon fields are greater than 800 m, which ensures that the CO₂ would be stored in the supercritical phase. 179

CO₂ sequestration projects have been applied by many countries, as listed in the ESI.† By October 2019, there were 19 large-scale CCUS projects operating around the world storing ~32 Mt of CO₂ per year.‡ In the past 40 years, more than 1 billion tons of CO₂ were injected for CO₂-EOR operations in the US, and more than 99% of the injected CO₂ remains safely trapped. 181 The development of CO₂ geological storage still needs supports from the government, such as the 45Q tax incentive in the US, 182 and tools to better characterize and understand large-scale sequestration.183,184

4 Role of SC-CO₂ in shale gas recovery and sequestration in shale gas reservoirs

When studying shale gas recovery, SC-CO₂ has the potential to support three different key aspects: drilling, fracturing and long-term storage (Fig. 5). In this section, the potential of the three aspects are discussed.

4.1 SC-CO₂ based drilling

The high-pressure water-jet technology has been widely used for drilling in the oil and gas industry since the 1950s. To further improve the drilling efficiency and rock cutting or breaking performance, structures and properties of the water jet have been optimized to develop various types of jets (e.g.
In an experimental study using artificial rock cores, Du, et al.\textsuperscript{193} found that a SC-CO\textsubscript{2} jet is able to achieve a higher rock-breaking depth than a water jet at the same pressure. Following these initial findings, a series of experimental and numerical studies were conducted to optimize the structure of nozzles which can improve the drilling ability of SC-CO\textsubscript{2} jets.\textsuperscript{190,194–196} Meanwhile, further investigations were performed to analyze the flow field of SC-CO\textsubscript{2} jets in wellbore conditions.\textsuperscript{197} It was found that the effects of pressurization,\textsuperscript{198} real gas behavior,\textsuperscript{199} and self-excited oscillations\textsuperscript{200} in SC-CO\textsubscript{2} jets are beneficial for rock-breaking, while the stagnation effect\textsuperscript{201} has a detrimental impact on drilling (Table 3). Considering the low viscosity, the feasibility of SC-CO\textsubscript{2} for carrying cuttings was experimentally and theoretically verified.\textsuperscript{202} The results showed that cuttings are difficult to transport when the well angle is between about 60° and 80°. Fortunately, the viscosity of SC-CO\textsubscript{2} can easily be increased by adding additives such as the fluoroether disulfate telechelic ionomer, to improve its ability to effectively carry cuttings.\textsuperscript{203} A comparison of drilling ability between water and SC-CO\textsubscript{2} is listed in Table 4.

### 4.2 Using SC-CO\textsubscript{2} as a fracturing fluid

SC-CO\textsubscript{2} fracturing has been investigated through experimental and numerical methods.\textsuperscript{204–207} Due to its low viscosity and lack of surface tension, SC-CO\textsubscript{2} used as a fracture stimulation fluid, has the potential to lower the formation breakdown pressure and create more irregular multiple fractures compared to liquid CO\textsubscript{2} or water. Wang, et al.\textsuperscript{208} used the Niobrara shale to conduct fracturing experiments with gaseous and SC-CO\textsubscript{2}, as well as slickwater with the same confining pressures and temperature. They found that gaseous and SC-CO\textsubscript{2} induced fracturing occurred at much lower pressures than slickwater fracturing, which were 6.6 MPa, 9.6 MPa and 11.0 MPa, respectively. In a numerical study, investigating the fracturing process with water, viscous oil and SC-CO\textsubscript{2},\textsuperscript{209} it was demonstrated that

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<td>Real gas effect\textsuperscript{198}</td>
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<td>The impinging peak pressure is higher than that of the continuous SC-CO\textsubscript{2} jet; the frequency distribution is different from that of the self-excited oscillation pulsed water jet.</td>
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<td>The increase of injection pressure presents a large increase of the stagnation pressure and a minor decrease of the ambient temperature; the stagnation temperature is mainly controlled by injection temperature.</td>
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<td>Water is better than SC-CO\textsubscript{2}\textsuperscript{202}</td>
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With the rapid development of deep resource exploration, more and more deep and ultra-deep vertical wells and long horizontal wells being used. This has intensified the demand for improving the rates of penetration (ROP) and minimizing the turn radius to reduce the cost of exploration and exploitation. The traditional high-pressure water jet offers few advantages for improving drilling efficiency because of the water-lock effect, the high threshold pressure for water jet erosion and the large pressure loss of coiled tubing.\textsuperscript{188,189} Air drilling fluids like foams and nitrogen can create satisfactory underbalanced drilling (UBD) conditions which in many subsurface conditions are beneficial for the improvement of ROP. However, their low density makes it difficult for such fluids to provide sufficient torque for bottom hole motors to operate efficiently.\textsuperscript{190} SC-CO\textsubscript{2}, which has liquid-like density, is an attractive choice by the drilling industry for certain sub-surface conditions. Above critical temperature and pressure for CO\textsubscript{2}, which is typically the case in shale gas reservoirs with horizontal wells, CO\textsubscript{2} is in the supercritical phase.

