Influence of supercritical, liquid, and gaseous CO2 on fracture behavior in sandstone

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Abstract
Storing CO2 in geological formations can reduce the amount of greenhouse gases in the atmosphere. In order to explore the fracture behavior of caprock during CO2 geological storage, three caprock adsorption experiments for supercritical, liquid, and gaseous CO2 were designed. The fracture toughness of mode I, mode II, and mixed-mode I/II of sandstone before and after the experiment was tested, and X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy (SEM) were used to examine the fracture mechanical characteristics of sandstone. Results showed that the pure mode I fracture toughness of sandstone immersed in supercritical CO2 (ScCO2), liquid CO2, and gaseous CO2 for 30 days decreased by 27.89%, 11.01%, and 17.43%, respectively, compared to nonimmersed sandstone. Pure mode I fracture toughness was more sensitive than mixed-mode I/II and pure mode II fracture toughness to the various CO2 phase states. Furthermore, the ability of sandstone to resist fracture and failure was significantly reduced by the adsorption of CO2 in different phases. The effects of the different phases were in the following order: ScCO2 > gaseous CO2 > liquid CO2. The decreased ability of sandstone to resist fracture was primarily due to the geophysical and chemical reactions between CO2 and minerals, the alteration of minerals, or the formation of new substances. SEM observations showed that liquid CO2 adsorption caused the sandstone to undergo intergranular fracture, and the adsorption of gaseous CO2 promoted the occurrence of transgranular fractures. In particular, due to the ScCO2 adsorption, various fracture forms such as intergranular fractures, transgranular fractures, and mutual coupling fractures existed simultaneously. Sandstone exhibited numerous fractures and pores, and fracture resistance was weakened. Results of this study have important significance for evaluating the stability and safety of CO2 geological storage.

KEYWORDS
CO2 geological sequestration, corrosion mechanism, fracture toughness, mechanical properties, sandstone
1 | INTRODUCTION

Increase in greenhouse gases is a direct cause of global warming. In order to reduce the amount of greenhouse gases in the atmosphere, the capture and storage of carbon dioxide has become an important issue for many researchers. Carbon capture and storage (CCS) is a newly emerging large-scale emission reduction method recommended by the United Nations Intergovernmental Panel on Climate Change (IPCC), which provides the possibility of achieving near-zero CO₂ emissions during fossil energy utilization. CO₂ capture and storage technology can be divided into three categories: marine storage, geological storage, and mineralized storage. Geological sequestration involves long-term CO₂ storage in natural underground reservoirs and is one of the most economical and reliable practical methods. Effective CO₂ underground reservoirs primarily include oil and gas reservoirs, abandoned oil and gas reservoirs, unrecoverable coal seams, and deep saline aquifers. China has carried out a nationwide assessment of geological sequestration CO₂ storage capacity. As a country with large coal resources, China has considerable coal bed methane reserves of approximately 3.06 × 10¹² m³ which can store approximately 2.2664 × 10¹⁰ t of CO₂. These reserves are mainly concentrated in the Shanxi, Shaanxi, and Guizhou provinces. Shanxi has the largest coal bed methane reserves, accounting for 91.5% of the national total.  

Rock is damaged and destroyed to varying degrees under the influence of geological processes such as in situ stress, temperature, and hydrochemical corrosion. For example, Ma et al. used the Forchheimer coefficient as an index to investigate the influencing mechanism of erosion on the nonlinear hydraulic properties of the broken red sandstones. Their experimental results showed that, as erosion seepage processed, the porosity and permeability of all samples increased, while the non-Darcy factor decreased. During the process of geological storage of CO₂ (capture, injection, and storage), the phase state of CO₂ constantly changes due to varying temperature and pressure. The physical properties of CO₂ in different phases are not the same. When CO₂ exists in supercritical state (31.1°C, 7.38 MPa), it has high density, strong solubility, low viscosity, and diffuses easily. CO₂ can easily infiltrate into tiny pores and fissures within a rock, as well as absorb and dissolve nonpolar and weak polar substances, which can significantly influence the physical and mechanical properties of rock.  

Many scholars have performed numerous studies on the physical and mechanical properties of rock under the action of CO₂, such as elastic modulus, compressive strength, tensile strength, Poisson's ratio, and permeability. After immersion in subcritical CO₂ (SubCO₂) and supercritical CO₂ (ScCO₂), the uniaxial compressive strength (UCS) and elastic modulus (E) of organic-rich shales decreased significantly, and the weakening effect of ScCO₂ on the mechanical properties of shale was significantly greater than that of SubCO₂. After immersion in ScCO₂, the Brazilian splitting strength (BSS), splitting modulus (E), and absorption energy (U) of shale samples decreased by 46%, 22%, and 50%, respectively, with increasing immersion time. Ranjith et al. studied the effects of gaseous CO₂ and ScCO₂ on the mechanical properties of Australian lignite and bituminous coal. The UCS and elastic modulus (E) of coal saturated with gaseous CO₂ and ScCO₂ decreased to varying degrees, while Poisson’s ratio generally increased. The effect of CO₂ adsorption on coal mechanical properties depends largely on the CO₂ pressure and phase state. Ranathunga reported that the UCS and elastic modulus (E) of lignite under SubCO₂ decreased by 21.25% and 22.52%, respectively, and Poisson’s ratio increased by 30.09%. The primary reason was that the matrix expansion of lignite caused by subcritical CO₂ adsorption led to significant changes in coal mechanical properties. However, when CO₂ was in the supercritical state, the lignite UCS and elastic modulus (E) decreased by 46% and 22.71%, respectively, and Poisson’s ratio increased by 16%. Compared with SubCO₂, the elastic properties of lignite were improved by 20%. Rathnaweera et al. tested the UCS of sandstone samples saturated with water and ScCO₂. Results showed that the UCS of saturated sandstone samples decreased by 46.44% and the elastic modulus (E) decreased by 20.93% compared to dry sandstone samples. Vikram Vishal et al. studied the influence of liquid, gaseous, and supercritical CO₂ on the permeability of Indian bituminous coal samples. Their results showed that, under the action of CO₂ saturation in different phase states, the permeability of bituminous coal decreased to different degrees with increasing saturation time, which was manifested as supercritical CO₂ > gaseous CO₂ > liquid CO₂. The reason is that ScCO₂ has higher affinity with the porous matrix of coal than other phases, which leads to greater pore and crack expansion and closure in coal. Iglauer et al. found that the permeability of Berea sandstone reservoir decreased by 23% after ScCO₂ injection, potentially due to the release of fine grains and subsequent pore-throat blockage.  

