Swelling of Shales by Supercritical Carbon Dioxide and Its Relationship to Sorption

Xiang Ao,* Zhilin Qi, Zuping Xiang, Zhiqiang Li, Hai Qu,* and Ziyi Wang

1. INTRODUCTION

Because of the economic developments and standard of living improvements, natural gas demand is continuously increasing. Shale gas is considered a promising energy source capable of providing more energy security.2,3 The shale gas is extracted by hydraulic fracturing and horizontal drilling, both of which require large amounts of water, which, in turn, might cause damage, waste water resources, and pollute groundwater.4,5 In addition, because of the high clay content in shale gas formations in China,6 it is almost certain that drilling and hydraulic fracturing will be necessary. A related issue is the need to control swelling strain on clay-rich shale caused by adsorption of water. To avoid these issues, many researchers have focused on anhydrous fracturing,7–10 especially with carbon dioxide as fracturing fluid. Therefore, currently, CO2 injections into the shale formations to enhance the production of shale gas and CO2 sequestration are actively studied.11–15 Analysis of the CO2-induced swelling strain of shale is fundamental to select appropriate methods for methane seepage in shale pores as well as for shale gas diffusion and CO2 storage in shale formations.

A lot of current literature focuses on the swelling strain caused by the gases injected into coal formations or shales. For example, the maximum volumetric strain of Australian coals was 1.7–1.9%.16 The maximum volumetric strain of low-ranked coals caused by CO2 injection was 1.65%. In addition to experimental studies, a lot of works use theoretical modeling to describe CO2-induced swelling in coal.17 Shale expansion caused by other gases was also studied. For example, Chen et al. investigated the swelling strain on shale injected by CH4.18 Despite many articles reporting swelling strains caused by CO2 injections into the matrix, the adsorption of gases co-occurring with their injections was rarely reported.19–22

Typical temperatures and pore pressures of shales with high organic content shale formations are in the 370–550 K and 15–20 MPa ranges. Thus, the state of CO2 injected into shale formations under these conditions is, thus, supercritical. Supercritical gas adsorption on shale was reported previously.23 For example, the excess adsorption on shales was measured by volumetric and gravimetric methods.24 Chareonsuppanimit et al. measured shale adsorption of high-pressurized gas adsorption using the simplified local density model to fit the experimental data.25 Chalmers and Bustin reported that the storage capacity of CO2 in shale reservoirs based on the shale adsorption ability and that CO2 adsorption would reduce its surface energy.26 The tendency of the shale to restore this lost energy would lead to shale swelling,27 which might have severe consequences for CO2 storage or hydraulic fracturing, including shale structure damage, inducing fracture close, porosity, and permeability decrease.28–32 Therefore, the analysis of CO2-induced swelling of shale is fundamental.

This paper reports shale swelling strain caused by the injected CO2 at 0–16 MPa and 35–75 °C, and measurement
of the pressure-induced strain using He. We also show the analysis of the absolute adsorption on shale as well as its relationship with the gas adsorption-induced strain.

2. THEORIES

2.1. CO2 Adsorption by Shale. Among a variety of different models capable to accurately describe CO2 adsorption by porous media, we chose the supercritical Dubinin–Radushkevich (SDR) model

\[ n_{ex}^{n} = n_{max} \exp \left[ -D \ln \left( \frac{\rho_s}{\rho_g} \right)^{2} \right] \]

(1)

where \( n_{ex}^{n} \) is the excess adsorption; \( n_{max} \) is regular and the maximum excess adsorption; \( D \) is a fitting parameter; and \( \rho_s \) and \( \rho_g \) are densities of the adsorbed phase and CO2, respectively.

2.2. Absolute Adsorption. Absolute adsorption \( \left( n_{ab} \right) \) was calculated using the excess adsorption \( \left( n_{ex} \right) \) by the equation shown below:\n
\[ n_{ab} = n_{ex} - \frac{\rho_s}{\rho_a} \]

(2)

where \( \rho_s \) and \( \rho_a \) are the densities of the adsorbed phase and CO2, respectively.

2.3. CO2-Induced Strain. According to the research by Sakurovs, \( \delta_{eff} \) in relation to swelling, the modified SDR model is shown in eq 3

\[ S = S_{max} \exp \left[ -E \ln \left( \frac{\rho_a}{\rho_g} \right)^{2} \right] - k \rho_g \]

(3)

where \( S_{max} \) is the maximum swelling of the shale, \( \rho_a \) and \( \rho_g \) are densities of the adsorbed phase and gas, respectively; \( k \) is a constant related to the solubility of CO2, and \( E \) is a constant depending on adsorption heat and affinity of the gas to the adsorbent. For the swelling data, \( E \) acts as an empirical curve-fitting parameter.