Kolle\textsuperscript{189} was the first to conduct laboratory tests to evaluate the SC-CO\textsubscript{2} based drilling potential. The results show that the threshold erosion pressure for CO\textsubscript{2} is ~67% of water in the Sierra white granite and 44% of water in the Mancos shale. The specific energy for cutting granite with SC-CO\textsubscript{2} is 42% of granite and only 3% of granite in shale. Since then, other studies have used additional experimental and numerical methods to further investigate the SC-CO\textsubscript{2} jet. Gupta\textsuperscript{191} developed a circulation model to calculate the SC-CO\textsubscript{2} jet impact force and the cuttings transport ratio. Results show the advantage of SC-CO\textsubscript{2} drilling, specifically that its liquid-like density can turn the downhole motor and gas-like viscosity can maintain underbalanced conditions. Al-Adwani, et al.\textsuperscript{192} simulated the erosion rate of pure SC-CO\textsubscript{2} in UBD operations, concluding that SC-CO\textsubscript{2} is a viable UBD fluid.
SC-CO$_2$ has the lowest and viscous oil the highest breakdown pressure. Fernandez, et al.\textsuperscript{165} used numerical and experimental methods to investigate the fracability of a CO$_2$-reactive polymer (CO$_2$ + nontoxic poly(allylamine)). They found that this nontoxic SC-CO$_2$-based fracturing fluid could be used to fracture rock cores at lower net pressures, which was caused by the CO$_2$-triggered volume expansion and the reduction in pore invasion pressure caused by the lower interfacial tension. Zhang, et al.\textsuperscript{210} found that SC-CO$_2$ fracturing was more likely than hydraulic fracturing to create fractures, especially secondary fractures near the tail end of the transverse fractures that connect with natural fractures and bedding planes to form a more complex and interconnected fracture network. These results were confirmed by using coupled modelling to simulate shale fracturing using SC-CO$_2$, liquid CO$_2$, and water (Fig. 6).\textsuperscript{210,211} SC-CO$_2$ fracturing can create rougher and more complex fracture surfaces than hydraulic fracturing, resulting in higher tortuosity of fractures created by SC-CO$_2$ compared to freshwater (Fig. 7).\textsuperscript{212–215} While keeping the fracturing conditions the same, SC-CO$_2$ induced an artificial fracture area, which was 60% higher than that induced by hydraulic fracturing.\textsuperscript{213} In addition, the fractal dimension of SC-CO$_2$ induced fracture surface ranged from 2.2314 to 2.2660, higher than that of the water fractured surface (ranged from 2.0855 to 2.1058),\textsuperscript{215} indicating more complex rough surfaces. Generally, shale is an anisotropic sedimentary rock with geomechanics and transport properties varying significantly in the horizontal compared to the vertical direction. As such, the orientation of bedding related to the vertical load affects fracture propagation.\textsuperscript{77} It was found that the breakdown pressure with SC-CO$_2$ fracturing was higher than that with freshwater fracturing when the bedding plane orientation varied from 0° to 90°.\textsuperscript{212} The reservoir stress and temperature, which also affect the fracturing characteristics, have been investigated by some researchers.\textsuperscript{78,216,217} The increase of temperature reduced the viscosity of SC-CO$_2$ which can easily permeate into the microcrack tip and promote fracture propagation. The SC-CO$_2$ flow in newly created void fractures will enhance fracturing because of the thermo-mechanical effects caused by the Joule-Thompson throttling process.\textsuperscript{218}

Similar to N$_2$, the low viscosity of SC-CO$_2$ limits its transport capacity for proppants. However, SC-CO$_2$ is a good solvent for synthetic polymers,\textsuperscript{219} which allows the viscosity to be modified by adding CO$_2$-philic chemicals (e.g. fluoroether disulfate telechelic ionomer) to enhance proppant lifting, transport and delivery under borehole conditions.\textsuperscript{22,220,221} The composition of the natural gas in shale reservoirs, specifically its natural gas liquid concentrations, is also likely to impact the physical properties of SC-CO$_2$ injected into gas-rich formations. For example, varying concentrations of methane, ethane, propane and nitrogen are known to impact the minimum miscibility of CO$_2$-rich fluids with oil\textsuperscript{222} and are likely to impact SC-CO$_2$ properties as it penetrates into a shale gas formation.

Field tests conducted in the Yan-2011 shale gas well in China showed that SC-CO$_2$ fracturing was able to create a more complex fracture network than hydraulic fracturing.\textsuperscript{223} However, field tests for SC-CO$_2$ fracturing are still limited. The microseismic response distributions after SC-CO$_2$ fracturing
need to be mapped and evaluated in more detail for a range of shale formations to better define the fracture network development potential SC-CO₂ fracturing. Further field-scale studies are required to obtain additional information on actual shale gas recovery from real anisotropic shale formations, not just laboratory tests.

4.3 CO₂ storage in shale gas reservoirs

When injected into shale gas reservoirs, CO₂ is preferentially adsorbed over methane on organic and inorganic pore surfaces, resulting in methane desorption and CO₂ storage within these formations. In addition, natural and induced fractures offer additional volumes for CO₂ storage, in combination making shale gas reservoirs a potential sink for CO₂ sequestration. Godec, et al. estimated the theoretical CO₂ storage capacity in the Marcellus shale in the Eastern US at 4.915 m depth. Considering reservoir properties (depth, thickness, total organic carbon, effective porosity, apparent gas saturation, CO₂ and methane adsorption isotherms, and permeability), the adsorbed CO₂ storage capacity is about 0.92 million tons per square kilometer (Mt per km²). Based on the statistical data from the US Energy Information Administration (EIA) which assesses the technically recoverable shale gas resource around the world, nearly 70 types of shale gas formations from 48 shale gas basins in 32 countries represented primary gas productions ranging from 20% to 35%. The reservoir characteristics of the Marcellus shale are similar to the shale gas basins with an average production of 25%. Assuming an additional 7% of shale gas production enhanced by CO₂ injection, the total shale gas production for Marcellus shale is 32%. As such, it can be calculated that nearly 55 Gt of CO₂ could potentially be sequestered in the Marcellus shale. This CO₂ storage capacity is 1.7 times larger than the world’s CO₂ emissions in 2019. In additional to the Marcellus shale, other shale formations such as the Barnett Shale in the US, the Montney Shale in Canada, and the Longmaxi shale in China which also show considerable technically recoverable shale gas resources, could potentially be used to sequestrate substantial quantities of CO₂. It was therefore concluded that the potential of CO₂ storage in shale gas reservoirs can fulfill the target of reducing 14% of CO₂ which is and will be produced before 2050.