The physical and mechanical properties of rock change significantly under the influence of CO₂. This may be due to a series of physicochemical-mineralogical reactions between CO₂ and minerals in the rock with water participation, which leads to pore and crack formation in the rock and causes structural changes. Cui et al. studied reactions of injected CO₂ with water and rocks during geothermal energy exploitation. X-ray diffraction analysis indicated that the mineral particles in sandstone react with CO₂ and water.
to form carbonate precipitate, while clay minerals, feldspar minerals, and siderite in sandstone are dissolved. Wan et al. conducted an experimental study on the mineral capture mechanism during CO₂ sequestration in the Shiqianfeng aquifer in the Ordos Basin. They found that, under the action of ScCO₂ and water, plagioclase, hematite, illite, and clay minerals in the sandstone dissolved, while quartz and kaolinite precipitated. Olabode et al. investigated the microstructure of CO₂-water saturated clay-rich caprock and showed that pore size and specific surface area of the caprock changed after contact with CO₂. In addition, CO₂-water-rock interactions commonly cause changes in rock strength and deformational response, which further affects the stability and quality of CO₂ storage. Yin et al. studied the effect of ScCO₂ on mineral composition and pore structure in shale. Results showed that ScCO₂ dissolved some organic and mineral components in shale, such as montmorillonite, kaolinite, and calcite. The effect of ScCO₂ on micropores in shale samples was significantly greater than that on mesopores and macropores. SEM analysis of SubCO₂ and ScCO₂ saturated shale samples showed that different pore sizes were present on the surface of shale samples. SubCO₂ and ScCO₂ adsorbed in the shale interact with the minerals and water inside the rock. This leads to mineral dissolution or precipitation, thus altering the pore structure inside the shale.

CO₂ geological storage is a long-term process, and its safety and stability are important factors that determine whether the technology can be accepted and implemented. During coalbed methane exploitation, large-scale CO₂ injection leads to excessive formation pressure and changes in the in situ stress state, which may cause cracks in the caprock and activate originally inactive faults. In particular, expansion caused by CO₂ injection into coal seams may impose loads on the overlying caprock of the nonideal coal seam (such as thin, low-permeability, fault-height development coal seams, or shale formations), which may activate faults and increase gas leakage channels. The bottom of the caprock is commonly affected by the aquifer or CO₂ for a long time, indicating that the geophysical and chemical reactions between them play an important role in CCS. Rock physical and chemical properties are affected by CO₂ intrusion into the caprock through different mechanisms. Under the action of CO₂ corrosion and external load, microdefects or cracks in the caprock begin to propagate, expand, connect, and finally form macrofractures and seepage channels. The integrity and stability of the caprock are weakened and leakage is accelerated, which are potential risks of long-term CO₂ storage.

Griffith believes there are always a number of cracks of different sizes either on the surface or inside of a material. In particular, natural rock materials inevitably have a variety of initial microcracks, pores, and defects. Temperature, chemical corrosion, or external loading may induce cracks of various sizes in rocks. According to mechanical characteristics of cracks, the basic crack propagation modes can be roughly divided into three categories: mode I (tensile mode), mode II (in-plane shear), and mode III (antiplane shear). In engineering practice, rock is commonly in a composite stress field. Due to asymmetries in load, crack position, rock geometry, and anisotropy, composite cracks commonly form, of which (I + II) composite cracks are the most common. Rock failure is a process of crack interaction and propagation, and the fracture toughness of rock reflects the ability of rock materials to resist crack propagation. Many scholars have carried out research on variations in rock fracture behavior under different conditions. Feng et al. tested the effect of temperature on mode I, mode II, and mixed-mode I/II fracture toughness in sandstone. Results showed that the threshold temperature range for the sharp decrease in fracture toughness of sandstone is 500°C-600°C for the mixed-mode I/II. Also, mode II fracture toughness is identical to pure mode I fracture toughness. Yang et al. studied the response of the fracture characteristics of Shanxi bituminous coal saturated with ScCO₂, and found that bituminous coal fracture toughness gradually decreased with increase in immersion time. In particular, pure mode I fracture toughness was affected more by ScCO₂ than pure mode II and mixed-mode I/II fracture toughness. Ma et al. investigated the impacts of different height/diameter ratio (H/D) on the fracture failure characteristics of granite disk samples and carried out out bending tests. The test results suggested that, the sample with the H/D less than 0.4 primarily fractured under bending deformation. Once the H/D exceeded 0.4, the fracture failure mode changed to split tensile failure pattern.

