


Geo-Energy Research

Invited review

Supercritical CO₂ fracking for enhanced shale gas recovery and CO₂ sequestration: Results, status and future challenges

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Abstract:

Supercritical carbon dioxide (ScCO₂)-based fracturing technology associating with CO₂ enhanced shale gas recovery is a promising technology to reduce the water consumption and could provide the potential for CO₂ sequestration. Advancing the understanding of complex gas shale reservoir behavior in the presence of multiphase and multicomponent gases (ScCO₂, gaseous CO₂ and CH₄ etc.) via laboratory experiments, theoretical model development and field validation studies is very important. In this paper, the progress of some key scientific problems such as the mechanism of ScCO₂ drilling and completion, the ScCO₂ fracturing technology, the competition adsorption behaviors of CO₂/CH₄ in shale, the coupled multiphase and multicomponent CO₂/CH₄ flow during the CO₂ enhanced shale gas recovery process and the CO₂ sequestration potential in shale formation were discussed. The results indicated that the ScCO₂ jet has a stronger rock erosion ability and requires much lower threshold pressure than water jet. The fracture initiation pressure of ScCO₂ is about 50% lower than that of hydraulic fracturing, and the volume of rock fractured by ScCO₂ is several times larger than that of hydraulic fracturing. Field test shown that the shale gas production rate was significant increased by the ScCO₂-based fracturing technology. Finally, the challenges of the technique will face and the further research is needed in the future is exposed.

1. Introduction

The recoverable reserve of shale gas is approximately 207×10^{12} m³, accounting for 32% of the total natural gas resources of the world (EIA, 2011; Melikoglu, 2014), which plays an important role in world energy supply. The United States is the first country achieved large-scale commercial production of shale gas. Inspired by the shale gas revolution in the US, China is trying to replicate the success of shale gas exploitation. Jiaoshiba shale gas field, which located in southwest China, has becoming the biggest gas field outside North America (Hu et al., 2018; Ma and Xie, 2018). The rapid development of shale gas relies on the breakthrough and development of horizontal drilling and hydraulic fracturing technologies (King, 2010; Rafiee et al., 2012; Nagel et al., 2013; Rutqvist et al., 2015; Wang et al., 2018a; Rahimi-

Aghdam et al., 2019; Nguyen-Le and Shin, 2019). Currently, the most common working fluid used for the commercial shale gas development is slick-water. However, the aqueous-based drilling and fracturing fluids show some notable drawbacks, including but are not limited to: 1) clay minerals are generally distributed in shale gas reservoir, water-based working fluids will induce the hydration of swelling clay, which may damage shale gas formation, and cause the collapse of wellbore and the blockage of gas percolation channel (Dehghanpour et al., 2012; Distefano et al., 2019); 2) hydraulic fracturing consumes large amount of water resources in shale gas development. Limited water availability may restrict shale gas production in water-scarce regions. The fracturing of a typical shale gas well requires 14000 to 24000 m³ of water depending on the drilling depth of the well, number of fracturing stages, and length of laterals (Nicot and Scanlon, 2012; Scanlon et



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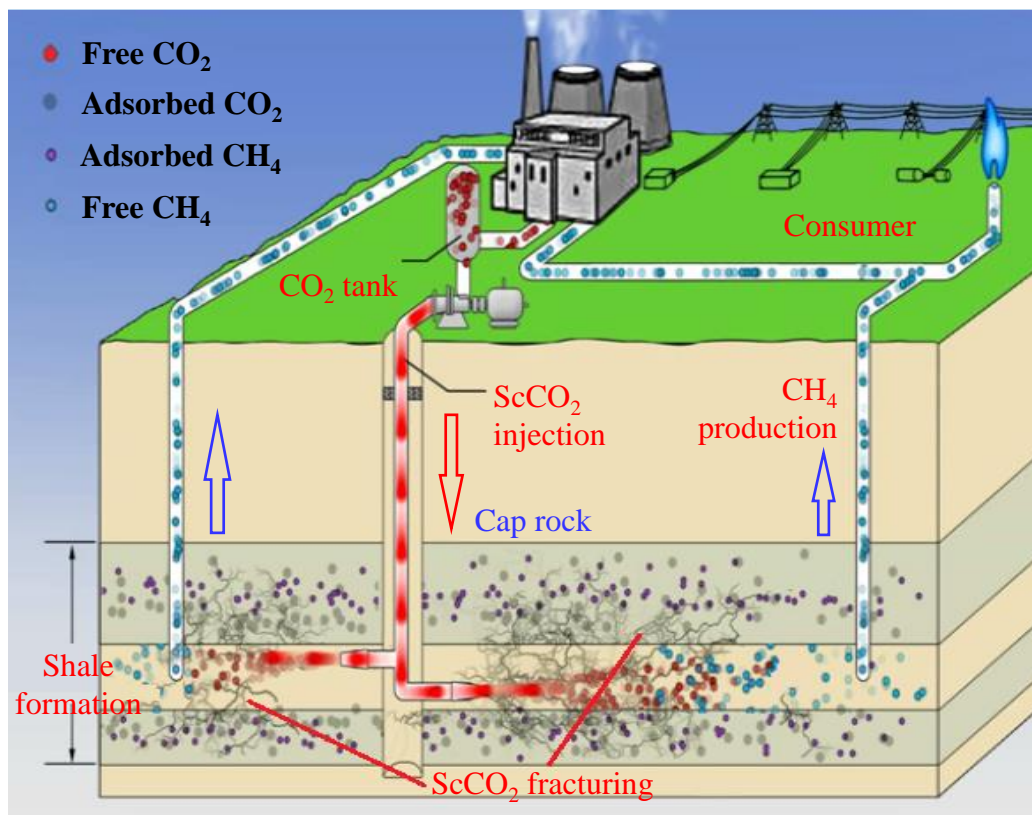


Fig. 1. Schematic diagram of ScCO₂ fracturing for enhanced shale gas recovery and CO₂ sequestration (developed after Li and Kang, 2018).

al., 2014; Vengosh et al., 2014; Kondash et al., 2018; Zou et al., 2018). Especially for China, the shale gas reservoirs are located in the area or adjacent area which are short of water resources, the scarcity of water resources is an obvious challenge for shale gas development in China; 3) in addition to water, the fracturing fluids contain a variety of chemical additives (e.g., friction reducers, thickening agents, gelling agents, crosslinkers, swelling inhibitors, corrosion inhibitors, breakers, biocides, and stabilizers) and proppants, which may have adverse effects on the groundwater and surface water environment (Gregory et al., 2011; Osborn et al., 2011; Estrada Bhamidimarri, 2016; Kondash et al., 2018). To overcome these drawbacks, an increasing number of researchers are exploring less water-intensive or waterless fracturing technologies for the shale gas development.

When the temperature and pressure of CO₂ are over the critical points (critical temperature of CO₂ $T_c = 31.05$ °C, critical pressure of CO₂ $P_c = 7.38$ MPa), CO₂ will achieve its supercritical state (ScCO₂). ScCO₂ has some unique and interesting properties, such as low viscosity and high diffusivity, which can be used as an ideal non-aqueous drilling and fracturing fluid for shale gas and oil exploitation (Mo et al., 2014; Jia et al., 2019). Compared with aqueous fluids, the unique properties of ScCO₂ present more advantages for shale gas development. First, rock breaking with ScCO₂ jet has a low threshold pressure and a high rate of penetration compared with water jet. Furthermore, it can induce more complicated fractures due to its low viscosity, enhance shale gas recovery by displacing adsorbed methane in shale, reduce

the water footprint, and minimize environmental impacts (Pei et al., 2015; Zhou et al., 2016; Peng et al., 2017; Zhang et al., 2017a; Jiang et al., 2018). Moreover, ScCO₂-based fracturing technology offers the opportunity for CO₂ sequestration in shale gas reservoirs (Zhou et al., 2012, 2018a; Middleton et al., 2015).

Based on the above advantages of the ScCO₂ in the shale gas development, an innovative idea that integrated the ScCO₂ fracturing technology for shale gas recovery and CO₂ sequestration was proposed. The main idea of the research is that using ScCO₂ to replace the water as drilling and fracturing fluids to enhance the permeability of shale gas reservoir, then utilizing the preferential adsorption behaviors of CO₂ over CH₄ in shale to enhance the recovery of shale gas, and simultaneously sequester CO₂ in shale gas formations (Fig. 1). This paper describes the results and accomplishments achieved to date in this field and some of the future activities being considered.