The sustainability and safety of geological CO₂ storage in shale reservoirs are the most important issues requiring careful assessments. The CO₂ trapping mechanisms in saline aquifers are structural and/or stratigraphic trapping, residual (capillary) trapping, solubility trapping, and mineral trapping. However, adsorptive trapping plays a significant role in shale gas reservoirs due to their high clay and organic matter contents, providing significant internal surface area. Liu, et al. simulated the feasibility of CO₂ storage in the New Albany Shale and found that more than 95% of the injected CO₂ was stored in the form of sorbed gas. As methane can be safely stored in the shale reservoir for long periods of time, the adsorption of CO₂ is also expected to be safe and stable and CO₂ has the potential to penetrate some of the nano-pores that hydrocarbon gases are unable to reach. This property is already exploited in gas adsorption studies to measure the nano-porosity distributions of shale. Liu, et al. solubility trapping and mineral trapping are more effective over longer timescales. However, the
matrix swelling and mineral dissolution that cause permeability variations strongly affect the cap sealing performance. The risk that some shale reservoirs may not be sealed adequately to prevent long-term seepage of CO₂ needs to be carefully evaluated in detail for each formation and potential trap. To date studies addressing long-term seepage of CO₂ from shales are limited.

5 Concerns of SC-CO₂ enhanced shale gas recovery and sequestration in shale gas reservoirs

5.1 Diffusion and adsorption of CO₂ in shale gas reservoirs

5.1.1 Advective and diffusive flow in shale gas reservoirs.

The Knudsen number (Kn) is a commonly used parameter to classify flow regimes in porous media. It is a dimensionless parameter, which is defined as the ratio of the molecular mean free path of gas and the characteristic pore size. Accordingly, continuum, slip, transition, and Knudsen flow can be distinguished as summarized in Table 5.

Typically, shale formations are multi-scale porous media, particularly thermally mature organic-rich shales. The space for gas storage and migration within shale reservoirs varies from meter scale to nanometer scale (Fig. 8). At the reservoir scale, gas moves through the reservoir (through the matrix and along connected fracture networks) and eventually flows into the wellbore due to pressure gradients. At the mesoscale, free gas in hydraulic fractures, natural fractures and macropores migrates following Darcy’s law. At the microscale, the slippage effect and Knudsen diffusion become significant, because at that scale continuum assumptions for the pore space are partly invalid. At the nanoscale, gas adsorption and desorption and surface diffusion are primary mechanisms controlling gas migration. Certain gases such as CO₂ and He, due to their molecular structure and size enter and move more easily than others at the nanopore scale. In adsorption tests on organic-rich shales with abundant nanopores, CO₂ and CH₄ penetrate the nanoscale pores more easily than N₂.

(1) Stress sensitivity effect. During shale gas production, the effective stress of the formation will increase continuously due to a reduction in pore fluid pressure. At higher effective stresses, hydraulic fracture apertures decrease, resulting in a decrease in fracture transmissivity. Therefore, understanding the permeability variations of shale gas reservoirs in terms of effective stress is essential for long-term shale gas production, especially for stress-sensitive formations.

To accurately estimate formation properties and shale gas production forecasts, various studies report permeability models coupled to mechanical effects. Liehui, et al. compared the different models and found that the Palmer and Mansoori model is suitable to describe permeability variations of a shale gas well over its entire production life span. Because of gas desorption in shale gas reservoirs, shale matrix shrinkage progressively occurs but particularly during the late production stage which can lead to an increase in permeability.

(2) Slippage effect. In conventional oil and gas reservoirs, fluid flow can be described according to Darcy’s law where it is assumed that fluid flow occurs in an unimpeded continuum. However, in shale gas reservoirs, micropores and nanopores account for a non-negligible percentage of the total pore volume. At depth, gas flow paths in micropores are comparable to the gas mean free path length. Darcy’s law, therefore, needs to be modified in such media because the continuity assumption is invalid.

According to the continuity assumption, the velocity of gas on the pore wall is zero. However, in micropores or nanopores, a non-zero molecular velocity should be considered at the pore wall, which is called the slippage or Klinkenberg effect. The slippage effect strongly affects the gas flow in shale reservoirs. Therefore, theoretical and experimental studies have been performed to describe the gas flow behaviors and a comprehensive summary is provided in Liehui, et al. There,

![Fig. 8](image-url) Gas storage and migration in shale reservoirs occurs at multiple pore scales with at least four distinct flow and gas movement mechanisms involved.