To the best of the authors’ knowledge, the current research primarily focuses on macroscopic mechanical properties and deformation mechanisms of deep strata under the long-term influence of CO₂, concentrating on rock macrofailure and instability modes. When evaluating the stability and safety of geological storage, the rock formation fracture characteristics and damage mechanisms should be considered. Exploring the response of deep rock formations to CO₂ injection from the perspective of fracture mechanics would be beneficial for understanding rock mechanical failure characteristics during CO₂ sequestration. Moreover, it can provide a theoretical and practical basis for effectively and safely storing CO₂. In addition, a few scholars have considered the reduction of rock fracture resistance induced by ScCO₂ saturation. However, when CO₂ is injected into the formation, its phase state changes due to the influence of the formation environment. The process of phase change is often accompanied by physical endothermic and exothermic processes, which increases the probability of temperature and pressure change in the local area of the reservoir. At this time, the CO₂ in the formation may not be in single state, but may exist in multiple phase states. Little is known about the variation of mixed-mode I/II and mode II fracture toughness in rock formations when saturated with...
different CO₂ phases, especially for sandstone overlying a deep coal seam, which can be used as a caprock. This study examined a coal seam roof sandstone, developed a series of immersion experiments with different CO₂ phase states, carried out three-point bending fracture experiments and related micro-analysis, and explored the fracture behavior of rocks.

2 | EXPERIMENTAL METHODS AND PROCEDURE

2.1 | Fracture toughness determination

In this study, three-point bending fracture experiments of sandstone before and after immersion are carried out using the method recommended by ISRM. Semicircular bend (SCB) samples are used (Figure 1).

The specimen used in the SCB test is a semicircular disk with radius $R$ (mm) and thickness $B$ (mm). There is a prefabricated radial edge manual groove with length $a$ (mm). The prefabricated manual groove has an angle $\beta$ (°) relative to the loading direction. $2S$ is the distance between the two idlers (mm). Fracture toughness tests are performed by applying a vertical load ($P$) along the specimen axis using a three-point bending device. $K_I$ and $K_{II}$ represent the stress intensity factors of mode I and mode II, respectively, and the critical stress intensity factors ($K_{IC}$ and $K_{IIIC}$) are determined by the external critical load, dimensionless stress intensity factor, and specimen size. The fracture toughness of mode I and mode II can be calculated by substituting the measured data into Equations (1) and (2). The specific formulas are as follows:

\[
K_I = \frac{P \sqrt{\pi a}}{2RB} Y_I \left( \frac{a}{R}, \frac{S}{R}, \beta \right) \tag{1}
\]

\[
K_{II} = \frac{P \sqrt{\pi a}}{2RB} Y_{II} \left( \frac{a}{R}, \frac{S}{R}, \beta \right) \tag{2}
\]

In the above formulas, $P$ is the peak load on the SCB specimen under uniaxial compression; the thickness of the specimen ($B$) is 20 mm; the length of the precrack ($a$) is 12.5 mm; $Y_I$ and $Y_{II}$ are defined as mode I and mode II geometric factors, which are functions of geometric parameters $a/R$, $S/R$, and $\beta$, respectively. Lim et al. and Ayatollahi and Aliha used a large number of finite element modes to analyze SCB specimens and calculated $Y_I$ and $Y_{II}$ values for pure mode I, pure mode II, and mixed-mode I/II under various combinations of $a/R$, $S/R$, and $\beta$. When $a/R = 0.5$ and $S/R = 0.61$, the corresponding $\beta$ value of SCB specimens under pure mode II loading is 54° (Figure 2). When the $\beta$ value varies between 0°-54°, SCB specimens are loaded using mixed-mode I/II. In this experiment, the pure mode I and mode II fracture toughness values of SCB specimens are determined by choosing $\beta$ values of 0° and 54°, respectively, and the mixed-mode I/II fracture toughness values are determined by choosing $\beta$ values of 15° and 30°, respectively (Figure 3). The effective stress intensity factor ($K_{eff}$) is used to characterize the composite fracture toughness, which is calculated as follows:

\[
K_{eff} = \sqrt{K_I^2 + K_{II}^2} \tag{3}
\]
2.2 Specimen preparation

The rock used in this experiment was from a deep coal seam roof sandstone in the Datong mining area of China, a medium-fine grain arkose with a medium-fine grain sandy structure. The sandstone was composed of 45%-50% monocrystalline quartz, 35%-40% plagioclase with a small amount of K-feldspar, and 15%-20% debris. Minor components included clay hybrids.
(1%-5%) and trace calcareous cements. Secondary minerals included kaolin, chlorite, and mica. The size of the mineral particles ranged from 50 to 500 µm and cement particles were mainly 1-50 µm. Sandstone density was 2.51 g cm⁻³, and the mechanical characteristics included a uniaxial unconfined compressive strength of 64.7 MPa, uniaxial tensile strength of 6.8 MPa, cohesive force (c) of 25 MPa, and internal friction angle (φ) of 16°. The sandstone moisture content measured via the drying method was 3.43%.