2. Supercritical carbon dioxide as a working fluid for shale gas development

2.1 Shale breaking with supercritical CO₂ jet

In the early days, high-pressure water jet technology was widely applied in the well drilling of the oil and gas development. However, to some extent, the commonly used water jet technology can't match the demands of low cost and high efficiency for drilling. ScCO₂, as its unique properties of a gas

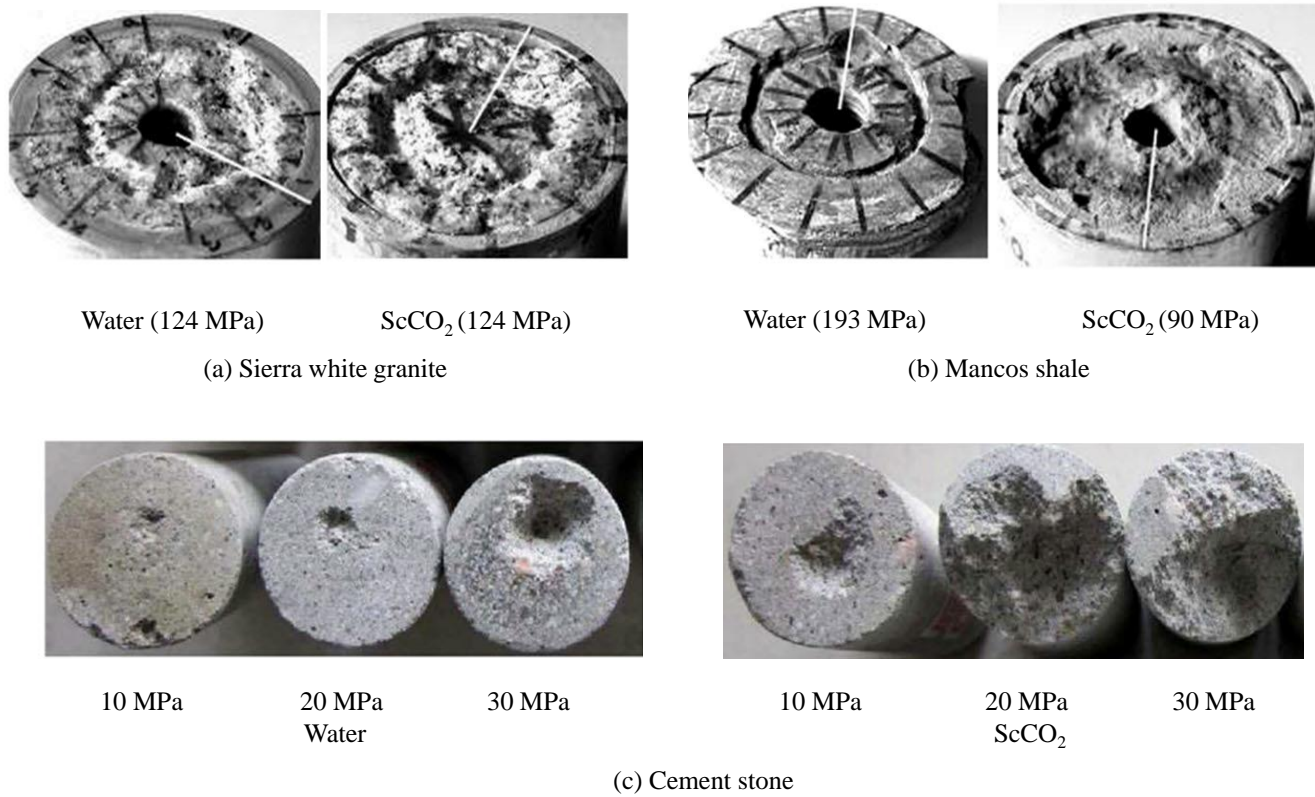


Fig. 3. Rock-breaking performance between water jet and ScCO₂ jet (Kolle, 2000; Li et al., 2018a).

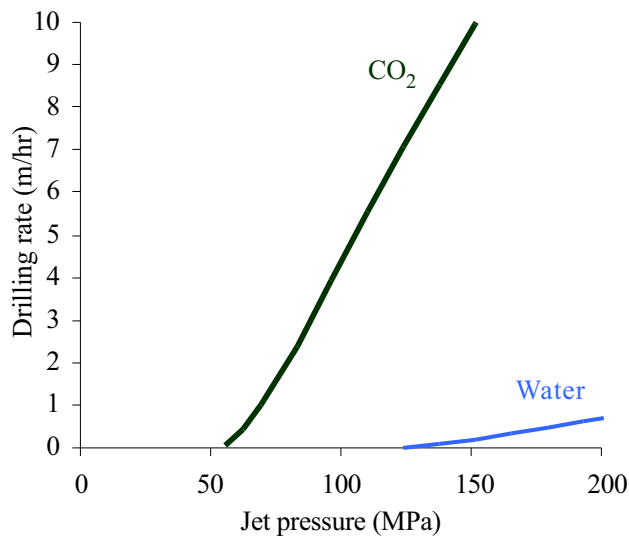


Fig. 2. Projected jet-erosion drilling rates in hard shale (Kolle, 2000).

-like viscosity and a liquid-like density, it can be used to break rock like water, and could decrease the dissipation of energy from the nozzle to the rock. Moreover, the high diffusivity allows ScCO₂ to enter tiny spaces and transmit the fluid static pressure, which is beneficial to improve the rock-erosion efficiency (Du et al., 2012; He et al., 2015, 2016a, 2016b;

Song et al., 2016; Cai et al., 2017, 2018, 2019; Huang et al., 2018b, 2019; Wang et al., 2018a, 2019b). Thus, ScCO₂ jet-assisted radial drilling technology is regarded as a potential alternative drilling method as its higher efficiency in rock-erosion efficiency than water jet.

The first research on the rock erosion characteristics of a ScCO₂ jet was conducted by Kolle in the late 1990s, stimulated by the demand of improving the drilling efficiency and reducing the working pressure in coiled-tubing drilling (Kolle, 2000). The results indicated that the ScCO₂ jet has a stronger rock erosion ability and requires much lower threshold pressure than water jet. The threshold pressure for ScCO₂ jet is just 2/3 for water jet when breaking the granite and even less than half for water jet when breaking the shale. The specific energies for eroding granite and Mancos Shale using ScCO₂ jets are less than 50% and only 3% those of water jets, respectively. The rate of penetration in Mancos shale applying a ScCO₂ jet was 3.3 times that observed while drilling with a water jet (Fig. 2). The results have also been confirmed by other researchers by using different rocks (Fig. 3). As can be seen from Fig. 3, ScCO₂ appears to be more efficient than water jet in slim-hole radial drilling and it has a lower rock breaking threshold pressure than that of water jet (Kolle, 2000; Li et al., 2018a).

With the rapid development of shale gas in china, some exploratory studies on the mechanism of shale breaking by supercritical CO₂ jet were conducted (Wang et al., 2012,

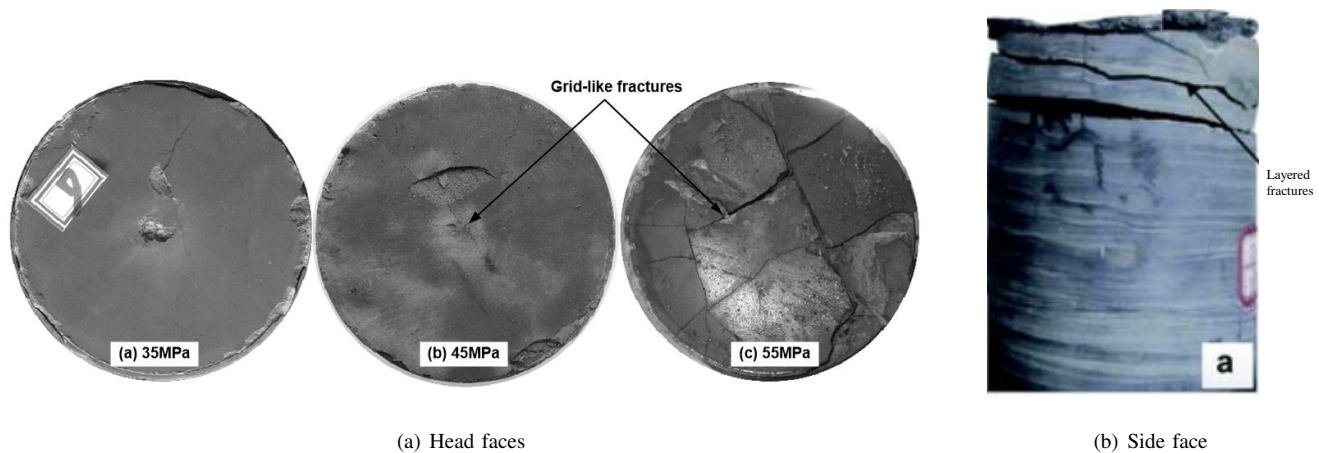


Fig. 4. Shale-cores impacted by ScCO₂ jet (Huang et al., 2018a).

2015a). He et al. (2016a) conducted rock erosion experiments using ScCO₂ jets on different rocks and made subsequent in-depth SEM observation and analyses. They demonstrated that a ScCO₂ jet erodes rock substances mainly in the brittle tensile failure mechanism and facilitates the rock to be further broken, accompanied with the shear failure mechanism in particular locations of the erosion hole. Huang et al. (2018a) studied the microstructure changes between the original shale sample and the eroded sample after ScCO₂ jet by using the methods of CT, SEM/EDX, XRD and XRF. The results illustrated that the surface of shale sample shot by a ScCO₂ jet shows a grid-like breakage, and the sample was broken into layers with a large volume overall (Fig. 4). The erosion of shale mineral induced by the ScCO₂ jet impingement can also change the microstructure of shale and then reduce its mechanical strength.