### Table 5 Flow-regime classifications based on Knudsen number

<table>
<thead>
<tr>
<th>Flow regime</th>
<th>Knudsen number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuum (viscous) flow</td>
<td>Kn &lt; 0.01</td>
<td>Darcy’s equation for laminar flow, Navier–Stokes equations for turbulent flow</td>
</tr>
<tr>
<td>Slip flow</td>
<td>0.01 &lt; Kn &lt; 0.1</td>
<td>Darcy’s equation with Klinkenberg correction</td>
</tr>
<tr>
<td>Transition flow</td>
<td>0.1 &lt; Kn &lt; 10</td>
<td>Darcy’s law with Knudsen correction*</td>
</tr>
<tr>
<td>Knudsen’s (free molecular) flow</td>
<td>Kn &gt; 10</td>
<td>Knudsen diffusion, usually occurs in nanopores</td>
</tr>
</tbody>
</table>

* The details for Knudsen correction are provided in ref. 236. The details for Knudsen correction are provided in ref. 237.
it was pointed out that the two most commonly used methods for modeling gas flow including slippage are an empirical Klinkenberg correction and slippage modification based on slip boundary conditions. For the empirical Klinkenberg correction, the intrinsic permeability is corrected by an equation that includes pore pressure, the slippage factor, and apparent permeability.252 For the slip boundary conditions, the first order, second (or higher) order and Langmuir slip boundary conditions are used to describe the gas flow in a transitional flow regime.253,254

5.1.2 Sorption capacities and competitive adsorption of CO2 versus CH4

5.1.2.1 Shale gas sorption capacities. Shale gas is commonly stored in reservoirs as dissolved gas, in the sorbed and in the free gas state. Sorbed gas accounts for 20 to 85% of the total shale gas storage capacity235 and is therefore important in the shale gas resource assessment. The gas sorption capacity of shales has been widely recognized as being closely related to moisture content, surface area, pore size distribution, total organic carbon (TOC) content, organic matter type and maturity, as well as clay mineralogy and clay content.256–262

TOC content is considered the most significant control on methane sorption capacity.263–265 Organic matter, typically quantified as TOC, is the source of the hydrocarbon gases present in a shale, while gas generation is mainly controlled by temperature and time during burial. Micropores in organic matter (<2 nm) provide high specific surface areas in comparison to macropores (>50 nm), particularly in thermally mature shales.261,266 Therefore, the methane sorption capacity correlates positively with TOC.259,267 Organic matter type and thermal maturity play complex roles in methane sorption capacity. For gas shales in the gas window, the sorption capacity shows a positive relationship with maturity because microporosity increases with maturity. Source rock organic matter can be classified in three types, which are found to generally show different sorption capacities, with Type I (lacustrine) < Type II (marine) < Type III (terrestrial).268 The micropores in clay minerals are also able to adsorb significant amounts of methane. For clay-rich shale, the methane sorption capacity can significantly contribute to the total sorption capacity.261,269–271 found that different types of clays have different sorption capacities: smectite > mixed layer illite/smectite > kaolinite > chlorite > illite. Busch et al. found a similar relationship with smectite > illite > kaolinite > chlorite.226 It should be noted that although water has a negative effect on the sorption capacity,272 most sorption tests have been carried out on dry samples which are not representative of reservoir conditions and should be treated carefully.

5.1.2.2 Competitive adsorption of CO2 versus CH4. While injecting CO2 into shale reservoirs for gas recovery and CO2 sequestration, the sorption ability of CO2 in shales should be considered. Various studies investigated the CO2 adsorption capacity of shales and clay minerals.30,236,273–278 They all found that the sorption capacity of CO2 in shale samples was higher than for CH4. The CO2/CH4 sorption ratio ranges between 1.3 and 10 for dry shale samples (Fig. 9).276 The molecular diameter of CO2 (0.33 nm) is slightly smaller than for CH4 (0.38 nm), which allows access to narrower pores and therefore higher surface area. In addition, CO2 has a higher sorption enthalpy resulting in a higher sorption capacity of CO2 over CH4.227,279

In the process of CO2-enhanced shale gas recovery, the competitive adsorption of CO2 and CH4 are essential to understand the efficiency of shale gas recovery and CO2 storage.30 Various studies report experimental CO2–CH4 competitive adsorption in shale samples.25,280–287 Here, shale samples are pressurized with CO2 and CH4 mixed gases at different molar ratios. With the increase in saturation pressure, the sorption volume of CO2 increases, while the sorption volume of CH4 decreases.281 As shown by nuclear magnetic resonance (NMR) studies, CO2 competitively sorbs over CH4.281 With an increase in reservoir pressure, CO2 shows better sorption ability than CH4.281,283,288 However, CO2 enhanced CH4 extraction exists in an optimal pressure range. In the study of Lee, et al.289 the suggested pressure range was 7 to 9 MPa. Other factors such as pore volume and pore size distribution (PSD), also affect shale sorption capacity.283

5.2 CO2–shale or CO2–liquid–shale interactions

When CO2 is injected into shale gas reservoirs, geochemical CO2–water–rock interactions occur over a period of time. This might cause physical properties of shale to change, potentially affecting the shale gas recovery efficiency and CO2 storage process.