2.4. Density of the Adsorption Phase. Because the density of the adsorbed phase cannot be experimentally obtained, it was assumed to be equal to the density of liquid CO2, which is independent of temperature, pressure, and the adsorbent type. However, in many research, it is incorrect for the adsorbed phase density as a constant. The adsorbed phase density can be determined by fitting adsorption isotherms with models such as the Dubinin–Radushkevich (DR) model. Therefore, we determined the adsorbed phase density from the adsorption isotherms fitted using the DR model.

2.5. Effective Stress. The effective stress was calculated as shown below:\n
\[ \sigma_{eff} = \sigma - \alpha p \]

(4)

where \( \sigma_{eff} \) and \( \sigma \) are the effective and total stresses, respectively; \( p_i \) is pore pressure; and \( \alpha \) is the Biot coefficient, which is specific for a given rock and is typically independent of stress and pore pressure. However, Ma and Zoback reported that the Biot coefficient was dependent on the pore pressure.

3. MATERIALS AND METHODS

3.1. Characteristics of Shale. The subject of this work was shale from an outcrop of the Longmaxi Formation of the lower Silurian near Yibin City, Sichuan Province, in the Sichuan Basin. The total organic carbon content (TOC) and the vitrinite reflectance \( (R_0) \) values (which were equal to 7.88 and 2.85%) were optimal (TOC \( \geq 2\% \), \( 3\% \geq R_0 \geq 1\% \)) for the shale gas occurrence of shale gas. The major phases of the shale, determined using powder X-ray diffraction (XRD) performed by the Siemens D5000 instrument, were quartz (40.2%), calcite (11.7%), and clay (15.1%) (see Table 1). XRD was performed in the 2θ range at 0.02° step and 2 s dwell time.

| mineral name          | content, wt % |
|-----------------------|---------------|
| quartz                | 40.2          |
| clay                  | 15.1          |
| calcite               | 11.7          |
| plagioclase           | 3.8           |
| iron pyrites          | 2.7           |
| barite                | 1.0           |
| K-feldspar            | 0.8           |
| karstenite barite     | 0.41          |
| clay                  | 15.1          |

The shale matrix pores range from micro- to nano-meters and relatively large surface area (SA), which were determined using mercury porosimeter and by recording N\(_2\) adsorption/desorption isotherms at 77 K using a Micromeritics ASAP2020. The SA was calculated at \( P/P_0 \) N\(_2\) pressure equal to 0.14. Pore size distribution was obtained using a Barrett–Joyner–Halenda (BJH) model.

3.2. Experiments. 3.2.1. Shale Samples. Shale samples were collected using a cylindrical core 100 mm long and 50 mm in diameter inserted perpendicular to the shale. Precautions were taken to avoid cracks and external contamination to ensure sample contents and properties to be as close to each other as possible. The sample surfaces were polished using (consequently) 60, 120, 200, 600, 2000, and 3000 mesh sandpaper, after which the samples were rinsed and dried at 110 °C for 24 h. Altogether, 15 samples were used in this study, and every temperature condition used three samples. Because of the CO2 isotherm adsorption curve always using the crushing sample, in this work, sample 1 was crushed to the powder after the test of adsorption-strain. The crushing sample was used to measure the CO2 isotherm adsorption curve at 35 °C (Figure 1).

3.2.2. Experimental Setup and Procedures. We used a high-pressure and high-temperature adsorption deformation setup described by Ao et al. to measure the gas-induced shale strain and the excess CO2 adsorption (see Figure 2).

The measurements were performed using the following steps:

1. Strain gauges were attached to the samples, rinsed with absolute ethanol, using Omega SG496 glue (see Figure 2B).
2. The sample was mounted inside the test cell to determine the void volume (composed of pore volume and free space inside a sample), which was performed using He.

3. The system was then heated to the target temperature using a water bath. The setup was allowed to equilibrate to ensure that the temperature-induced expansion took place. The maximum swelling was assumed to be reached after the strain gauges showed no significant changes, after which the system was evacuated. Prior to the tests, the samples were degassed for 24 h, during which the samples shrank slightly. The adsorption measurements and data processing were conducted as described by Chen et al. The amount of the Gibbs excess adsorption \( \Delta n^{ex} \) was obtained as shown below

\[
\Delta n^{ex} = \frac{1}{m} [V_R (\rho_{R,Fi} - \rho_{R,F}) - V_{void} (\rho_{S,Eq,i} - \rho_{S,Eq,i-1})]
\]

where \( m \) is the sample weight, \( V_R \) is the volume of the reference cell, \( V_{void} \) is the void volume of the system, and \( \rho \) is the density of CO2 (taken from the US National Institute of Standards and Technology Chemistry WebBook) (NIST, 2019). The indices "R", "F", and "Eq" refer to the initial, final, and equilibrium conditions, "i" and "i-1" refer to the corresponding experimental steps, respectively.