Downhole field sampling and core drilling were conducted in the same rock mass. Cores were processed into disk samples with a diameter (D) of 50 mm and thickness (B) of 20 mm (Figure 4). Disk sandstone samples were cut into two semicircular disks of equal thickness. A 12.5-mm-long straight groove crack with a width of less than 2 mm was prefabricated for each semicircular specimen using a 0.5-mm diamond-embedded metal saw blade. All sample processing was in strict accordance with ISRM standards. Specimen surfaces were smooth with no visible microcracks.

2.3 | SCB specimen immersion process

In order to investigate the effect of different CO₂ phase states on sandstone fracture mechanical properties, sandstone specimens were immersed in liquid, gaseous, and supercritical CO₂. The temperature and pressure at the CO₂ triple-phase point are −56.4°C and 0.518 MPa, respectively, while the critical points are 31.1°C and 7.38 MPa (Figure 5). In this experiment, the immersion time was selected according to the test results. Results show that when the immersion time reaches 30 days, the fracture toughness deterioration degree of the sandstone tends to be stable. Therefore, in order to effectively saturate SCB specimens, the immersion time is 30 days.

The CO₂ immersion experiment system is shown in Figure 6. Before beginning the experiment, SCB specimens were first placed in a high-temperature-high-pressure reactor, which was evacuated for 24 hours to form a vacuum in the reactor and gas pipeline. Then, the temperature control system was adjusted to increase the temperature in the reactor at a rate of 1°C/min to the required temperature for the experiment, at which point the temperature was held constant. The CO₂ gas injection valve was slowly opened to inject CO₂ into the reactor through the compression and gas injection system to avoid any damage to the sandstone sample caused by a sudden pressure increase. When the pressure in the reactor reached the predetermined value, the gas injection was stopped, and the temperature and pressure stability was monitored for 30 minutes to ensure that the reactor was sealed. After 30 days of saturation, the pressure relief valve was opened to slowly discharge the CO₂ in the reactor and bring the pressure in the reactor down to atmospheric level. Finally, the SCB sandstone samples were taken out and sealed using a polyethylene film for subsequent fracture toughness tests.

2.4 | Fracture toughness test

The dip angle of the artificial crack and the CO₂ phase state were the primary variables in the experiment. Each group of variables used three identical control specimens, and artificial cracks at different inclination angles and nonimmersed SCB specimens were selected as the control group. A total of 48 sandstone SCB specimens were tested to evaluate artificial crack angles (0°, 15°, 30°, 54°) and phase state changes (liquid, gaseous, and supercritical). Due to the large number of samples tested in this experiment, these samples were labeled as “A-B-C,” where A denotes the different CO₂ phase states (L, G, S), and nonimmersed samples were denoted by “N.” B represents the artificial crack angle, and C represents the sample number. For example, “L-15°-1” represents the first SCB specimen with a precracking angle of 15° under liquid CO₂ immersion.

The fracture toughness test was conducted using an INSTRON 5544 materials testing machine (Figure 7). The loading rate was 0.0002 mm s⁻¹ with constant displacement. The load and displacement data were recorded synchronously during the testing process.

3 | FRACTURE TOUGHNESS AND LOADING CURVE

3.1 | Pure mode I and mode II fracture toughness

After the sandstone fracture toughness test was completed, the test data were input into Formulas (1) and (2) to calculate

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**FIGURE 5** Phase diagram of CO₂
$K_I$ and $K_{II}$, respectively. Then, the effective stress factor ($K_{eff}$) was calculated using Formula (3), and the average value of each variable was obtained (Table 1).

Figures 8 and 9 respectively show the pure mode I and pure mode II fracture toughness test results for sandstone samples immersed in liquid, gaseous, and supercritical CO$_2$.

The average pure mode I fracture toughness for nonimmersed sandstone samples was largest, which was about 23.90 MPa-mm$^{1/2}$ (Figure 8). After immersion in liquid, gaseous, and supercritical CO$_2$ for 30 days, the average pure I fracture toughness decreased to 21.27 MPa-mm$^{1/2}$, 19.74 MPa-mm$^{1/2}$, and 17.24 MPa-mm$^{1/2}$, respectively. Compared with the nonimmersed sandstone specimens, the pure I fracture toughness of sandstone specimens immersed in liquid CO$_2$ decreased by 11.01%, indicating that liquid CO$_2$ played a deteriorating role in pure I fracture toughness of sandstone specimens. The pure mode I fracture toughness of sandstone specimens was affected by gaseous CO$_2$ more than liquid CO$_2$. However, when sandstone specimens were immersed in ScCO$_2$, the average pure mode I fracture toughness was the lowest, which was about 27.89% lower than that of the sample without immersion. In other words, ScCO$_2$ caused the highest reduction in pure mode I fracture toughness in sandstone specimens.

The average pure mode II fracture toughness of nonimmersed sandstone specimens was 6.25 MPa-mm$^{1/2}$ (Figure 9). For liquid, gaseous, and supercritical CO$_2$, the average pure mode II fracture toughness of sandstone samples was...
5.95 MPa·mm$^{1/2}$, 5.37 MPa·mm$^{1/2}$, and 4.70 MPa·mm$^{1/2}$, respectively. After immersion in liquid and gaseous CO$_2$, the
pure II fracture toughness decreased by 4.76% and 13.97%, respectively, compared to nonimmersed sandstone samples. Pure mode II fracture toughness of specimens immersed in supercritical CO$_2$ decreased most significantly, by 24.69%. These results indicate that the influence of supercritical CO$_2$ on pure mode II fracture toughness of sandstone specimens is much greater than that of gaseous CO$_2$ and liquid CO$_2$.