5.2.1 Carbonic acid in water + CO2. The dissolution of gaseous CO2 in water creates a weak carbonic acid (H2CO3), which is in dynamic equilibrium with its dissociated forms (HCO3− and CO32−).290–293 The microsolvation of H2O and CO2 and the formation/decomposition of carbonic acid have been extensively studied by means of density functional theory (DFT), Hartree–Fock (HF), ab initio molecular dynamics, matrix isolation IR experiments, phase molecular beam, etc.293–298 However, the widely accepted reaction between H2O and CO2 in gaseous and aqueous conditions may be different in SC-CO2. The structural feature of SC-CO2 is that each CO2 molecule is surrounded by six other CO2 molecules configured in a distorted T-shaped configuration around the carbon.299 The reaction between H2O and CO2 to form H2CO3 in supercritical condition has a higher barrier than that of gaseous condition because H2O has to displace the surrounding CO2 molecule’s out of their equatorial positions and align them with the reacting C.293,298 Glezakou, et al. used an ab initio molecular dynamics method to examine the structure, dynamics, and vibrational spectra of SC-CO2/H2O (n = 0–4).288 They found that the strongest interactions between SC-CO2 and H2O occur in the case of monomeric water. The dynamic hydrogen bonds with the oxygens are mostly formed between the equatorial and polar coordinating CO2 molecules. For the decomposition of H2CO3, the enthalpy and entropy terms are similar in SC-CO2, but that is not the case for gaseous CO2. The formation of H2CO3 in SC-CO2 is thermodynamically unfavorable. Once formed, H2CO3 will probably be the...
undissociated form while the water is likely to remain unsaturated. The low solubility of water in SC-CO₂ resulted in the water clustering when the water concentration in SC-CO₂ was high. In the reservoir condition, the water usually contains brines like NaCl, the formation/decomposition of carbonic acid will be more complex and need further investigation.

5.2.2 Chemical reactions. Although well-defined concepts in aqueous solutions such as mineral solubility and ion activity do not have corresponding thermodynamic meaning in water-based SC-CO₂, McGrail, et al. demonstrated that water-based SC-CO₂ can be reactive with different mineral phases. Many scholars have proved the mineral dissolution and precipitation in such acidic fluids. Busch, et al. investigated the CO₂-shale interactions with temperatures between 45 °C and 50 °C and pressures up to 20 MPa. Minor geochemical reactions such as the dissolution of silicates and precipitation of carbonates were observed after sorption experiments. Alemu, et al. selected two caprock shale samples (a carbonate-rich and a clay-rich shale) to study the reactions between rocks and a mixture of brine and SC-CO₂ (the pressure was 11 MPa, the temperature ranged from 80 to 250 °C). By analyzing fluid major element concentrations as well as SEM and XRD tests, they indicated dissolution and re-precipitation of carbonates, dissolution of plagioclase, illite, chlorite and the formation of smectite. When shale rocks are exposed to CO₂–water mixtures, chemical reactions such as the dissolution of calcite, carbonates and clay minerals could be observed. If the imbibition time is long, quartz could also be dissolved. The geochemical reactions can potentially affect petrophysical properties which will be discussed below.

5.2.3 Physical changes. Mineral dissolution creates additional porosity within rock formations, whereas precipitated minerals can block the connection of pores. These chemical processes can change the petrophysical properties of shales. Therefore, investigating shale properties following CO₂–water–rock interaction can help predicting potential causes and consequences over long timescales, using advanced experimentation and reactive transport or batch modelling. This will promote the assessment of the suitability for CO₂ enhanced shale gas recovery and CO₂ sequestration of specific shale gas reservoirs. In the following, the macro and microscale changes of shale properties after reaction with CO₂ and carbonated fluids are reviewed.

5.2.3.1 Macroscale variations. Important macroscale properties of shales include mechanical (strength, brittleness, hardness/toughness) or petrophysical properties (permeability, porosity). Significant changes of these properties due to
CO₂–water–rock interactions might impact reservoir performance in terms of mechanical stability and recovery rates.

(1) Mechanical properties. Strength is a fundamental mechanical property of a rock. Previous studies report uniaxial compressive strength (UCS) and tensile strength (TS) tests to determine the variation of a shale's strength after CO₂–water–rock reaction. The experimental conditions and major results are shown in Table 6 and Fig. 10. It can be seen that CO₂ and its saturated fluids decrease the strength of shale samples. With 30 days of imbibition, the strength of shales reacted with sub/supercritical CO₂, sub/supercritical CO₂ + water, and sub/ supercritical CO₂ + brine decreased by 20% and 30%, 56% and 66%, and 61% and 70%, respectively. Longer imbibition time leads to more extensive CO₂–shale or CO₂–water/brine–shale reactions and a higher reduction of stress. With a lower pH value than pure CO₂, CO₂ saturated water or brine yields conditions where chemical reactions are more violent. Therefore, the strength of shale samples with CO₂ + water/brine imbibition is lower than that with CO₂ imbibition. SC-CO₂ has no capillary force and lower values of viscosity than subcritical CO₂. With the same reaction time, SC-CO₂ penetrates into shale samples and reduces their strength more than subcritical CO₂. The trends of strength variation vary among shale types. Different shales have distinct anisotropy, mineral composition, and thermal evolution, which leads to differences in the mechanical changes caused by CO₂ and CO₂ + water/brine imbibition.

The shale–CO₂ or shale–water/brine–CO₂ interactions influence the brittleness index (BI) of shale. BI is usually used to characterize the potential of fracability, that is, a higher value BI means a better fracability, which is beneficial for reservoirs with re-fracturing treatment. Lyu, et al. used the energy-based method to calculate the BI values of shale samples with different soaking times in subcritical CO₂, SC-CO₂, subcritical CO₂ + water, and SC-CO₂ + water. The results showed that, with 30 days of imbibition, subcritical CO₂ and SC-CO₂ imbibition resulted in 13% increase of the BI values of shale, while samples with subcritical CO₂ + water and SC-CO₂ + water imbibition displayed 17% reduction of BI values. It can be deduced that CO₂ imbibition enhances a shale's fracability, while CO₂ + water imbibition lowers the fracability. The fracability can also be characterized by the variations of toughness and hardness. If the toughness decreases, the brittleness increases. A low value of hardness means fractures can be created more easily. Based on the study of Ilgen, et al., with 7 days of CO₂–brine imbibition, quartz-rich shales showed a small decrease, while dolomite- and muscovite-rich shales showed about 50% decrease in toughness and hardness. However, the fracability of shale reservoirs cannot be determined using BI, toughness, or hardness alone. As reported in Lyu, et al. and Lyu, et al., samples soaked in CO₂ + water were weakened more than those soaked in CO₂. The weakening of shale which caused by imbibition induced cracks and pores also contributes to better fracability.