Through theoretical analysis and numerical simulation, some research explored the properties of the ScCO₂ jet flow field, and the influencing factors on the flow field of the ScCO₂ jet (Hu et al., 2016; Zhou et al., 2017a; Huang et al., 2018b). The results indicated that the velocity and the pressure of the ScCO₂ jet could be converted to each other, and the ScCO₂ jet has a stronger impact pressure and a higher velocity than those of the water jet under the same conditions, the maximum velocity and the impact pressure of the ScCO₂ jet increase with the increase of the nozzle pressure drop, ScCO₂ impacting jet has a more obvious thermal effect on the wall without any phenomena of CO₂ freezing and blocking nozzle.

However, though theoretical, experimental and numerical simulation studies were conducted to disclose the main factors, including the jet pressure, jet temperature, confining pressure, jet distance, rotary speed of core samples and jet time, which influence the rock-breaking performance and efficiency (Hu et al., 2016; Shi et al., 2016; Zhou et al., 2017a; Huang et al., 2018b; Li et al., 2018b; Sun et al., 2018a), further works on the wellbore pressure control theory, the rock-erosion rules and the cutting-carrying ability of supercritical carbon dioxide drilling especially at horizontal section are needed to understand the

mechanisms of shale breaking with ScCO₂ jet for promoting the engineering application of this technology.

2.2 Mechanism of supercritical carbon dioxide fracturing in shale gas reservoir

As most shale formations in China have high clay contents and low or ultra-low permeability (Xiong et al., 2015; Zhou et al., 2017b), the water-based fracturing technology will cause clays swelling, which may lock the gas channels and further decrease the gas production. As a non-aqueous fracturing fluid, ScCO₂-based fracturing technology has shown a promising application in shale gas development (Zhou et al., 2016; Zhang et al., 2017a).

Experiments has been conducted to reveal the mechanism of ScCO₂ fracturing in shale (Zhou et al., 2016; Zhang et al., 2017a; Jia et al., 2018a; Jiang et al., 2018; Zhao et al., 2018; Zhou et al., 2018b, 2019b; Zhang et al., 2019). The results were indicated that the ScCO₂ fracturing induced more complicated and rough fractures than that of induced by hydraulic fracturing, thus ScCO₂ fracturing are more likely to form complex fracture networks. The volume of rock fractured by ScCO₂ is several times larger than that of hydraulic fracturing. Compared with hydraulic fracturing and liquid CO₂ (L-CO₂) fracturing, the fracture initiation pressure of ScCO₂ is the lowest, which was about 15% lower than that of L-CO₂, and almost 50% lower than that of hydraulic fracturing (Fig. 5) (Wang et al., 2017; Zhang et al., 2017a). The acoustic emission (AE) sources of the Sc- and L-CO₂ injections tend to distribute in a larger area than those of water injection, and furthermore, ScCO₂ tended to generate cracks extending more three dimensionally rather than along a flat plane than L-CO₂ (Ishida et al., 2012, 2016; Zhang et al., 2017a). The results are also consistent with the results of the fracturing experiments conducted by using cubic granite blocks (Ishida et al., 2012; Inui et al., 2014; Chen et al., 2015b).

The fracture extension model with ScCO₂ appeared to be different from that of water (Ishida et al., 2012; Zhang et

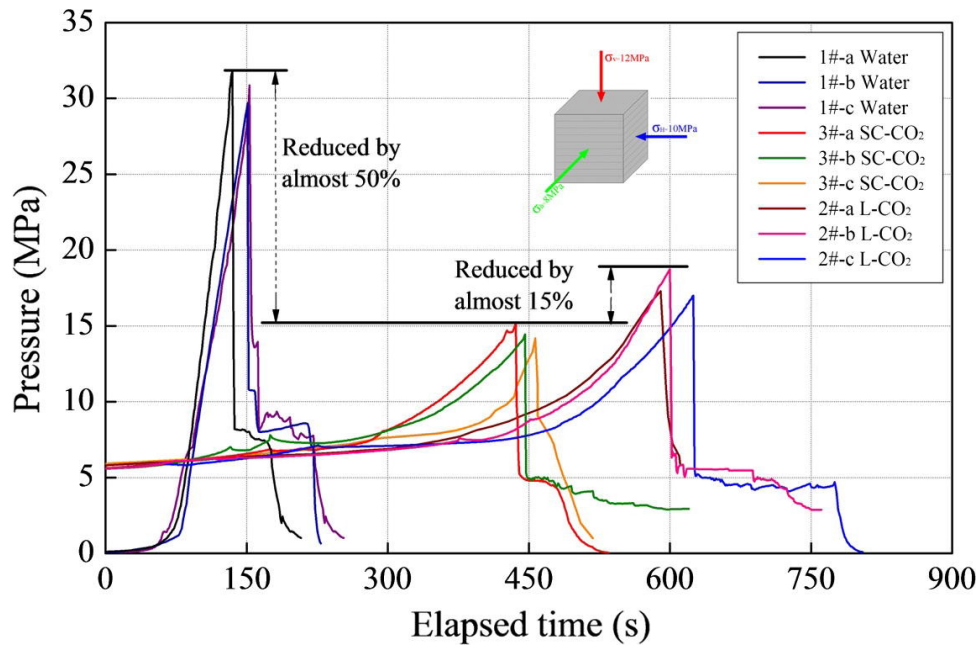


Fig. 5. The fracture initiation pressures for water, L-CO₂ and ScCO₂ fracturing in shale (Zhang et al., 2017a).

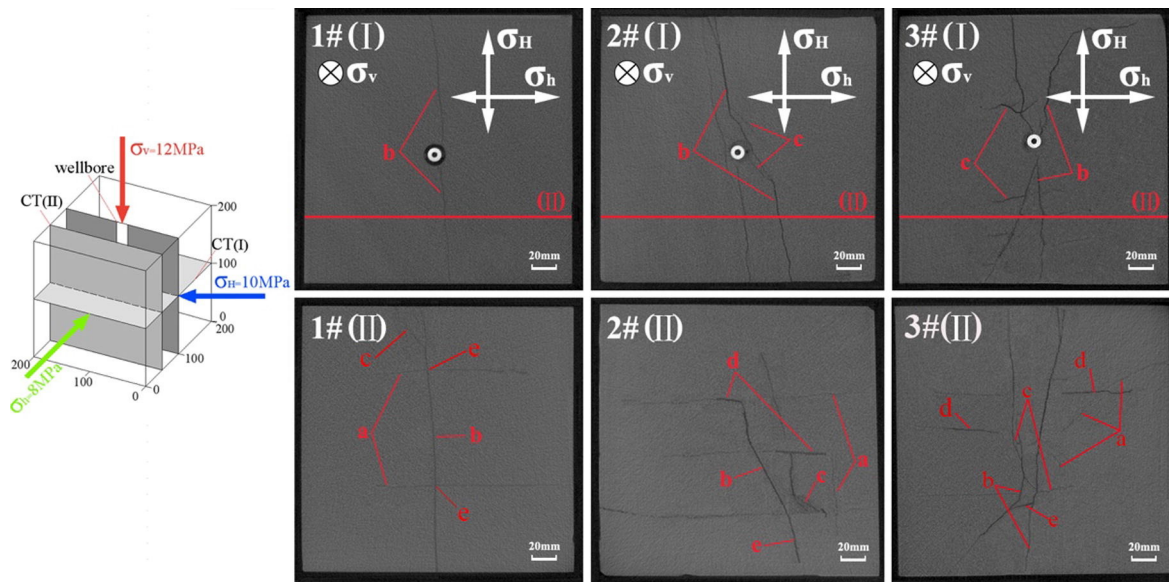


Fig. 6. CT scanning images of specimens using different fracturing fluids. 1# (with water), 2# (L-CO₂), 3# (ScCO₂). (I) images recorded from the scan CT (I) plane, (II) vertical images recorded from the CT (II) plane (Zhang et al., 2017a).

al., 2017). ScCO₂-induced fractures are dominated by shear fractures, including tensile fractures. Fracture extension with shear dominant fractures, which occurred during the CO₂ injection, is likely sensitive to defects, such as bedding weak planes, in a core. The difference in the fracturing modes of ScCO₂ and water seems to be significantly affected by the viscosity. Unlike water, ScCO₂ has a high diffusivity, low viscosity, and low surface tension. It thus can penetrate into micro defects and even smaller pore spaces of the shale samples. Moreover, when the pressure of CO₂ drops as the fractures extending during the fracturing process, ScCO₂ could suddenly change to the gaseous state. As the compressibility of the gas state is much larger than that of the supercritical state,

this phase transition could lead to the expansion of ScCO₂ and induce further fracturing, which is beneficial to the fractures extension and could create more fractures in all directions. Thus, compared to the conventional slick-water fracturing, ScCO₂ injection induces more widely extended fractures with multiple branches (Fig. 6) (Zhang et al, 2017a).