3.2 Mixed-mode (I/II) fracture toughness

Figures 10 and 11 respectively show the effect of the phase change of CO$_2$ on the effective stress intensity factor ($K_{eff}$) of sandstone at the precracking angles of 15° and 30°.

When the precracking angle of the sandstone specimen was 15°, the average effective stress intensity factor of the nonimmersed sandstone specimens was largest, 22.38 MPa·mm$^{1/2}$ (Figure 10). When specimens were immersed in liquid CO$_2$ for 30 days, the average effective stress intensity factor was 18.87 MPa·mm$^{1/2}$, which was 15.67% lower than nonimmersed specimens. After immersion in supercritical CO$_2$, the effective stress intensity factor of sandstone specimens
continued to decrease to 14.99 MPa·mm$^{1/2}$, a 33.03\% decrease and the largest decrease observed.

The effective stress intensity factor of nonimmersed specimens with a precracking angle of 30° was the maximum value of 13.40 MPa·mm$^{1/2}$ (Figure 11). After immersion in liquid CO$_2$, the average effective stress intensity factor of the specimens was 12.61 MPa·mm$^{1/2}$, which was 5.93\% lower than that of the nonimmersed specimens. When sandstone samples were immersed in gaseous CO$_2$, their average effective stress intensity factor decreased to 11.69 MPa·mm$^{1/2}$, which was 12.79\% lower than that of the nonimmersed sandstone samples. The average effective stress intensity factor of sandstone specimens immersed in supercritical CO$_2$ was the smallest, 8.96 MPa·mm$^{1/2}$, a decrease of 33.17\%. Supercritical CO$_2$ had the most obvious influence on the mixed-mode I/II fracture toughness of sandstone (Figures 10 and 11).

### 3.3 Load-displacement curve

The load-displacement curve can be directly obtained by testing the fracture toughness of sandstone samples. The load-displacement curve of sandstone directly reflects sandstone failure characteristics and helps us understand the sandstone’s ability to resist fracture. In this experiment, sandstone deformation and failure experienced four stages: crack compaction stage (OA), linear elastic deformation stage (AB), crack stable growth stage (BC), and crack instability and failure stage (CD) (Figure 12). The rock is compacted during the initial loading, internal microcracks close quickly under the external force, and the load-displacement curve becomes concave. The crack compaction stage accounts for a small proportion of the whole deformation and failure process. When the loading process reaches point A, the linear elastic deformation stage begins (from A to B), and the load-displacement curve is approximately linear, which becomes the primary part of the deformation and failure process. When the load reaches the crack propagation critical stress at point B, the fracture begins to form. As the load increases, internal cracks in the rock undergo stable growth or expansion. As axial load continues to increase, it is quickly unloaded after the peak load at point C is reached. This indicates that the unstable crack growth inside the sandstone causes considerable damage to the sandstone specimen and will eventually lead to specimen failure. For this research study, the plastic stage was assumed to be the elastic deformation stage. In other words, the study assumed that points B and C coincide.

Figure 13A shows the load-displacement curves for the pure mode I fracture toughness test with a precracking angle of 0°. Figure 13D shows the load-displacement curves of the pure mode II fracture toughness test, with a precracking angle of 54°. Figure 13B,C shows the load-displacement curves for the mixed-mode I/II fracture toughness test, with precracking angles of 15° and 30°, respectively. The peak load of pure mode II is always higher than that of pure mode I, indicating that open-type cracks (mode I) in sandstone are more likely to form than slip-type (mode II) cracks. The shape of load-displacement curves for mixed-mode I/II and mode II fracture toughness is similar to that of pure mode I fracture toughness. The peak load of the sandstone after immersion is smaller than that of nonimmersed sandstone. Moreover, the peak load is positively correlated with fracture toughness, which may be closely related to the closure of microcracks or pores in sandstone by external forces. In the initial loading stage, displacement of immersed sandstone specimens is significantly greater than that of nonimmersed sandstone specimens, which may be due to the formation of new pores.
or cracks in the sandstone after immersion. Compaction and closure of these pores and microcracks significantly increase the strain, further indicating that the brittleness of sandstone samples decreases and the original toughness changes in the initial loading stage under CO₂ immersion. Crack compaction varies with CO₂ phase state. The displacement of supercritical CO₂ is significantly higher than that of liquid CO₂ and gaseous CO₂, indicating that after immersion in supercritical CO₂, more new microcracks are formed inside the sandstone.

As axial load continues to increase, sandstone samples show a linear elastic behavior. However, in the elastic deformation stage (AB), the slope of the load-displacement curve of the immersed sandstone sample is significantly lower than that of the nonimmersed sandstone sample. The slope is lowest after immersion in supercritical CO₂, followed by gaseous CO₂, then liquid CO₂. After the elastic stage, the sandstone specimen undergoes sudden brittle failure.

4 DISCUSSION

4.1 Fracture toughness changes with CO₂ phase state

In order to better understand the variations in pure mode I, pure mode II, and mixed-mode I/II fracture toughness of sandstone with CO₂ phase state, their effective stress intensity factors were studied. Figure 14 shows the variation in average value of the effective stress intensity factors for pure mode I, pure mode II, and mixed-mode I/II with change in the CO₂ phase state.