As discussed before, four types of gas flow should be considered when CO₂ is injected into shale reservoirs: viscous flow, Knudsen diffusion, molecular diffusion, and surface diffusion.  

![Fig. 10 Compressive and tensile stress of shale samples after CO₂ and CO₂ saturated water or brine imbibition.](image-url)
different reaction time, temperature, and pressure. They found that the permeability of both shales increased with increasing reaction time, temperature, and pressure. This was caused by the dissolution of carbonates, which creates more pores and improved pore connectivity.

However, the experiments conducted by Zhou, et al.\textsuperscript{323} showed that CO\textsubscript{2} adsorption leads to shale swelling and a decrease in permeability. The permeability reduction is more likely to occur in ultra-low permeability shales where fluids flow paths are more sensitive to CO\textsubscript{2} sorption-induced swelling.\textsuperscript{324}

The published experimental results, therefore, provide complex results suggesting that permeability of shale after CO\textsubscript{2} and CO\textsubscript{2} based fluids imbibition can either increase or decrease depending on shale properties and a range of factors. The complex trends are not just affected by the processes of adsorption/desorption and dissolution/precipitation. The composition of the samples and the bedding angles, testing methods, and imbibition conditions are also important factors. The salinity of the formation fluids and the temperature of the injected SC-CO\textsubscript{2} fluids impact interfacial tension (IFT) of the shale-water/brine-CO\textsubscript{2} solutions in the reservoir, which in turn impacts the relative permeability of the water/brine-CO\textsubscript{2} rich phase versus the hydrocarbon-rich phase in the reservoir.\textsuperscript{325} More experimental and analytical studies are required to better quantify and rank the significance of these factors on permeability changes in a wide range of shales following SC-CO\textsubscript{2} imbibition.

5.2.3.2 Microscale variations. The macroscale changes of shale are accompanied by microscale variations. Pore sizes of microporous systems like gas shales are classified into three distinct groups: micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm).\textsuperscript{326,327} CO\textsubscript{2}, with linear molecular geometry, can access a certain fraction of micropores that other naturally-occurring gases cannot access. Jiang, et al.\textsuperscript{328} experimentally investigated the microstructure of shales after treatment with SC-CO\textsubscript{2} at different pressures (8–18 MPa), reaction times (0–5 days) and temperatures (40–90 °C). The specific surface area and porosity increased slightly with an increase in temperature and reaction time. Higher pressure significantly promoted an increase in specific surface area and porosity. Similarly, the increasing trends of porosity have also been observed in shales with SC-CO\textsubscript{2} saturated brine imbibition.\textsuperscript{312} Pan, et al.\textsuperscript{329} used marine and terrestrial shale samples to conduct similar tests but increased the soaking time to 14 days. After SC-CO\textsubscript{2} imbibition, the number of micropores and mesopores in the marine shale (with low clay contents) decreased, while the number of macropores increased, resulting in a higher porosity overall. However, the terrestrial shale with high clay content exhibited the opposite trend of porosity changes to the marine shale after SC-CO\textsubscript{2} imbibition. This was interpreted to be mainly caused by clay swelling during imbibition.

The increase in porosity occurs mainly because of the chemical reactions between CO\textsubscript{2}/CO\textsubscript{2} based fluids and shale minerals during the process of fracturing and sequestration. The dissolution of calcite, quartz, illite/smectite, and chlorite and the precipitation of iron-rich carbonate(siderite), illite, and smectite have been observed when shale samples are exposed to CO\textsubscript{2}.\textsuperscript{330–333}

5.3 Further concerns

5.3.1 Costs of using SC-CO\textsubscript{2} in shale gas recovery. During the process of SC-CO\textsubscript{2} enhanced shale gas recovery, the CO\textsubscript{2}-related costs are related to CO\textsubscript{2} capture, transport, and storage. CO\textsubscript{2} can be obtained from power plants and transported by pipelines, trucks or ships.\textsuperscript{334,335} Pipeline corrosion caused by CO\textsubscript{2} can be prevented by surface coating and cathodic protection.\textsuperscript{336} CO\textsubscript{2} should be compressed to a liquid phase which can be stored near the well. For SC-CO\textsubscript{2} fracturing, CO\textsubscript{2} will be compressed to a high pressure and injected into shale wells. The energy requirement for CO\textsubscript{2} compression is about 1.2 to 1.5 kW h per t-CO\textsubscript{2} per 1 MPa.\textsuperscript{337,338} The flowback gas which mixes with natural gas and CO\textsubscript{2} need to be separated. The CO\textsubscript{2} content in natural gas should be decreased to 2–5% to meet typical pipeline specifications.\textsuperscript{339} The major separation processes of CH\textsubscript{4} and CO\textsubscript{2} are chemical and physical adsorption, low temperature distillation, and membrane separation.\textsuperscript{340} Membrane separation represents commercial advantages and has become a major industrial application.\textsuperscript{341} The cost of the gas separation system is not a one-time investment, the operation and maintenance cost, the natural gas lost, and the gas processing cost should also be considered.\textsuperscript{342} The separated CO\textsubscript{2} can be reused for fracturing. The cyclic injection process should be optimized based on the net present value (NPV).\textsuperscript{343}