The experimental and numerical results commonly indicate that significant fluid permeation during ScCO₂ fracturing is a primary reason for its lower breakdown pressure and more distributed fractures compared with hydraulic fracturing (Li et al., 2016; Zhang et al., 2017a; Ha et al., 2018; Jia et al., 2018a; Jun et al., 2018; Wang et al., 2018b; Wang et al., 2019a). ScCO₂ may also more effectively fracture shale rock due

to coupled compressibility-thermal shock effects. Specifically, strong Joule-Thompson cooling effect may enhance fracturing due to thermal stress created as CO₂ expands into a new fracture volume and cools the crack tip (Middleton et al., 2014).

For shale gas reservoirs, fracturing often aims to create propped fractures with a certain flow conductivity, the distribution of proppant is the key factor that influences the flow conductivity of the fracture. Thus, the proppant carrying capacity of ScCO₂ is a key factor should be considered for the engineering application of ScCO₂ fracturing in unconventional gas reservoir development (Song et al., 2018a; Sun et al., 2018b). However, the low viscosity of ScCO₂ in reservoir conditions prevents effective transport of proppants deep into stimulated fractures, and the volume of injected proppant by ScCO₂ during the fracturing is limited (Wang et al., 2014; Hou et al., 2015, 2017a, 2017b; Dai et al., 2018; Du et al., 2018; Li et al., 2019). To overcome this limitation, two general strategies are commonly pursued: Thickening CO₂ and foaming CO₂ (Ribeiro et al., 2017; Jing et al., 2019). In future, developing an effective, economical and environmentally friendly thickener for ScCO₂ is needed to enhance its proppant carrying capacity. For foaming CO₂, as conventional foams still contain significant fractions of water by volume (one tenth to one quarter) that can contribute to formation damage, ultra-dry foams containing less water should be developed.

2.3 Competition adsorption behaviors of CO₂/CH₄ in shale

Since a large proportion of gas in shale reservoirs is stored as an adsorbed state, competitive adsorption behaviors involving CO₂ and CH₄ are of key importance for the optimal of CO₂-enhanced shale gas recovery and CO₂ sequestration processes (Sun et al., 2013; Xu et al., 2017; Myshakin et al., 2018; Zhou et al., 2018a). Extensive investigate efforts have been conducted to study the adsorption of CH₄ and CO₂ on shales under single gas environment and binary gas environment, and the influence of different affecting factors, such as total organic carbon (TOC) content, organic matter type, thermal maturity, clay mineral content, and pore structure on the selective behavior of CH₄ and CO₂ adsorption on shales were also determined (Cancino et al., 2017; Gu et al., 2017; Wang et al., 2018c, 2018d; Huang et al., 2018c, 2019; Zhou et al., 2018a). The main results indicated that the adsorption capacity of CO₂ on shale is always greater than that of CH₄, and the adsorption ratios of CO₂ to CH₄ ($\alpha_{\text{CO}_2/\text{CH}_4}$) show widely varying ranges for different shales. Nuttall et al. (2005) observed that CO₂ is adsorbed approximately 5 times more than that of CH₄ for Devonian black shales. Weniger et al. (2010) reported $\alpha_{\text{CO}_2/\text{CH}_4}$ varied between 1.9 and 6.9 for several carbonaceous shale samples from Paraná Basin, Brazil. Similar study of preferential adsorption was conducted by Kang et al. (2011) on two Barnett shale samples from USA. It was found that CO₂ adsorbed 5-10 times more than CH₄. The CO₂ adsorptive capacity for Barnett, Eagle Ford, Marcellus and Montney shales from USA was measured to be 2-3 times higher than that of CH₄ (Heller et al., 2014a). For

Sichuan Basin shale, the value of $\alpha_{\text{CO}_2/\text{CH}_4}$ ranges from 2.5 to 6.9 (Duan et al., 2016; Qi et al., 2018). Heller et al. (2014a) obtained that CO₂ has approximately 2-3 times the adsorptive capacity of CH₄ in both the pure mineral constituents and actual shale samples. Gu et al. (2017) hold that shale with high clay contents and more micropores is more likely has a greater $\alpha_{\text{CO}_2/\text{CH}_4}$. Huang et al. (2018c) obtained that the adsorption ratios of $\alpha_{\text{CO}_2/\text{CH}_4}$ are in the order of kerogen IA < IIA < IIIA for different organic types. For CO₂/CH₄ mixtures adsorption in shale, CO₂ also preferentially adsorbs over CH₄ in the competitive adsorption process (Luo et al., 2015; Duan et al., 2016; Niu et al., 2018; Wang et al., 2018d). The competition adsorption behaviors of CO₂/CH₄ are influenced by many factors, such as the reservoir pressure and temperature, pore structure and mineral composition of shale (Luo et al., 2015; Hong et al., 2016; Gu et al., 2017; Psarras et al., 2017; Zhou et al., 2019a). As the many affecting factors mentioned above contribute to the variability of $\alpha_{\text{CO}_2/\text{CH}_4}$ in different shales, thus, it is important to study this on a case by case basis.

The gas retention capacity of a shale gas reservoir under simulated geological temperature and pressure conditions can be estimated from an adsorption isotherm. Finding an optimized adsorption model to estimate the true adsorbed quantity of CH₄ and CO₂ in shale at reservoir conditions is fundamental for estimating the CO₂ storage capacity and analyzing the shale gas production. To date, many gas adsorption isotherm models have been developed to describe the experimental adsorption data. For single gas adsorption, these include the Langmuir, Dual-Langmuir, Dubinin-Radushkevich (D-R), Dubinin-Astakhov (D-A), BET, Lattice Density Functional Theory (LDFT) and Ono-Kondo Models (Charoensuppanimit et al., 2016; Tang et al., 2016, 2017a, 2017b; Xiong et al., 2017; Chen et al., 2018b; Singh and Cai, 2018; Song et al., 2018b; Zhou et al., 2019a). Whereas for multicomponent gas adsorption their combination with the extended Langmuir equation, multicomponent potential theory of adsorption (MPTA), ideal adsorbed solution (IAS) theory have been applied (Ambrose et al., 2011; Fathi and Akkutlu, 2014; Wang et al., 2015b; Ren et al., 2017; Kulga and Ertekin, 2018). Among these models, Langmuir isotherm model is the most common model used to describe adsorption of methane and CO₂ on shales, its relatively simple form allows for direct implementation in reservoir simulators describing enhanced shale gas recovery (ESGR) processes. However, some exceptional trends have also been reported. Bi et al. (2017) hold that both Langmuir and Ono-Kondo models exhibit excellent correlation with the experimental adsorption data of CH₄, and the Ono-Kondo model appears to be more reliable for supercritical adsorption. Rexer et al. (2013) observed that the modified D-R model is superior to the Langmuir model for supercritical CH₄ adsorption. Wang et al. (2016) observed that both D-A and Langmuir models performed well CH₄ adsorption on organic-rich shale samples, while the BET model show a poor performance for CH₄ adsorption on shale. All these studies indicated that the modeling exercise should be continued to evaluate the relative accuracy of various models in predicting the adsorption behavior of shales, especially for supercritical CO₂ and multi-component gaseous systems in shale.

Overall, majority of the studies focus adsorption for pure gas components, while on mixed gas adsorption studies in shale are rare, further work is needed to perform rigorous laboratory test to obtain more multicomponent adsorption data, and develop more rigorous, theory based, thermodynamically consistent adsorption model to improve the capability in predicting multi-component adsorption behavior in shale (CH_4 , gaseous CO_2 and ScCO_2). In addition, in most of the shale gas reservoirs, carbon dioxide exists in supercritical condition and more studies should be addressed on ScCO_2 adsorption in shale.

2.4 CO_2 -shale interaction

2.4.1 The CO_2 -shale interaction on the physical and chemical properties of shale

The injected CO_2 will interact with shale components (i.e. clays, organic matter) and affect rock properties and fluid transports through chemical alteration, matrix swelling/shrinkage, and related geo-mechanical effects. As changes in rock properties will impact both CO_2 sequestration and hydraulic fracturing, it is imperative to increase our understanding of the CO_2 -shale interactions.

Many characterization methods such as scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, X-ray fluorescence (XRF) spectrometer, low-pressure gas (N_2 and CO_2) adsorption, (ICP-MS), Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) technology were used to investigate the effects of CO_2 -shale interactions on the microstructure and chemical properties of shale (Yin et al., 2016; Ao et al., 2017; Jiang et al., 2016; Pan et al., 2018a; Hui et al., 2019). The results indicated that CO_2 -shale interactions can alter the microstructure and geochemical properties of shale, and this alteration is related to the temperature, pressure, phase states of CO_2 and the type of shale (Qin et al., 2017; Zhou et al., 2017b; Pan et al., 2018a; Goodman et al., 2019).

