Different Effect Mechanisms of Supercritical CO₂ on the Shale Microscopic Structure

Yiyu Lu, Jiankun Zhou, Honglian Li,* Xiayu Chen, and Jiren Tang

1. INTRODUCTION

Shale gas reservoirs contain spontaneously generated natural gas stored within shale rocks of low porosity and low permeability, where methane (CH₄) exists mainly as free gas and adsorbed gas. Horizontal well fracturing is currently the main technique used for shale gas production. However, because of the very high water consumption involved in this process, which is typically in the range of 15,000–30,000 tons of water per shale gas well, its application is severely limited in regions with water scarcity. As an alternative, supercritical CO₂ can be used as a new anhydrous fracturing fluid to extract shale gas. It has the characteristics of a low-viscosity gas and a high-density liquid, with superior fluidity, permeability, and transmissivity. Further, CO₂ is more easily adsorbed than CH₄ by shale rock, which is not only a source of CH₄ but also a gas reservoir. Studies have shown that using supercritical CO₂ to extract shale gas can not only improve the recovery rate of shale gas but also effectively store CO₂ underground, which alleviates the greenhouse effect.

When CO₂ is injected into a shale gas reservoir, shale is exposed to supercritical CO₂ at high temperature and pressure. On the one hand, this causes supercritical CO₂ to react with carbonates and clay minerals within the reservoir, resulting in changes in mineral contents; on the other hand, a large amount of injected CO₂ increases the pore pressure and changes the pore structure of shale. Microscopic pores adsorb gas and are channels for gas migration; thus, the study of the effect of supercritical CO₂ on shale microstructure is of much significance for the efficient production of shale gas and CO₂ storage. At present, several test methods are used to analyze the interaction between supercritical CO₂ and the shale microstructure, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), nuclear magnetic resonance (NMR), and low-pressure nitrogen gas adsorption (N₂GA). Some studies have shown that supercritical CO₂ can extract water molecules from minerals to form carbonic acid and dissolve carbonate minerals. Lyu et al. found that new pores appeared on the surfaces of shale slices after being saturated with sub-/super-critical CO₂, and an increase in carbon content confirmed a chemical reaction between CO₂ and shale. Ao et al. found that supercritical CO₂ causes strain...
because of swelling and that high CO$_2$ pressure causes shale deformation; however, deformation also occurs at low pressure, mainly because of CO$_2$ adsorption. Yin et al.\textsuperscript{48} observed that after treatment with supercritical CO$_2$, the proportions of clay minerals, calcite, and dolomite in shale decreased, and the primary macropores and microcracks in shale were narrowed because of swelling induced by CO$_2$ adsorption. Lu et al.\textsuperscript{38} found that after CO$_2$ saturation, shale porosity and volume of macropores increased, but the volume of micropores and mesopores decreased, and that the effect of gaseous CO$_2$ on the pore structure of shale was weaker than that of supercritical CO$_2$. Jiang et al.\textsuperscript{49} noted that original pores and pre-existing fractures in shale could be eroded because of the effect of dissolution by supercritical CO$_2$, and new pores could form. Zhou et al.\textsuperscript{50} remarked that dissolution due to supercritical CO$_2$ led to a reduction in the number of shale micropores, and that the effect of swelling transformed macropores into mesopores; also, supercritical CO$_2$ could decrease the surface roughness of shale pores and the complexity of pore structures.

Although several studies have been conducted on the effect of supercritical CO$_2$ treatment on shale microstructures, the factors that affect these changes differ and have not been adequately studied. In addition to differences in shale specimens and experimental conditions, the mechanisms of microstructure changes are important and have not yet been well-understood. For example, it is unclear whether CO$_2$ pressure or mineral dissolution has a greater effect on porosity. To explore the different mechanisms by which supercritical CO$_2$ changes shale microscopic structure, several methods including XRD, SEM, NMR, N$_2$GA, and fractal theory were used in this study to determine the effects of different gas and pressure conditions on the shale microstructure. The results and significance for improving shale gas recovery are discussed in this paper.