Currently, the investments required for SC-CO\textsubscript{2} fracturing are significantly higher than for hydraulic fracturing. However, if the SC-CO\textsubscript{2} fracturing process is combined with CO\textsubscript{2} sequestration, costs can be lowered when the operation is part of a CO\textsubscript{2} tax scheme. Shafeen, et al.\textsuperscript{344} calculated the investment of a CO\textsubscript{2} sequestration project. A total of US$257 million dollars is needed for a project with 1 off shore platform, 10 injection wells, and 112 kilometers of pipelines, the CO\textsubscript{2} capture costs ranging from US$30 per ton to US$60 per ton, are not included.\textsuperscript{345} For hydraulic fracturing, the total costs of disposal, basic separation, and desalination of flowback water range roughly between $78 000 and $1460 000 for each well.\textsuperscript{346} The costs for groundwater and surface water cleanup add significant expenses to this operation.\textsuperscript{347} Till now, hydraulic fracturing is still the appropriate technique for shale gas recovery. The application of SC-CO\textsubscript{2} fracturing together with CO\textsubscript{2} sequestration relies on the supporting policy from the government, more capital channels, and the integration of social resources.

5.3.2 Induced seismicity and environmental impacts. Similar to hydraulic fracturing, extracting hydrocarbons from low permeability shale formations through SC-CO\textsubscript{2} fracturing may also cause environmental impacts and induce or trigger earthquakes. During the fracturing process, SC-CO\textsubscript{2} can penetrate the unconnected micropores in the formation more easily than the water-based fracturing fluid, form a high pore pressure area around the wellbore, and may transfer the fluid pressure to the farther and deeper part of the formation. Numerous
fracturing. It is worth noting that CO2-based fracturing cycle assessments (LCA) of using SC-CO2 in shale gas recovery or in CO2 sequestration might therefore be a considerable adsorption capacity of CO2. Water-based fracturing consumes achieved net carbon offsets as shale pores show considerable adsorption capacity of CO2. Water-based fracturing consumes large amount of water. The transfer to CO2-based fracturing avoids high-volume surface and groundwater extractions and further minimizes active fluid management over the well’s lifetime, including produced water storage, transport, and treatment at the wellhead. CO2-based fracturing is region-specific. It is much more suitable for regions where the extractions and disposal of high volumes of water are constrained and CO2 sources are accessible.

The public concerns of hydraulic fracturing focus on the large amount of water consumption, drinking water contamination, fugitive methane emissions, seismic events, noise pollution, and truck traffic. Although CO2-based fracturing avoids water consumption and contamination, the increase of total truck trips (100% higher than water-based fracturing) will lead to high public health risks. The construction of CO2 pipelines can help to reduce the risks and increase the fluid transport efficiency. Depleted shale well can be used for CO2 sequestration. A design of collocated parallel pipelines for both CO2 and natural gas transport is beneficial for CO2 fracturing/sequestration and natural gas supply. The advanced pipeline strategy requires the coordination between CO2 sources, field services suppliers, and producers. Although CO2-based fracturing shows advantages for shale gas recovery, the effective large-scale deployment of this technique should consider social, technical, and environmental trade-offs.

5.3.4 Further investigations

5.3.4.1 Laboratory study. Previous work has shown some advantages of SC-CO2 enhanced shale gas recovery. However, the changes to shale properties, fracturing results, and drilling ability after imbibition with CO2 or CO2-based fluids are complex. Generalization of established trends is not yet possible using information from studies published to date. This is because the laboratory tests are limited by several factors:

(a) Sample anisotropy. With the process of deposition, burial, and lithification, shale can be divided into three types: marine shale, continental (lacustrine) shale, and transitional facies shale. The mineral composition and porosity of the three types of shales are different, which results in variable adsorption abilities. Even for one type of shale, the clay minerals assemblage can vary by location. The methane adsorption ability of each clay mineral assemblage tends to be different (e.g., where smectite ⇠ illite compared to smectite mixed layers > kaolinite > chlorite > illite). Therefore, it is necessary to determine the types of shale and characterize its clay mineralogy and heterogeneity before imbibition tests.

(b) Sample Size effect. The mechanical properties of rocks are closely related to the size (diameter, height-diameter ratio) of samples. The bedding angles of shale formations also affects rock properties. More importantly, the size scale of samples used in laboratory tests is typically too small to reliably represent the real reservoir conditions. Therefore, comparisons of reaction results between samples with different sizes are necessary. Despite the difficulty of sample preparation, large shale samples are suggested for conducting robust SC-CO2 imbibition tests.