ScCO_2 -shale interactions had a more significant effect on the pore structure of shale than that of SubCO_2 -shale interaction, which was attributed to the greater dissolution and expansion effect as well as the extraction ability associated with supercritical CO_2 (Yin et al., 2016; Zhou et al., 2017b; Pan et al., 2018b; Lu et al., 2019). Rezaee et al. (2017) observed that there is a reduction in the capillary threshold pressures and an increase in pore volume for most of the shale samples exposed to ScCO_2 . Pan et al. (2018a, 2018b) found that the SubCO_2 and ScCO_2 exposures had different influences on the micro-, meso- and macropore structure of marine and terrestrial shales. Specifically, the specific surface area (SSA), pore size distribution (PSD) as well as the porosity of the SubCO_2 -treated shale samples were lower than those of the raw samples. However, ScCO_2 -shales interactions created a more significant influence on the pore structure compared to those of subcritical CO_2 -shale interactions, and it should be noted that the variation trend of pore structure parameters for different types of shale samples was quite different, which was related to the huge discrepancies in terms of mineralogy and geochemical properties between them. For marine shale

samples, the pore surface area and pore volume obviously decreased after a relatively short period of ScCO_2 treatment, whereas an opposite trend was observed in a terrestrial sample after long-term ScCO_2 treatment. In addition, an obvious decrease in fractal dimensions for marine Longmaxi sample was also observed after ScCO_2 exposure, reflecting the degree of pore surface roughness, and pore structure complexity were reduced, whereas the terrestrial sample exhibited an opposite trend. The changes in the pore structure of shale associated with ScCO_2 -shale interactions could be interpreted by two mechanisms: The dissolution effect of ScCO_2 , which enlarged the pore size; and the CO_2 adsorption-induced swelling, which narrowed the pores. The CO_2 -shale interactions induced the changes to the pore structure in the shale may modify the flow pattern of the gas in the process CO_2 enhanced shale gas recovery (CO_2 -ESGR), which need further research in the future.

CO_2 -shale interactions also altered the chemical properties of shale, chemical reactions include dissolution and precipitation of several authigenic minerals such as kaolinite, natrojarosite, silica and gypsum. Sanguinito et al. (2018) found that carbonate formation and dissolution occurs in shale exposed to dry CO_2 , and etching and pitting occur, with minor calcite precipitation along the surface of the shale sample. Yin et al. (2016) observed that montmorillonite, kaolinite and calcite content in shale sample decreases due to the dissolution induced by ScCO_2 . Ao et al. (2017) observed that the mineral content of all the shale minerals except quartz decreased after ScCO_2 exposure. Luo et al. (2019) measured the element mobilization and pore structure before and after the ScCO_2 -water-shale reaction using the shale samples of Qaidam Basin and Ordos Basin in China. The results indicated that the major elements, including Ca, Mg, Na, K, and Al, exhibit varying degrees of mobilization after the interactions because of dissolution of carbonate and silicate minerals in shale samples. Compared with the major elements, trace elements have a lower mobility, quantified as $< 13.97\%$. However, the trace elements Sr, Zn, Co and Ba that mainly exist in carbonate and sulfide minerals are more easily mobilized than other trace elements. Thus, under the conditions of ScCO_2 fracturing or CO_2 sequestration in shale gas reservoirs, the underground water below the operating regions must be monitored because trace elements such as Sr, Zn, Co, and Ba can be mobilized and potentially contaminate groundwater.

As the CO_2 -shale interactions has different influence on the different types of shale samples, and the reservoir temperatures and pressures also have significant impacts on the ScCO_2 -shale interactions. Thus, it is necessary to study shale- CO_2 interactions on a case by case basis. Furthermore, the interactions of CO_2 -shale are also time dependent, then further research on the reaction kinetics of shale- CO_2 in different time scales is also needed in future.

2.4.2 The CO_2 saturation on the mechanical properties of shale

The CO_2 -shale interactions induced microstructure and mineral composition alteration may have significant influence on the mechanical properties of shale, which should be crit-

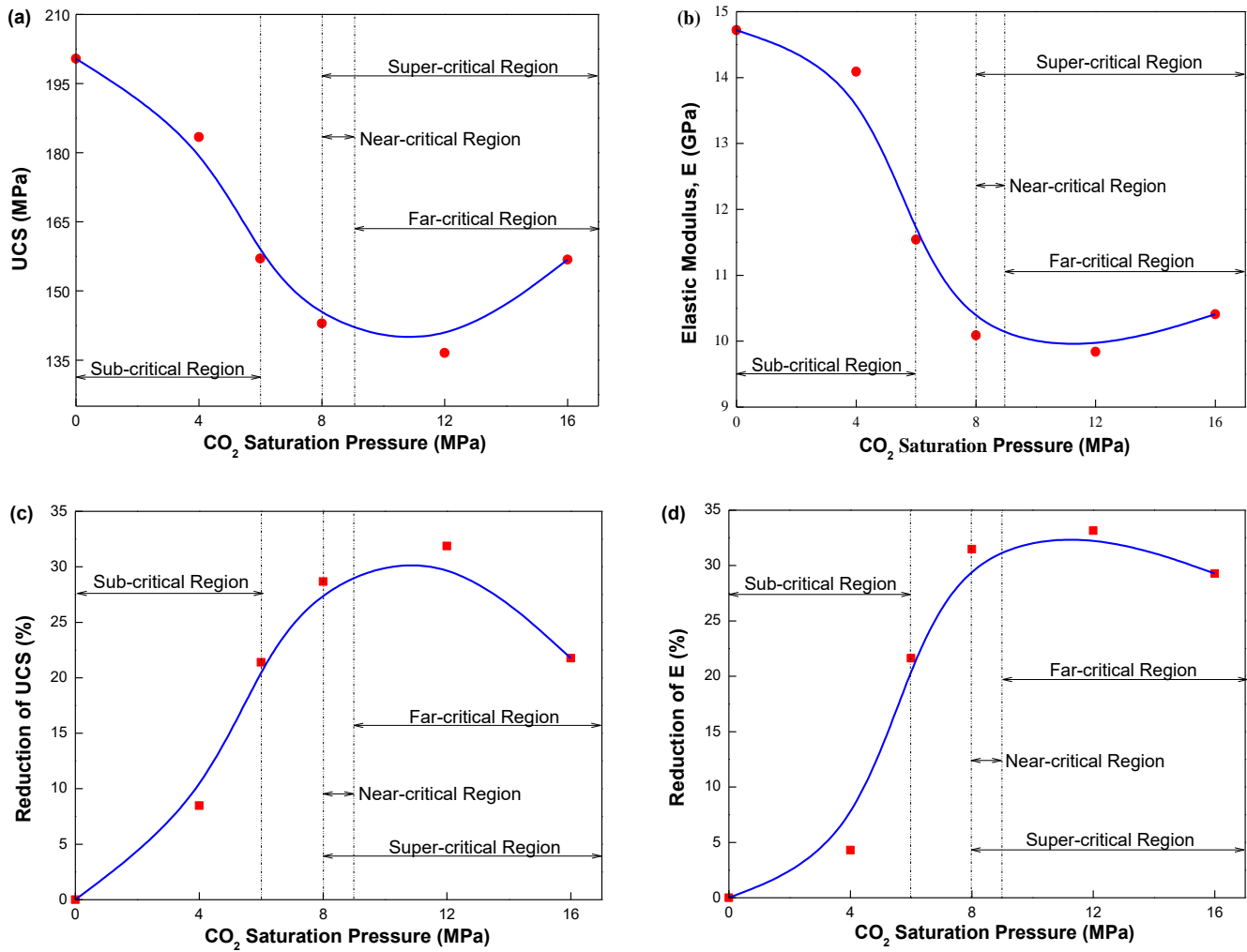


Fig. 7. Effect of CO₂ adsorption pressure and phase change on UCS and Young's modulus of shale (Yin et al., 2017).

ically evaluated to enhance the efficiency of CO₂-ESGR and CO₂ sequestration processes, and mitigate associated hazards. Many laboratory studies testing the interaction of shale between different saturation fluids (water, SubCO₂, ScCO₂) on the mechanical properties of shale. Both of sub-/super-critical CO₂ saturation weaken the strength and increase the ductility of the shale, as the uniaxial compressive strength (UCS) and Young's modulus (E) were decreased after CO₂ saturation (Yin et al., 2017; Zhang et al., 2017b; Lyu et al., 2018a, 2018b, 2018c; Feng et al., 2019; Lu et al., 2019). However, ScCO₂ saturation causes a greater reduction of shale's mechanical properties than that of subCO₂, which indicated that the influence of CO₂ saturation on mechanics of shales is also highly depending on the saturation pressure and the phase state of CO₂ (Yin et al., 2017; Lu et al., 2019). Yin et al. (2017) observed that ScCO₂ saturation caused a reduction of 33.89% in UCS of organic-rich shales, which is higher than that of 22.86% caused by SubCO₂ saturation. The reduction in E of organic-rich shales caused by ScCO₂ saturation is 33.97%, which is higher than that of 23.10% caused by SubCO₂ saturation (Fig. 7). Lyu et al. (2018b) observed that the UCS and E of shale decrease with the increase of

saturation time, and ScCO₂ saturation creates more AE energy than SubCO₂ saturation (Fig. 8). The macroscopic mechanical properties alteration of shale caused by CO₂ saturation can be interpreted by the microscopic changes induced by CO₂-shale interactions, as previously mentioned. The discrepancies of mechanical behavior of shale caused by SubCO₂ and ScCO₂ saturation is also consistent with the microstructure alteration of shale caused by SubCO₂ and ScCO₂. In addition to the adsorption-induced swelling effect, the extraction and dissolution effects of ScCO₂ induced microstructural alterations could cause more additional damages, which caused a greater weaken of shale.