2. METHODOLOGY

2.1. Specimen Preparation. Shale for this study was obtained from the Fuling area of the Sichuan Basin in China, which is currently the largest shale gas producing area in China, and the shale has an average total organic carbon content of 3.47\% and a vitrinite reflectance ($R_o$) of 2.56\%.\textsuperscript{48,51} The shale was processed into standard cylindrical specimens with a diameter of 50 mm and a length of 25 mm (Figure 1). The parallelism of the end faces of each cylindrical specimen was not greater than 0.01 mm, and the vertical deviation was not greater than 0.05°. To eliminate experimental errors caused by differences among the specimens, an NMR analysis was conducted to select specimens with the closest pore characteristics and thus maximize the reliability of the test results (Figure 2). To meet different experimental requirements, some select shale samples were crushed, and the powder was mixed evenly. Powder finer than 200 mesh was used for XRD, powder in range of 20–60 mesh was used for N$_2$GA tests, and cuboid samples of size less than 8 mm × 8 mm × 3 mm were used for SEM tests. All processed shale samples were wrapped and sealed with a plastic wrap to prevent moisture and contamination.

2.2. Experimental Procedure. Experiments with the shale samples were conducted in a high-pressure reactor system designed at our facility (Figure 3a). It consists of a high-pressure vessel with a maximum working pressure of 32 MPa, a Teledyne ISCO 260D syringe pump (Teledyne, Thousand Oaks, CA, USA) with a maximum working pressure of 51.7 MPa and a flow rate range of 0.001–107 mL/min, and a thermostatic water bath with a fluctuation of less than 0.1 °C. The experimental temperature was set at 60 °C to simulate real reservoir environment, and the exposure time was set to be 10 days, as per the time required for the interaction between shale and CO$_2$ to reach equilibrium. Argon (Ar) gas has also been used in these experiments. Being an inert gas, Ar does not react with shale and can thus be used to isolate the effect of pressure from a gas on the pores in shale, as opposed to the effects of CO$_2$, which not only include pressure from the gas, but also adsorption, dissolution, extraction, and other factors. To study the mechanisms by which supercritical CO$_2$ changes the shale pore structure, the exposure conditions (Table 1) of shale to gas treatments were set as follows: untreated sample (reference group), 4 MPa Ar, 16 MPa Ar, 4 MPa CO$_2$ (gaseous state), and 16 MPa CO$_2$ (supercritical state). Before each experiment, the shale sample chamber was subjected to vacuum for at least 2 h to avoid the experimental error caused by air.

An “X-Max20/W500X” X-ray diffractometer (Co Ka radiation, 40 kV, 40 mA) was used for the XRD analysis of the 200 mesh shale powder to determine the change in the mineral content of shale before and after exposure. The micromorphology of shale was observed using a "JSM6610LV" scanning electron microscope (JEOL, Japan). The aperture distribution of shale was tested by a "MacroMR12-150H-I" low-field NMR core analysis system (Niumag Analytical Instrument Corp., China). The NMR analysis is based on the principle of using the hydrogen-containing fluid in pores to determine the pore structure of rocks.\textsuperscript{52} Therefore, it was...
necessary to fully saturate the shale specimens with water before performing an NMR analysis. The N₂ adsorption–desorption isotherms were obtained at a temperature of −196 °C at a relative pressure (p/p₀) range of 0.01–0.99 using a Micromeritics ASAP 2020 system.

3. RESULTS AND DISCUSSION

3.1. XRD and SEM. Table 2 and Figure 4 show the results for the mineral content in shale under different treatment conditions. It can be seen that the shale was mainly composed of quartz, dolomite, and calcite. The mineral content of shale did not change appreciably because of treatment with Ar, but did change significantly after treatment with CO₂. The change in the mineral content of shale after treatment with CO₂ is likely due to the chemical reactions of minerals in the CO₂-water system (eqs 1 and 2). The dissolution of calcite (CaCO₃) in acid solution occurs before that of dolomite (CaMg(CO₃)₂) (eqs 3 and 4), while quartz (SiO₂) is stable and remains almost undissolved. Therefore, it is believed that the change in the proportion of calcite indicates the degree of dissolution, and the change in the proportion of quartz indicates the degree of the overall chemical reaction. The calcite content is the lowest, and the quartz content is the highest after treatment with 16 MPa CO₂, indicating that when shale is exposed to supercritical CO₂, the dissolution of calcite

| specimen groups | gas | pressure (MPa) | temperature (°C) | time (d) | state |
|-----------------|-----|----------------|-----------------|----------|-------|
| A               | untreated |  | | | |
| B               | Ar   | 4             | 60              | 10       | gaseous |
| C               | Ar   | 16            |                 |          |       |
| D               | CO₂  | 4             |                 |          |       |
| E               | CO₂  | 16            |                 |          | supercritical |