After immersion in CO₂ with different phase states, sandstone fracture toughness curves show a similar variation trend of decreasing with varying CO₂ phase state (Figure 14). Under the same phase of CO₂, sandstone fracture toughness decreases with increase in precracking angle. The fracture toughness of pure mode I is greater than that of pure mode II. In mixed-mode I/II fracturing, the fracture toughness of specimens with a precracking angle of 15° is greater than that of specimens with a precracking angle of 30°.

4.2 Influence of CO₂ immersion on sandstone mineral composition

The mechanical properties of rock primarily depend on its internal mineral composition and structure. Sandstone is mainly composed of quartz, feldspar, clay minerals, and other mineral debris, which can be detected using XRD and XRF. These minerals are capable of physical and chemical reactions in a CO₂-rich environment. Table 2 shows the mineral composition and content of sandstone specimens analyzed using XRD and XRF.

Generally, a small amount of free water is present, and crystalline water does not easily evaporate. When sandstone specimens are immersed in CO₂, the water combines with CO₂ entering the pores and cracks of the sandstone, forming an acidic environment (Equation 4).

\[
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+; \quad \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \quad (4)
\]

Dissolving CO₂ in water releases H⁺, which causes a series of complex geochemical reactions between minerals in sandstone and H⁺ (Table 3).

The dissolution of these minerals and the formation of new materials may cause secondary fractures and pores in the sandstone, thus having a significant influence on the sandstone mineral structure. According to the composition and content of sandstone minerals measured using XRD, silicate
minerals (such as quartz and feldspar minerals) account for a large proportion of the sandstone composition, while the amount of clay minerals (such as chlorite and kaolinite) is relatively small. These silicate minerals are inherently strong and act as a skeleton within the sandstone, while clay minerals act as a cement. Siliceous minerals rich in Mg, Al, and other elements are considered to have great mineralization and capture potential. However, CO₂ corrodes and dissolves the skeleton particles, damages the contact surfaces between the particles, and weakens the pore structure bond energy to a large extent. As a result, the overall structure of the sandstone becomes loose and rock strength decreases. The alteration of clay minerals such as kaolinite changes the accumulation of Mg, Al, Si, and other elements in the pore fluid, which also weakens the macroscopic mechanical properties of sandstone.

The viscosity of liquid CO₂ (20°C, 6 MPa) is higher than that of gaseous CO₂ (40°C, 6 MPa). Therefore, it may be more difficult for liquid CO₂ to penetrate small pores and cracks inside the sandstone, allowing for insufficient contact between the mineral components and liquid CO₂. This reduces the probability of liquid CO₂ combining with water inside the sandstone, which makes the alteration of minerals in sandstone much smaller compared to gaseous CO₂. Similarly, the degree of damage from liquid CO₂ on the cement between skeleton particles and the particles in the sandstone specimens is not as large as that of the gaseous CO₂. Consequently, the mechanical properties of sandstone after immersion in liquid CO₂ are higher than those of sandstone after immersion in gaseous CO₂. When temperature and pressure exceed 31.1°C and 7.38 MPa, respectively, CO₂ changes into a supercritical state.

**FIGURE 13** Experimental load-displacement curves for sandstone specimens with varying precracking angles

(A) pure mode I ($\beta = 0°$)

(B) mixed-mode I/II ($\beta = 15°$)

(C) mixed-mode I/II ($\beta = 30°$)

(D) mode II ($\beta = 54°$)
where the intermolecular force of CO\textsubscript{2} is very small and the surface tension is 0. Although its viscosity is higher than that of gaseous CO\textsubscript{2}, the viscosity of supercritical CO\textsubscript{2} is significantly lower than that of liquid CO\textsubscript{2}. Moreover, its diffusion ability is 10-100 times that of liquid CO\textsubscript{2}, which has an extremely strong solubility.\textsuperscript{64} ScCO\textsubscript{2} is more likely to enter into micropores and cracks compared to gaseous and liquid CO\textsubscript{2}, allowing the minerals in the sandstone to fully come into contact with ScCO\textsubscript{2}. This greatly increases the probability of mineral dissolution or precipitation, weakens skeleton particles and cemented mineral strength, and severely threatens the stability of the overall sandstone structure. Compared with liquid CO\textsubscript{2} and gaseous CO\textsubscript{2}, ScCO\textsubscript{2}-immersed sandstone has the lowest macroscopic fracture resistance.

### 4.3 Influence of CO\textsubscript{2} immersion on the microscopic structure of sandstone

Griffith\textsuperscript{51} believes that rock fracture is the result of stress concentration caused by microcracks. When rock deforms under stress, if the elastic strain energy released is larger than the surface energy needed to form a new crack surface, cracks begin to expand. Gibbs\textsuperscript{65} proposed that when a porous dielectric material adsorbs a liquid or gas, its surface energy changes. These two theories can be expressed by Equations (5) and (6), respectively:

\[
d\gamma = - \sum (\gamma_i d\mu_i) d\gamma
\]

\[
\sigma = \sqrt{\frac{2E\gamma}{\pi a}}
\]