The results of the experimental investigation provide persuasive evidence to conclude the fact that CO₂ interaction causes significant mechanical degradation in shale. However, the degree of strength reduction is influenced by multiple factors, including geo-environment characteristics of shale formations, CO₂ phase, adsorption pressure, interaction time, etc. The micro-cracks caused by the CO₂ adsorption induced heterogeneous swelling and chemical interactions, contribution to the overall mechanical degradation in the shale mass. For in-situ reservoir environment, during the fracking or sequestering

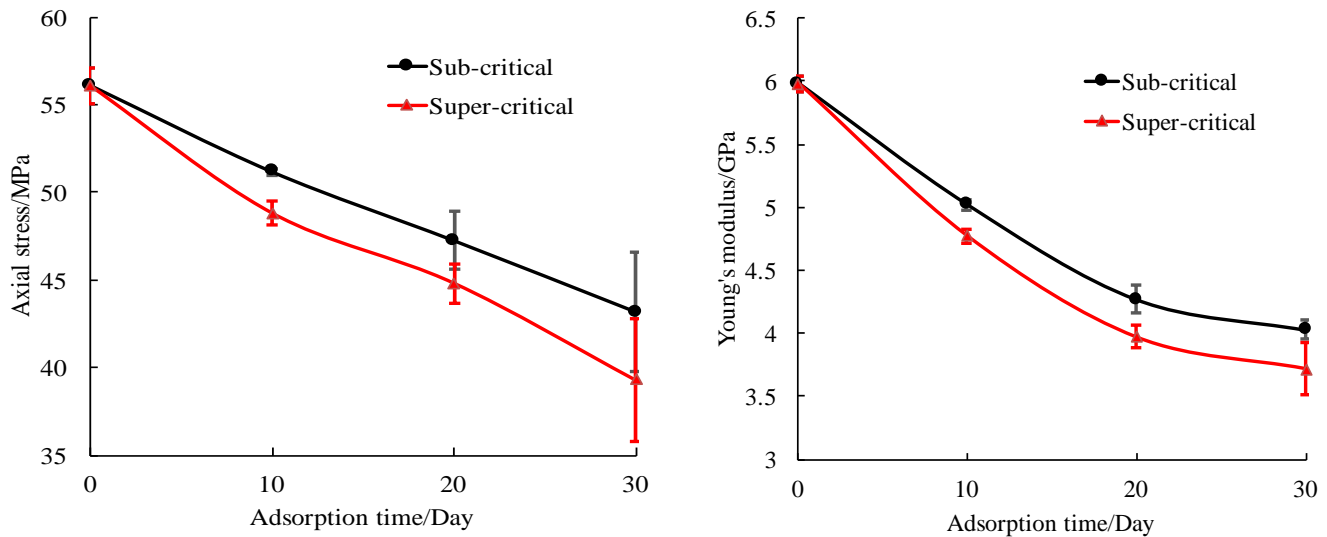


Fig. 8. Effect of CO₂ adsorption time on UCS and Young's modulus of shale (Lyu et al., 2018b).

process, CO₂ will form carbonic acid when meeting water or brines and dissolving into it, which leads to the dissolution and precipitation of minerals. Thus, more attentions are needed to focus on the effect of CO₂-brine-rock interactions on shale samples' mechanical properties (Lyu et al., 2016, 2018a; Zhang et al., 2017b). In addition, the CO₂-shale reaction in reservoir condition covers a long-term timescale, thus the influence of the long-term shale-CO₂ interactions induced strength alterations should be investigated more rigorously. Moreover, the risk of the strength weakening associated with CO₂-shale interaction on the borehole stability of horizontal wells, and the collapse of the induced fractures should be evaluated. Finally, shale is an extremely heterogeneous and anisotropic material, the mechanical alteration can be varied, thus should be evaluated targeting the specific reservoir characteristics, prior to implementation of CO₂-ESGR projects.

2.5 Gas flow in shale during the process of CO₂-ESGR

The gas flow in shale gas reservoirs is controlled by the permeability of shale, during the CO₂-ESGR process, the permeability of shale gas reservoir is influenced by multiple factors, including geo-stress, pressure, temperature, Klinkenberg effect, CO₂/CH₄ competition adsorption induced differential swelling, CO₂-shale interaction induced damage and fracture (Bhandari et al., 2015; Moghaddam and Jamiolahmady, 2016; Zhou et al., 2016; Li et al., 2017; Wu et al., 2017; Yang et al., 2017; Chen et al., 2019; Lan et al., 2019).

During the CO₂-ESGR process, with the injection of CO₂, the variation of gas pressure will induce the change in geo-stresses, then caused the changes of permeability in shale. The impacts of effective stress on the gas permeability have been studied extensively in the laboratory. For the low effective stress range, an exponential decrease trend of shale can be observed between the permeability and effective stress, the permeability of organic-rich shale decreases rapidly with

the increased effective stress especially for the shales with permeability less than 1 μ D (Heller et al., 2014b; Gutierrez et al., 2015; Pan et al., 2015; Moghadam and Chalaturnyk, 2016; Zhou et al., 2016). While at high effective stress range, the gas permeability change behavior shows a two-stage characteristic and nonlinearly decreasing trend with the increase of effective stress, the permeabilities of the intact and fractured shale samples decreased rapidly at low effective stress and decrease slowly at high effective stress at the semi-log plot (Chen et al., 2019). During the CO₂ injection, the effective stress will change with the variation of injection pressure, thus the influence of injection regime and the stress path on the permeability is also should be considered in further research.

In addition, the shale matrix swelling or shrinkage is will also impact on the dynamic evolution of gas flow in shale. It is well-known that the adsorption of gases as CO₂ and CH₄ can cause swelling of shale with decreasing void volume in cleats and fracture networks, which may have a significant impact on gas transport in shales (Lu et al., 2016; Chen et al., 2018a). The amount of shale swelling varies with multiple factors, including the adsorbing gas type, pressure, temperature and the phase state of CO₂ (Fig. 9). Heller et al. (2014b) measured the swelling of pure minerals of gas shale, including carbon, illite and kaolinite, and investigated the relationship between the swelling of pure mineral and the amount of gas adsorption. Chen et al. (2015a) investigated the deformation of shale in Helium and CH₄ at constant confining pressure and different gas pressures, the results indicated that the adsorption induced shale swelling strain shows a Langmuir-like relationship with pressure and is proportional to the amount of methane adsorbed. Miedzińska and Lutyński (2018) measured the CO₂-CH₄ adsorption induced swelling of gas shales, the results indicated that swelling of shale in case of CO₂ adsorption was greater than in the case of CH₄ adsorption, and the swelling is also related to the mineral composition of shale, more swelling of the organic matter than of the clay matrix is occurred. Lu et al. (2016) measure CO₂-