Table 2. XRD Results

| treatment conditions | quartz | dolomite | calcite | TCCM | feldspar | pyrite | hematite |
|----------------------|--------|----------|---------|------|----------|--------|----------|
| untreated            | 42.7   | 30       | 16.2    | 9.3  | 0.8      | 0.5    | 0.5      |
| 4 MPa Ar             | 42.6   | 30.1     | 16.2    | 9.2  | 0.9      | 0.6    | 0.4      |
| 16 MPa Ar            | 42.7   | 29.8     | 16.3    | 9.3  | 0.9      | 0.5    | 0.5      |
| 4 MPa CO₂            | 43.3   | 30.2     | 15.1    | 9.8  | 0.8      | 0.4    | 0.4      |
| 16 MPa CO₂           | 45.5   | 30.1     | 12.4    | 10.4 | 0.6      | 0.5    | 0.5      |

*TCCM represents clay minerals such as kaolinite, illite, and montmorillonite.
and the overall chemical reaction between shale minerals and the CO$_2$–water system are the strongest compared to other conditions. This is because supercritical CO$_2$ can extract bound water from clay minerals (TCCM), which increases the amount of CO$_2$ in aqueous solution. The pH of the acid solution decreases, that is, the acidity increases, with an increase in the pressure of CO$_2$. Compared with a 4 MPa CO$_2$ environment, the 16 MPa CO$_2$ environment has a higher acidity, which results in a sudden decrease in calcite content and a sudden increase in quartz content.

\[
\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3
\]  

(1)

\[
\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^- = 2\text{H}^+ + \text{CO}_3^{2-}
\]  

(2)

\[
\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^- 
\]  

(3)

\[
\text{CaMg(CO}_3)_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} = \text{Ca(HCO}_3)_2 + \text{Mg(HCO}_3)_2
\]  

(4)

The microscopic morphologies (Figure 5) of shale samples under different treatment conditions show that compared with untreated and other treatment conditions, the pores on the shale surface seem to develop the most because of the dissolution of minerals when shale is exposed to a 16 MPa CO$_2$ environment.

3.2. NMR Analysis of Aperture Distribution. The aperture distribution of shale specimens was obtained from the distribution of the transverse relaxation time $T_2$. The pore size has a positive correlation with the transverse relaxation time. The relationship between pore size and transverse relaxation time can be expressed by eq 5 as follows:

\[
\frac{1}{T_2} = F_s \times \frac{\rho}{r}
\]  

(5)

where $T_2$ is the transverse relaxation time, ms; $F_s$ represents the shape factor of the pore; $\rho$ is the relaxation strength of the transverse surface, nm/ms; $r$ is the pore size, nm. For this study, $F_s = 2$ and $\rho = 10$ nm/ms.