(c) Reaction conditions. The CO2 injection and release rate, the heating rate, and the pressure/temperature stabilization in the imbibition process affect the actual sample test results. The soaking time in most published studies was less than 30 days. According to some published research, 358-359 30 days of imbibition is not long enough to affect the porosity of shale or coal. A shale gas well might remain productive for 5 to 40 years, and CO2 sequestration needs to be stable for thousands of years. While the diffusion of CO2 in shale rocks is as slow as millimeters per year. Therefore, to better understand the effects of SC-CO2 on shale reservoirs, longer soaking times in laboratory tests are required.
5.3.4.2 Field tests. Previous studies mainly focus on the laboratory tests of the possibility of using SC-CO₂ for shale gas recovery. Field tests for SC-CO₂ fracturing are still limited. More investigations should be conducted by field tests to promote the application of SC-CO₂ enhanced shale gas recovery. (a) Drilling. Laboratory tests have demonstrated the feasibility of SC-CO₂ based drilling. However, in the real condition of application, the drilling ability should consider both the fluids flow in the wellbore and the cutting-carry ability of fragments. The physical properties of SC-CO₂ is sensitive to the pressure and temperature that are related to the CO₂ injection, injection pressure and temperature, depth of the well, and the roughness of the well surface.³⁶⁰,³⁶¹ The change of physical properties will directly affect the drilling ability of SC-CO₂. Some researchers have investigated the SC-CO₂ flow by simplified models.¹⁹¹,³⁶²,³⁶³ However, these models have not been validated by field tests. To increase the drilling efficiency, the fragments produced by drilling need be cleaned immediately. The cutting-carry ability of SC-CO₂ was studied by laboratory experiments with a meter-scale. While a well for shale gas recovery is usually composed of a vertical well with hundreds of meters to several kilometers and several horizontal wells with more than one kilometer. The cutting-carry ability of SC-CO₂ at a kilometer-scale remains unknow. (2) Proppant-carry in fractures. Like hydraulic fracturing, SC-CO₂ fracturing also needs the propannt to hold the fractures open. However, SC-CO₂ has good diffusion ability, the filtrate loss is larger than using water. Thereby the proppant-carry ability decreases with a decrease in turbulence intensity in fractures. Meanwhile, the particle-fluid multiphase flow is also affected by temperature and pressure variations caused by the heat transfer between shale rocks and SC-CO₂.³⁶⁴,³⁶⁵ (3) Fracturing equipment. Before fracturing, sands should be continuously be added to the liquid CO₂. It is very difficult to control the high-pressure sand-CO₂ mixing process. Sands in the well can block perforation nozzles resulting in overpressure of the fracturing equipment.³⁴⁹,³⁶⁶ Therefore, a sand-adding equipment is necessary to fulfil the demand of large-scale SC-CO₂ fracturing.

6 Conclusions, challenges, and perspectives

Based on the review of the current literature, we conclude that it is feasible to use SC-CO₂ to enhance shale gas recovery instead of using conventional water-based fracturing fluids. SC-CO₂ might be applied with three distinct objectives: (1) Drilling. The rock-breaking threshold pressure and cutting energy required for SC-CO₂ jets are lower than those of water jets. However, the capacity of SC-CO₂ to carry cuttings still needs to be improved. (2) Fracturing. SC-CO₂ fracturing can create more irregular multiple fractures and rougher and more complex fracture surfaces than liquid CO₂ or water. (3) Sequestration. Shale gas reservoirs have substantial potential for CO₂ sequestration. CO₂ injected into reservoirs could be safely and stably stored by solubility, adsorption, and mineral trapping. Considering the large quantities of CO₂ consumed during each SC-CO₂ fracture stimulation operation, the large-scale application of SC-CO₂ enhanced shale gas recovery is restricted by the high expense of CO₂ capture and transportation to supply CO₂ to many injection sites.

Although SC-CO₂ shows significant benefits in enhancing shale gas recovery, there are still some challenges that need to be addressed. Firstly, CO₂–shale or CO₂–water/brine–shale interactions strongly affect the properties of shale. The direct and indirect effects of these interactions on the recovery of shale gas and CO₂ sequestration are still unknown. More work is required to better quantify and model such effects. Secondly, the mechanism of SC-CO₂ fracturing is still unclear. The fracturing process is affected by the variations in pressure and temperature, the physical properties of SC-CO₂, the leak-off of SC-CO₂ and the physical and chemical reactions between shale and SC-CO₂. It is totally different from hydraulic fracturing. The numerical simulation methods such as the extended finite element method, boundary element method and other advanced methods can be used together with delicate laboratory tests to reveal the mechanism of fracture initiation and propagation during SC-CO₂ fracturing. Thirdly, more data from field tests is necessary to demonstrate the feasibility of SC-CO₂ enhanced shale gas recovery and CO₂ sequestration in a wide range of potential shale gas reservoirs. The proppant-carry and sand-carry abilities of SC-CO₂ are poor. Proppant and sand could therefore potentially accumulate in the wellbore or the tips of cracks which would be detrimental to perforation and fracturing. The flow resistance of SC-CO₂ in the wellbore and the bit nozzles is very high. To fulfill the injection volume, a higher pumping pressure is therefore needed. This risks causing overpressure in the surface equipment.³⁴⁹ Moreover, induced-seismicity monitoring is required. This involves multi-disciplinary inputs from geophysics, geology, and reservoir engineering, which are required for advanced identification, processing, and interpretation of induced seismicity. Such monitoring and recorded signal interpretations are essential to ensure the safe and effective production and sequestration of shale gas over long time periods.

Author contributions

Jingqiang Tan conceived the idea and organized writing. Qiao Lyu, Jingqiang Tan, and Yiwen Ju led the preparation of the manuscript. Lei Li, Andreas Busch, David A. Wood, Pathgama Gamage Ranjith, and Richard Middleton helped to revise and edit the article. Biao Shu and Qiao Lyu conducted a literature review of CO₂ emissions and CO₂ capture, utilization, and storage. Chenger Hu helped to summarize the costs of using SC-CO₂ in shale gas recovery and field tests. Zhanghu Wang and Ruining Hu drew and improved some of the figures. All authors contributed to the study with valuable discussions.

Conflicts of interest

There are no conflicts to declare.
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