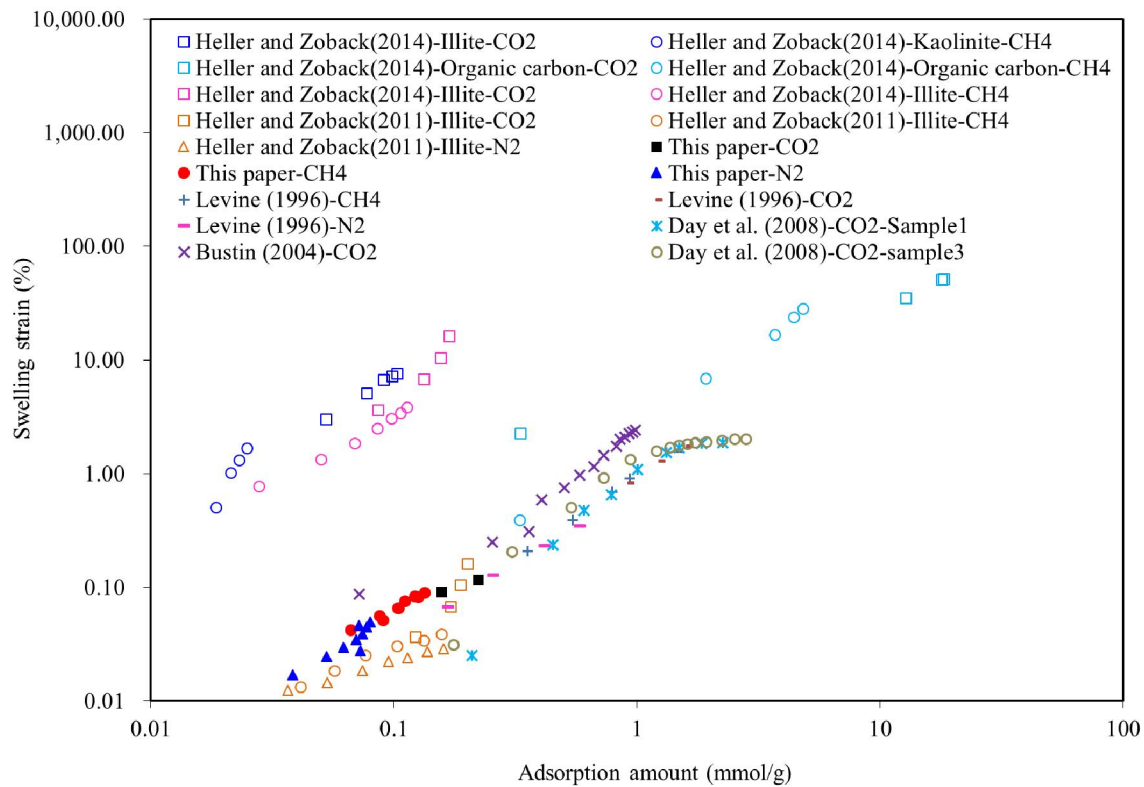


Fig. 9. Relationship between adsorption-induced swelling and the absolute adsorption amount in different types of gases (modified from Chen et al., 2018a).

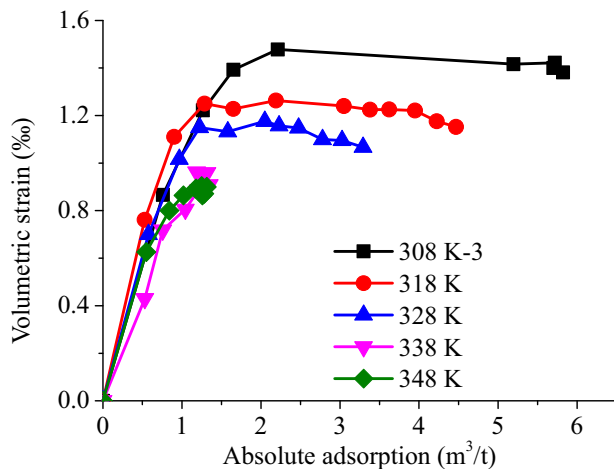


Fig. 10. Influence of adsorbed amount and the temperature on CO₂ induced shale swelling (Lu et al., 2016).

induced swelling in shale samples at temperatures between 308 and 348 K and pressures up to 15 MPa, which covers the pressure range from subcritical to supercritical CO₂. The results indicated that the swelling of shale is related to the temperature, gas pressure and phase of CO₂, with increasing CO₂ pressure, the swelling of shale samples initially increases and then lessens, and the swelling of shale can be described well by a simplified local-density model. With increasing CO₂ temperature, the maximum swelling of the shale gradually decreases (Fig. 10). In addition, shale exhibited anisotropic

swelling in response to CO₂ injection, with the swelling strains always being less in the direction parallel to the bedding plane (Lu et al., 2016; Pluymakers et al., 2018). Furthermore, the water saturation inside the shale matrix may influence the swelling effect of CO₂-shale matrix interaction, thus, it should be considered at the real reservoir conditions as well.

All these studies were focused on the final strain at the adsorption equilibrium, however, gases are not at adsorption equilibrium during production or CO₂ injection. Based on this, Chen et al. (2018a) investigated the kinetic swelling of organic-rich shale in different gases (CO₂, CH₄ and N₂), they found that the shale swelling rate and the gas uptake rate show a linear relationship and both are affected by gas type and phase state of CO₂, adsorption induced swelling of shale are successively increased in order of N₂, CH₄ and CO₂ (Fig. 11). The phase change of CO₂ is also resulting in the change of kinetic swelling rate. Moreover, the anisotropic swelling behavior is also observed, and the anisotropy ratio is related to the adsorbing gas type as well, with the anisotropy ratio for shale swelling decreases in the order of He, N₂, CH₄ and CO₂. In the CO₂-ESGR process, the adsorption induced swelling may change the porosity of shale, then induce the change of the permeability of shale, the phase change of CO₂ will lead different variation characteristics of permeability in shale reservoir, as CO₂ adsorption induced swelling is dependent to the phase state of CO₂. Furthermore, the adsorption induced swelling may also influence the gas flow mechanism in shale. As the pore size distribution of shale changed by adsorption,

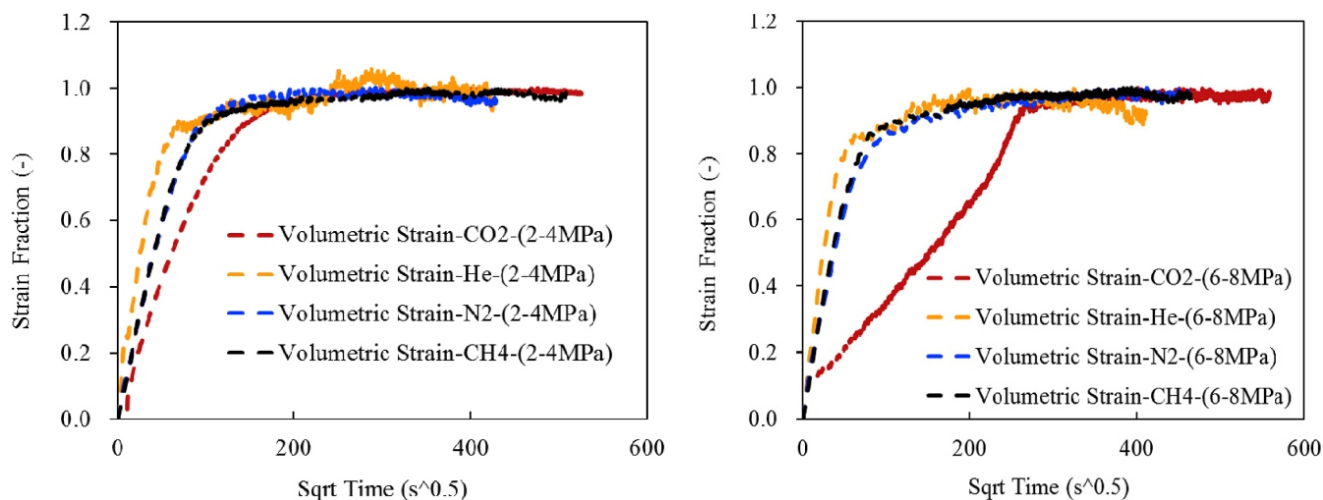


Fig. 11. Evolution of volumetric strain fraction with time (Chen et al., 2018a).

the Knudsen number and the Klinkenberg coefficient will be changed, thus, the gas flow behavior or surface diffusion behavior is varied with the adsorption (Cui et al., 2009; Jia et al., 2018b, 2018c).

Temperature variation is also an important parameter which may influence the shale permeability at a particular stress state (Perera et al., 2012). Adsorption and its consequent adsorption induced swelling, decrease at elevated temperatures. Reduction of swelling effect lowers the pore volume changes and increases the permeability. The temperature difference between the injected CO₂ and shale gas reservoir may induce thermo-mechanical effects in shale. If the temperature difference is significant then it can induce thermal stresses greater than fracture strength of shales. The thermally induced fractures can therefore increase the permeability significantly.

The interaction of ScCO₂-shale induced physical and structural changes is another important factor which has significant influence on gas flow in the process of CO₂-ESGR. First, the extraction and dissolution effects of ScCO₂ will induce damage and secondary fracture on shale, which is beneficial to enhance the permeability of shale. Second, the ScCO₂-shale interaction induced alteration of mechanical properties in shale will change the stress sensitivity of shale, which also has a significant impact on the permeability of shale (Jia et al., 2018a). Moreover, chemical reaction of CO₂-rich aqueous fluids may increase the permeability of fractured shale due to the dissolution effects. Thus, the permeability of shale is competitively controlled by shale swelling, mineral dissolution and chemical reaction effects. The combined effects on shale permeability variation is still not clear, comprehensive and systematic research studies need to be carried out to fully appreciate these influences on permeability changes of shale during the CO₂-ESGR processes.

Over all, during the CO₂-ESGR processes, the permeability of the reservoir is influenced by multiple factors, thus, the fluid flow behavior of shale is controlled by the complex coupled thermo-hydro-mechanical-chemical (THMC) processes associated with CO₂ injection. The coupling framework and relationship are shown in Fig. 12. In future, the coupled

multicomponent, multiphase flow behaviors considering the phase change of CO₂ in shale during the CO₂-ESGR process should be further investigated.