where \(\gamma\) is the surface energy per unit crack length; \(\Gamma_i\) is the surface concentration; \(\mu_i\) is the change of chemical potential energy; \(a\) is the crack length; and \(\sigma\) is the critical stress for crack growth. From these two equations, the relationship between sandstone strength and adsorbent can be inferred. When the rock surface adsorbs a liquid or gas, if the rock surface energy can be reduced, the stress required for crack growth will be reduced, and vice versa. In other words, when the rock breaks, the required external load decreases. Yin Hong et al,\textsuperscript{31} Perera et al,\textsuperscript{34} and Ma Li et al\textsuperscript{66} have shown that the CO\textsubscript{2} adsorption of rocks can significantly reduce the surface energy of rocks, especially for ScCO\textsubscript{2}. A strong adsorption capacity has the most significant effect on reducing rock surface energy and has the most prominent rock strength deterioration. Due to CO\textsubscript{2} adsorption in the liquid or gas phase, the surface energy of sandstone can only be reduced by expanding itself to increase the surface area.\textsuperscript{67} However, the expansion coefficients and elastic-plastic properties of various minerals in sandstone are different and have a random distribution, so that inconsistency in deformation between particles is inevitable. This can also lead to changes in sandstone structure and overall strength reduction.

In addition, Vikram Vishal et al\textsuperscript{38,39} studied the permeability of coal under the action of CO\textsubscript{2} in different phase states. They concluded that the main reason for the decrease in coal permeability was that expansion of the coal matrix under the action of ScCO\textsubscript{2} reduced the space of pores and cracks and also blocked the seepage channel in the coal matrix. The permeability of coal under the action of ScCO\textsubscript{2} was larger than that of gaseous and liquid CO\textsubscript{2}. In other words, the expansion effect of ScCO\textsubscript{2} on coal was also greater than that of gaseous and liquid CO\textsubscript{2}. Results also indirectly indicated that the weakening effect of ScCO\textsubscript{2} on sandstone strength was significantly greater than that of liquid and gaseous CO\textsubscript{2}. In order to further explain the influence of CO\textsubscript{2} of different phase states on the microstructure and strength of sandstone, sandstone specimen surface morphology and fractography were observed using SEM.

The SEM observation results showed that different CO\textsubscript{2} phase states had significant influence on the surface morphology of sandstone specimen. The surface of the non-immersed sandstone specimen was flat and smooth, with faint scratches on the surface (Figure 15A). Pores and cracks on the specimen surface were not well developed. Mineral
particles had sharp edges and corners, and the particles were bonded well. The filling between minerals was clear and distinguishable, and the overall structure was relatively complete. After immersion in liquid CO₂, the sandstone sample began to become rough and uneven, with numerous potholes or bulges (Figure 15B). Mineral boundaries were blurred by the influence of liquid CO₂, and the shape of specific mineral particles cannot be easily distinguished. At the same time, many tiny new pores began to appear on the surface and are randomly distributed across the specimen surface. When the sandstone specimen was immersed in gaseous CO₂, surface roughness increased, mineral particles were no longer complete, and the surface was subjected to varying degrees of corrosion (Figure 15C). Compared with the sandstone immersed in liquid CO₂, the number of pores on the surface of the sandstone increased and pore size gradually increased, with a small amount of fibrous-like substances appearing locally. This result indicated that gaseous CO₂ had a greater

| Reaction type             | Reaction formula                                                                 |
|---------------------------|---------------------------------------------------------------------------------|
| Quartz dissolution        | Quartz ↔ SiO₂                                                                     |
| Albite dissolution        | Albite + H⁺ ↔ 2H₂O + Na⁺ + Al³⁺ + 3SiO₂ (aq)                                     |
| Microcline dissolution    | Microcline + 4H⁺ ↔ 2H₂O + K⁺ + Al³⁺ + SiO₂ (aq)                                 |
| Kaolinite dissolution     | Kaolinite + 6H⁺ ↔ 5H₂O + 2Al³⁺ + 2SiO₂ (aq)                                      |
| Chlorite dissolution      | Chlorite + 8H⁺ ↔ 3SiO₂ + 2.5Fe²⁺ + 2.5Mg²⁺ + 8H₂O + 2AlO₂⁻ (aq)                 |

**FIGURE 15** SEM images of sandstone surface morphology before and after CO₂ immersion (red arrows indicate pores, and the red boxes indicate cracks)

**TABLE 3** Interaction of sandstone minerals and H⁺ ions in the CO₂ environment⁴¹
influence on sandstone surface morphology than liquid CO$_2$. When the sandstone specimen was immersed in ScCO$_2$, the roughness of the sandstone surface increased significantly, and gully depressions began to form across the specimen surface (Figure 15D). Mineral particles were not complete, and most of them were broken and loose. The number and size of pores further increased, and the local micropore groups even penetrated to form cracks of different sizes. The above comparison showed that ScCO$_2$ had the greatest influence on sandstone surface morphology. Rock surface roughness has a significant impact on rock strength. Therefore, the degradation degree of ScCO$_2$ to sandstone strength was higher than that of gaseous and liquid CO$_2$.