The aperture distribution of shale before and after exposure is shown in Figure 6. Before the tests were conducted, specimens with almost identical $T_2$ curves were identified and selected for testing. Hence, the $T_2$ curves for untreated shale in Figure 6 are identical. It can be seen that the aperture distributions of shale samples show a bimodal distribution, with two peaks located in the pore size ranges of 1–250 nm (main peak) and 250–2000 nm (secondary peak). After
treatment with 4 MPa Ar, the aperture distribution curve shows a slight shift to the left. Because Ar does not react with shale, the overall decrease in pore size for this condition is likely caused by the compression of shale pores because of the pressure of the gas. After treatment with 16 MPa Ar, the decrease in pore size corresponding to the main peak is more apparent, indicating that the increase in gas pressure causes a greater compression of shale pores. Also, some microcracks occur in shale because of the higher pressure of the Ar gas at 16 MPa; hence, the pore component corresponding to the secondary peak increases. It has been shown that when CO₂ is adsorbed on a shale surface, it causes an expansion and deformation of shale and a reduction in pore size.59–61 It can also be seen from Figure 6c that after treatment with 4 MPa CO₂, the main peak decreases, while the secondary peak increases because of the dissolution of minerals such as calcite. In addition to adsorption and the dissolution reactions with shale minerals, supercritical CO₂ also has the unique ability to extract organic matter, resulting in an increase in pore size and forming an acidic environment with higher solubility. Compared with other treatment conditions, when shale is exposed to a 16 MPa CO₂ environment, the magnitudes of both the main peak and the secondary peak increase significantly, which indicates that the extraction reaction of supercritical CO₂ has a greater effect on shale pore size than other factors.

3.3. Porosity and Average Pore Size. To further reveal the effect of different mechanisms on shale pores, a cumulative porosity diagram (Figure 7) was plotted based on NMR data.

As seen in this figure, the porosity of untreated shale was 3.46%, and after the treatments with 4 MPa Ar, 16 MPa Ar, and 4 MPa CO₂, the porosity had decreased in all cases, and the increments were −0.06, −0.15, and −0.25%, respectively. However, after being exposed to 16 MPa CO₂, the porosity of shale increased from 3.46 to 3.63%, which represents an increase of 0.17%. Combining the data of Figures 6b and 7, it can be inferred that although a high gas pressure induces microcracks in shale, the porosity of shale decreases, indicating that the impact of gas pressure on shale pores is mainly compressive, regardless of the magnitude of the pressure. According to Table 3 and Figure 8, it is seen that after treatment with 4 MPa CO₂, the gas pressure causes a reduction in shale porosity of 0.06%, and the combined effect of CO₂ adsorption and mineral dissolution causes the porosity to decrease by 0.19%. In general, the effect of CO₂ adsorption on shale porosity is opposite to that of mineral dissolution, that is, adsorption-induced expansion reduces porosity, and dissolution increases porosity. Therefore, it can be concluded that in a gaseous CO₂ environment, the adsorption of CO₂ has a greater effect on shale pores than gas pressure and dissolution reactions. By comparing the change in shale porosity after treatments with 16 MPa Ar and 16 MPa CO₂, it is found that after treatment with 16 MPa Ar, the shale porosity decreases by 0.15%, while after treatment with 16 MPa CO₂, the shale porosity increases by 0.17%. The increase in porosity in the latter case is because the effects of the extraction and dissolution reactions of supercritical CO₂ can not only overcome the effects of compression caused by gas pressure but also the compressive effects of CO₂ adsorption; this indicates that after treatment with supercritical CO₂, the change in shale porosity is mainly controlled by extraction and dissolution reactions. Consistent with the above effects on shale porosity, the average pore size of shale decreases after treatment with 4 MPa Ar, 16 MPa Ar, and 4 MPa CO₂, but increases after treatment with 16 MPa CO₂ (Figure 9).