2.6 CO₂ sequestration in shale formations

Shale gas reservoirs have proven the ability to retain the gas over geologic timescales. The generally low permeability of shales is ideal for caprocks, which contain injected CO₂. As long as the caprocks are not damaged by the hydraulic fractures introduced for shale gas production, CO₂ could be securely retained as shale gas has been. Recent studies have reported that the shale gas reservoir has a potential for large-scale sequestration of CO₂ with multiple sequestration mechanisms (Zhou et al., 2012; Edwards et al., 2015; Levine et al., 2016). Edwards et al. (2015) estimated that the CO₂ storage capacity is 7.2-9.6 Gt in the Marcellus shale and 2.1-3.1 Gt in the Barnett shale. Tao and Clarens (2013) estimated that 10.4-18.4 Gt of CO₂ could be stored in the Marcellus shale by 2030, and Nuttall et al. (2005) estimated that 28 Gt could be stored in the Devonian shale.

In shale gas plays, CH₄ exists both as a free phase in pores and fractures and as adsorbed gas on organic matter or clay surfaces. After the CH₄ is extracted, CO₂ could be stored by the same mechanisms as CH₄ in two populations. Theoretically, the total amount of CO₂, which can be stored, may be estimated from the CH₄ produced, as follows:

$$Q_{\text{CO}_2} = \left[\left(\frac{\rho_{\text{CO}_2}}{\rho_{\text{CH}_4}} \right) X + \left(\frac{A_{\text{CO}_2}}{A_{\text{CH}_4}} \right) (1 - X) \right] Q_{\text{CH}_4} \quad (1)$$

where Q_{CO_2} is the molar ratio of CO₂ to be stored over CH₄ produced. X is the fraction of free-phase CH₄ in the shale formation, ρ_{CO_2} and ρ_{CH_4} are the molar density of CO₂ and CH₄, respectively. A_{CO_2} and A_{CH_4} are the adsorption affinity of CO₂ and CH₄ on the shale, respectively. As CO₂ has higher molar density and adsorption affinity than CH₄, the produced methane could be displaced by a greater amount of CO₂ in the depleted shale gas reservoirs. First, we consider the space for

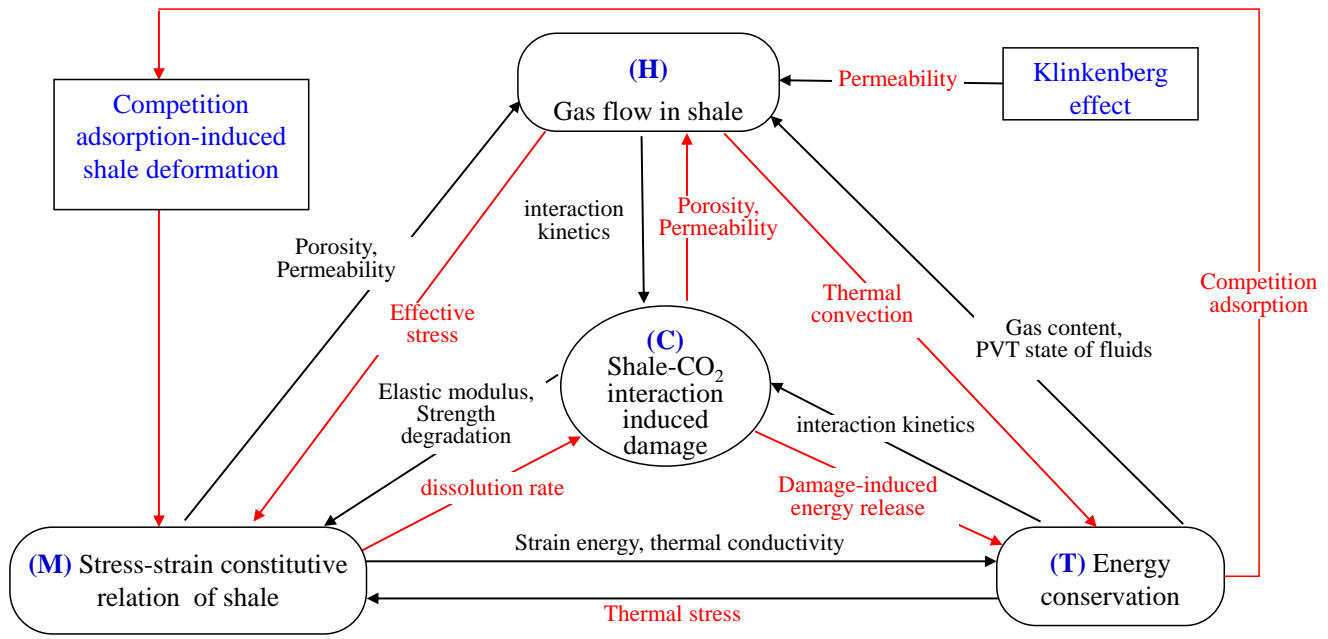


Fig. 12. Coupled THMC processes during the CO₂-ESGR.

free phase CO₂, the density of gases is dependent on pressure and temperature, which are functions of burial depth of shale gas reservoirs. In the depth range 1000 to 5000 m of the largest shale gas reservoirs in Chongqing, China, the molar density ratio $\rho_{\text{CO}_2}/\rho_{\text{CH}_4}$ (calculated assuming 0.01 MPa/m pressure gradient, 0.024 °C/m temperature gradient and 20 °C ground temperature) varies from 1.35 to 2.8, which means that one mole of produced CH₄ could create the space for 1.35-2.8 moles of CO₂. As for the adsorption affinity ratio of CO₂ over CH₄ on shale, the value varies between 2.1 and 7.2 for several shale samples from China (Zhou et al, 2018a), which means that the 2.1-7.2 moles of CO₂ can be adsorbed for one mole of CH₄ produced. As the adsorption affinity ratio of CO₂ over CH₄ is also a function of reservoir pressure and temperature, pore structure and mineral composition of shale, and shale is an extremely heterogeneous and anisotropic material, the CO₂ storage capacity of shale gas reservoirs should be evaluated targeting the specific reservoir characteristics for specific CO₂-ESGR and CO₂ sequestration projects.

In addition, it should be noted that in the Eq. (1), there are only two trapping mechanisms were considered: The structural mechanism (free phase CO₂) and adsorption mechanism. However, in the reservoir conditions, mineral trapping may also occur. Interactions between ScCO₂ and minerals of shale are important for the when CO₂ is injected into shale formations for storage and as working fluids for fracturing and enhanced shale gas recovery. In conventional wisdom, it is usually considered that only typical swelling clays such as smectites can take up CO₂ into interlayers at the reservoir condition. However, Wan et al. (2018) found that CO₂ can enter muscovite interlayers without bulk interlayer expansion, and the amount of CO₂ uptake by muscovite (a conservative proxy for illite and a non-swelling phyllosilicate) far exceeds the maximum adsorption capacity of its external surface area,

which constitutes a previously unrecognized potential trapping mechanism. As the non-swelling illitic clay is the major clay mineral in shale, the unexpected uptake of CO₂ by non-swelling phyllosilicates may significantly contribute to CO₂ storage capacity in shale. Thus, the CO₂ sequestration mechanism in shale formation warrants further indepth studies when estimating the CO₂ storage capacity.

2.7 Field test

The first ScCO₂ fracturing experiment with continental shale gas was successfully conducted in the Yan-2011 shale gas well in Shaanxi Province, China (Li and Kang, 2018). The field test confirmed that ScCO₂ fracturing technology can effectively form a complex fracture network and increase stimulated reservoir volume, as compared to the results of conventional hydraulic fracturing. After ScCO₂ fracturing, a continuous test of flowback indicated that the CO₂-retention rate was 39.5% and the shale gas production rate was increased 1.5 times. The test results show that ScCO₂ fracturing for shale reservoirs is an efficient method for enhancing gas recovery, reducing water consumption, and achieving geological sequestration of CO₂. So far, ScCO₂ fracturing has been applied in several other shale gas wells, enhanced shale gas recovery and CO₂ sequestration were also achieved in these wells, which confirmed the commercial application prospect of the technology as its superiority in improving shale gas recovery, CO₂ utilization and geological storage, and water conservation.

3. Conclusions

In this paper, the advancements in the integration technology of ScCO₂ fracturing, enhanced shale gas recovery

and CO₂ sequestration were reviewed. The progress of some key scientific problems associated with the technique such as the mechanism of ScCO₂ drilling and completion technologies, the supercritical carbon dioxide fracturing technology, the competition adsorption behaviors of CO₂/CH₄ in shale, the coupled multiphase and multicomponent CO₂/CH₄ flow during the CO₂ enhanced shale gas recovery process and the CO₂ sequestration potential in shale formation were discussed. The accomplishments via laboratory experiments, theoretical model development and field validation studies confirmed that the ScCO₂ fracturing enhanced shale gas recovery and CO₂ sequestration operations has commercial application prospect. However, as with any emerging technology, and particularly in a complex reservoir environment, many technical unknowns and challenges remain. Future work should be conducted to address these unknowns and challenges, and ultimately lead to commercial application of the technology.

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