Rock fracturing is closely related to the internal microstructure and microdefects. Rock fractography records the irreversible deformation during fracturing, as well as the initiation and propagation of cracks. Therefore, an analysis of sandstone fractography will be helpful in understanding the influence of CO$_2$ on the microscopic rock fracturing characteristics and reveal the degradation mechanism of sandstone fracture toughness caused by CO$_2$ in different phase states. Figure 16A-D shows SEM images of fractography of sandstone samples before and after CO$_2$ immersion. The fractography of the nonimmersed sandstone specimen was relatively flat, with few pores and cracks (Figure 16A). Only a small number of intergranular cracks were visible at local particle boundaries, which was due to the presence of cement. Under the external load, fractures easily occurred along particle boundaries. With the change of immersion environment, the number of pores and fractures on the fracture surface of sandstone samples increased gradually, which may be due to the different intensity of physical and chemical reactions between mineral particles and CO$_2$ in different phase states. The fractography of the sandstone specimen immersed in liquid CO$_2$ became rougher than that of the nonimmersed specimen (Figure 16B). A few micropores were visible on the surface of mineral particles and many intergranular cracks between particles were present. Also, a small amount of transgranular cracks were observed in some areas, indicating that liquid CO$_2$ acted on the surface of sandstone mineral particles, causing a certain degree of damage to the strength of mineral particles. When the sandstone specimen was
immerged in gaseous CO2, its fractography changed more significantly (Figure 16C). Under the action of gaseous CO2, the width of intergranular cracks between particles increased, and the mineral particles began to deform and separate from each other, causing the mineral structure to gradually loosen. The surface of the mineral particles corroded inward from the particle boundary. A large number of tiny pores (red boxes) appeared, and these pores had a clear tendency to expand into cracks. Moreover, “river-like” transgranular cracks appeared and spread across the mineral particles, making mineral particle surfaces rough. Mineral particles exhibited large plastic deformation locally, which greatly reduced mineral particle strength. However, through comparative analysis, the most prominent change in fractography correlated to immersion in ScCO2 (Figure 16D). The fracture morphology was messy and had a honeycomb-like structure, with ubiquitous ScCO2 corrosion and increased plastic deformation. Small cracks in the same direction gradually coalesced to form larger cracks. Mineral particles were seriously deformed and separated from each other. A large number of pores and cracks cause cracking of the sandstone structure and were more likely to break under external force. In addition, relevant studies have shown that the changes in the geometry of mineral particles and the volume of fractures between particles have a great influence on the porosity and seepage characteristics of the caprock. This may pose a threat to the effectiveness of CO2 sequestration in caprock.

3. Three different phases of CO2 had different effects on the sandstone load-displacement curve. Overall, the sandstone peak load and the slope of the curve both decreased. The crack compaction stage was the longest under the adsorption of ScCO2, followed by gaseous CO2, then liquid CO2, indicating that ScCO2 adsorption caused more microcracks and micropores in the rock. During the complete stress loading process, the change in CO2 phase state did not change the failure form of the rock. All specimens experienced brittle failure.

The three different CO2 phases caused different degrees of cracking in the sandstone. On the one hand, the chemical reaction between CO2, water, and mineral components in sandstone led to matrix dissolution or precipitation. On the other hand, CO2 adsorption caused heterogeneous expansion of mineral particles. For example, numerous intergranular cracks formed along fractures after liquid CO2 immersion and more transgranular cracks formed after gaseous CO2 immersion. Moreover, multiple mutual coupling fractures appeared after ScCO2 immersion, and pores and cracks became connected and penetrated each other, which significantly weakened the sandstone fracture resistance.

From the perspective of practical engineering applications, this study clearly shows that when CO2 is injected into the formation, CO2 in different phases reduce the fracture resistance of the caprock. ScCO2 has the most significant degradation effect. This may lead to large-scale crack development of the caprock under in situ stresses, increasing the risk of CO2 leakage. The investigations performed in this study are important for sandstone caprock stability in the CO2-ECBM and CO2 sequestration process.

5 | CONCLUSION

In order to better understand the impact of CO2 on fracture mechanical behavior in caprock sandstone during geological storage, this paper carried out a CO2 immersion experiment with CO2 different phase states on a caprock sandstone. Three-point bending tests were conducted on sandstone specimens before and after immersion. The microstructure and fracture characteristics of sandstone were studied using XRD, XRF, and SEM. The main conclusions are as follows:

The ability of sandstone to resist fracture is reduced by CO2 in all three different phase states. Mode I (β = 0°), mixed-mode I/II (β = 15°), mixed-mode I/II (β = 30°), and mode II (β = 54°) fracture toughness of sandstone decreased by 27.89%, 33.03%, 33.17%, and 24.69%, respectively, under the influence of ScCO2. Sandstone fracture toughness decreased by 11.01%, 15.67%, 5.93%, and 4.76%, respectively, under the influence of liquid CO2. Finally, sandstone fracture toughness decreased by 17.43%, 23.81%, 12.79%, and 13.97%, respectively, under the influence of gaseous CO2. ScCO2 adsorption led to the largest reduction in sandstone fracture toughness, followed by gaseous CO2, then liquid CO2.

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1. NOMENCLATURE
Abbreviations
ISRM, International Society of Rock Mechanics; SCB, Semicircular bend; XRD, X-ray diffraction; XRF, X-ray fluorescence; SEM, Scanning electron microscopy; R, Sample radius (mm); D, Sample diameter (mm); B, Sample thickness (mm); a, Precrack length (mm); 2S, Support span (mm); P, Load (N); Pmax, Peak load (N); β, Orientation angle of an artificial precrack with respect to the loading direction (°); Yf, Normalized mode I stress intensity factor; YfII, Normalized mode II stress intensity factor; KIC, mode I fracture toughness (MPa-m1/2); KICII, mode II fracture toughness (MPa-m1/2); Keff, The effective stress intensity factor (MPa-mm1/2).

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