3.4. Fractal Dimensions of T₂ Spectra. According to the International Union of Pure and Applied Chemistry (IUPAC) classification of pore sizes,62 pores of sizes 0–2 nm are defined
as micropores, pores of sizes 2−50 nm are defined as mesopores, and pores larger than 50 nm are defined as macropores. Adsorption in rocks mainly occurs in micropores and mesopores, while macropores are the main channels for gas migration. Therefore, according to the \( T_2 \) curves obtained from NMR tests, \( T_2 = 2.5 \) ms (corresponding to a pore size of 50 nm) is chosen as the demarcation point, and the fractal dimensions of shale adsorption pores and seepage pores are calculated using eq 6.63−66. Figure 10 and Table 4 present the results of the calculations of fractal dimensions. \( D_{N_2} \) obtained from adsorption pores represents the fractal dimension of the pore area, which reflects the roughness and heterogeneity of the surface of shale adsorption pores, and its value is typically between 1 and 2. \( D_{N_2} \) obtained from seepage pores is the fractal dimension of pore volume, which reflects the complexity of the flow channel of shale seepage pores, and its value is typically between 2 and 3. It can be seen from Table 4 that both adsorption pores and seepage pores show a good fitting effect and that the fitting coefficient of adsorption pores is higher than that of seepage pores, indicating that adsorption pores have more fractal characteristics than seepage pores. Figure 11 shows the variation of fractal dimensions of shale pores for different treatment conditions. For adsorption pores, \( D_{N_2} \) increases after treatment with 4 MPa Ar, 16 MPa Ar, and 4 MPa CO\(_2\), and the maximum value appears for the 16 MPa Ar environment, while \( D_{N_2} \) decreases only in the case of treatment with 16 MPa CO\(_2\), indicating that supercritical CO\(_2\) decreases the specific surface area and roughness of adsorption pores, which may weaken the adsorption capacity of shale. For seepage pores, there are no obvious changes in \( D_{N_2} \) after treatment with 4 MPa Ar, 16 MPa Ar, and 4 MPa CO\(_2\). However, after treatment with 16 MPa CO\(_2\), \( D_{N_2} \) decreases significantly, indicating that in a supercritical CO\(_2\) environ-
ment, the complexity of shale seepage pores declines, which is conducive for gas migration.

$$D = \frac{\ln(S_v)}{\ln(T_{2\text{max}}) - \ln(T_2)} + 3$$  \hspace{1cm} (6)

where $D$ represents the fractal dimension of pores; $S_v$ represents the pore volume component occupied in the wetting phase; $T_2$ is the relaxation time, ms; $T_{2\text{max}}$ represents the maximum relaxation time constant, corresponding to the capillary pressure. Besides the NMR method, it is worth pointing out that fractal theory has been effectively applied to natural porous media from different perspectives. Cai and Yu\textsuperscript{67} introduced fractal to modify the classical Lucas–Washburn equation, and the proposed fractal time exponent model presented a theoretical insight to the effect of tortuosity on capillary flow. Xia et al.\textsuperscript{68} employed three fractal structural parameters, fractal dimension, lacunarity and succolarity, to characterize scale-invariant complexity, heterogeneity, and anisotropy of rock microstructures, respectively.

### 3.5. N$_2$ Adsorption–Desorption Isotherms

The N$_2$ adsorption–desorption isotherms of shale samples under different treatment conditions are shown in Figure 12, where the shapes of the isotherms are found to be similar. When the relative pressure $p/p_0$ is in the range of $p/p_0 = 0$–0.45, the adsorption isotherms rise slowly with relative pressure, and the main type of adsorption is the monolayer adsorption of N$_2$, or microporous filling. When $p/p_0$ reaches 0.45, the monolayer adsorption of N$_2$ is considered complete. When $p/p_0$ exceeds 0.45, the adsorption isotherms continue to rise with relative pressure, the slope increases gradually, and the adsorption transforms from monolayer adsorption to multilayer adsorption. Also, when $p/p_0$ is more than 0.45, the isotherms of desorption show hysteresis loops because of capillary condensation. Also, compared with other treatment conditions, the volume of adsorption in shale samples, that is, the adsorption capacity, significantly decreases after treatment with 16 MPa CO$_2$. Figure 13 shows the specific surface area of shale measured by N$_2$ adsorption. It can be seen that the specific

### Table 4. Fractal Dimension of Shale Samples from NMR\textsuperscript{a}

| Treatment Conditions | Region 1 ($T_2 < 2.5$ ms) | Region 2 ($2.5$ ms $\leq T_2 < 100$ ms) |
|----------------------|-------------------------|----------------------------------|
|                      | $D_{\text{NMR}}$       | $R^2$                           | $D_{\text{NMR}}$       | $R^2$                           |
| Untreated            | $y = 1.797x - 1.902$    | 1.203                           | $y = 0.056x - 0.215$   | 2.944                           |
| 4 MPa Ar             | $y = 1.793x - 0.981$    | 1.207                           | $y = 0.046x - 0.178$   | 2.954                           |
| 16 MPa Ar            | $y = 1.718x - 0.905$    | 1.282                           | $y = 0.048x - 2.952$   | 2.952                           |
| 4 MPa CO$_2$         | $y = 1.755x - 1.099$    | 1.245                           | $y = 0.056x - 0.220$   | 2.944                           |
| 16 MPa CO$_2$        | $y = 1.845x - 1.537$    | 1.155                           | $y = 0.091x - 0.353$   | 2.909                           |

\textsuperscript{a}$T_2$ is the transverse relaxation time obtained from the NMR test.

Figure 11. Variation of fractal dimensions of shale pores.

Figure 12. Adsorption and desorption curves of shale specimens under different treatment conditions: (a) 4 MPa Ar; (b) 16 MPa Ar; (c) 4 MPa CO$_2$; and (d) 16 MPa CO$_2$. 

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In a supercritical CO2 environment, changes in the results of N2GA tests and fractal dimensions of T2 spectra both decreased, indicating that when shale is exposed to supercritical CO2, the spec content changed the most, particularly in the proportions of calcite and dolomite in shale, which decreased, after exposure to supercritical CO2; these conditions also resulted in the highest number of microscopic pores, as observed by SEM. The NMR test results revealed that gas pressure caused compression of shale pores. In a gaseous CO2 environment, the effect of CO2 adsorption on shale pores was found to be greater than the effects of gas pressure and dissolution reactions. In a supercritical CO2 environment, changes in the structures of shale pores were mainly controlled by the extraction and dissolution reactions of supercritical CO2. The results of N2GA tests and fractal dimensions of T2 spectra showed that adsorption pores have more fractal characteristics than seepage pores. After treatment with 16 MPa CO2, the fractal dimensions of the adsorption pores and seepage pores both decreased, indicating that when shale is exposed to supercritical CO2, the specific surface area and roughness of the adsorption pores decrease, the adsorption capacity is weakened, and the complexity of the seepage pores declines, which is conducive for gas migration. Therefore, when supercritical CO2 is used to extract shale gas, it reduces the adsorption capacity of shale for CH4 and promotes the conversion of adsorbed gas to free gas, thereby improving shale gas production.

**4. CONCLUSIONS**

To explore the different mechanisms by which supercritical CO2 changes the shale pore structure, this study uses shale specimens from the Sichuan Basin, China, and utilizes several methods such as XRD, SEM, NMR, N2GA, and fractal theory to analyze and compare the changes in shale pore structures under different gases and pressures. An analysis of XRD results showed that almost no changes in shale mineral content occurred after treatment with Ar, while the mineral content changed significantly after treatment with CO2. The mineral content changed the most, particularly in the proportions of calcite and dolomite in shale, which decreased, after exposure to supercritical CO2; these conditions also resulted in the highest number of microscopic pores, as observed by SEM. The NMR test results revealed that gas pressure caused compression of shale pores. In a gaseous CO2 environment, the effect of CO2 adsorption on shale pores was found to be greater than the effects of gas pressure and dissolution reactions. In a supercritical CO2 environment, changes in the structures of shale pores were mainly controlled by the extraction and dissolution reactions of supercritical CO2. The results of N2GA tests and fractal dimensions of T2 spectra showed that adsorption pores have more fractal characteristics than seepage pores. After treatment with 16 MPa CO2, the fractal dimensions of the adsorption pores and seepage pores both decreased, indicating that when shale is exposed to supercritical CO2, the specific surface area and roughness of the adsorption pores decrease, the adsorption capacity is weakened, and the complexity of the seepage pores declines, which is conducive for gas migration. Therefore, when supercritical CO2 is used to extract shale gas, it reduces the adsorption capacity of shale for CH4 and promotes the conversion of adsorbed gas to free gas, thereby improving shale gas production.

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**Notes**

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**NOMENCLATURE**

| Symbol | Description |
|--------|-------------|
| D     | fractal dimension |
| Dv1   | fractal dimension of pore area |
| Dv2   | fractal dimension of pores volume |
| Fr    | the shape factor of the pore |
| Sv    | the pore volume component occupied by the wetting phase |
| R2    | correlation coefficient |
| T2    | transverse relaxation time |
| T2max | maximum relaxation time constant |
| ρ     | relaxation strength of the transverse surface |
| r     | pore size |

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