4. The tests were performed at 35, 45, 55, 65, and 75 °C using 15 MPa pressure increments and equilibrated for 24 h before each measurement. The strain was recorded simultaneously with CO2 adsorption measurements.

5. For comparison, strain induced by He was measured at 35 °C and 0–16 MPa.

6. The step 3 and step 4 were used to measure the CO2 isotherm adsorption curve using the crushing sample.

4. RESULTS AND DISCUSSION

4.1. CO2 Adsorption Isotherms. For each temperature, the amount of excess adsorbed CO2 was measured in eight pressure intervals: from 0.02 to 2, from 2 to 4, from 4 to 6, from 6 to 8, from 8 to 10, from 10 to 12, from 12 to 14, and from 14 to 16 MPa. The resulting isotherms were then used to calculate an equilibrium adsorption gas content for each pressure and temperature step using eq 5 (Figure 3).

Supercritical adsorption occurs when a gas is adsorbed above its critical temperature. Thus, because our adsorption experiments were performed above the supercritical temperature of CO2, the curves shown in Figure 4 can be considered supercritical adsorption isotherms. The adsorption isotherms belonged to type I. Below the critical CO2 pressure, the amount of excess adsorption increased as CO2 pressure increased. It indicates that the adsorption is a monolayer–molecular layer adsorption. The reaction of solid–fluid and fluid–fluid interfaces is van der Waals force. Therefore, the gas molecules can be adsorbed on the solid and can also be adsorbed on the molecules. In addition, the interaction between the solid surface and the adsorbed molecules is weak, whereas the force between the adsorbed molecules is strong. In the 6–9 MPa range, the bulk density increased as CO2 pressure increased. These changes are equal to changes in the density of the adsorbed phase. Therefore, the maximum excess adsorption is obtained, and thereafter, as the pressure further increases, the adsorption decreases. In addition, it was found that the adsorption amount tends to zero, and the packing density is close to that of the adsorbed phase. The excess CO2 adsorption decreased as temperature increased (see Figure 4). The temperature during the tests was above the

---

2. The sample was mounted inside the test cell to determine the void volume (composed of pore volume and free space inside a sample), which was performed using He.

3. The system was then heated to the target temperature using a water bath. The setup was allowed to equilibrate to ensure that the temperature-induced expansion took place. The maximum swelling was assumed to be reached after the strain gauges showed no significant changes, after which the system was evacuated. Prior to the tests, the samples were degassed for 24 h, during which the samples shrank slightly. The adsorption measurements and data processing were conducted as described by Chen et al. The amount of the Gibbs excess adsorption \( \Delta n^{ex} \) was obtained as shown below

\[
\Delta n^{ex} = \frac{1}{m} [V_R (\rho_{R,Fi} - \rho_{R,F}) - V_{void} (\rho_{S,Eq,i} - \rho_{S,Eq,i-1})]
\]

where \( m \) is the sample weight, \( V_R \) is the volume of the reference cell, \( V_{void} \) is the void volume of the system, and \( \rho \) is the density of CO2 (taken from the US National Institute of Standards and Technology Chemistry WebBook) (NIST, 2019). The indices "R", "F", and "Eq" refer to the initial, final, and equilibrium conditions, "i" and "i-1" refer to the corresponding experimental steps, respectively.

4. The tests were performed at 35, 45, 55, 65, and 75 °C using 15 MPa pressure increments and equilibrated for 24 h before each measurement. The strain was recorded simultaneously with CO2 adsorption measurements.

5. For comparison, strain induced by He was measured at 35 °C and 0–16 MPa.

6. The step 3 and step 4 were used to measure the CO2 isotherm adsorption curve using the crushing sample.

4. RESULTS AND DISCUSSION

4.1. CO2 Adsorption Isotherms. For each temperature, the amount of excess adsorbed CO2 was measured in eight pressure intervals: from 0.02 to 2, from 2 to 4, from 4 to 6, from 6 to 8, from 8 to 10, from 10 to 12, from 12 to 14, and from 14 to 16 MPa. The resulting isotherms were then used to calculate an equilibrium adsorption gas content for each pressure and temperature step using eq 5 (Figure 3).

Supercritical adsorption occurs when a gas is adsorbed above its critical temperature. Thus, because our adsorption experiments were performed above the supercritical temperature of CO2, the curves shown in Figure 4 can be considered supercritical adsorption isotherms. The adsorption isotherms belonged to type I. Below the critical CO2 pressure, the amount of excess adsorption increased as CO2 pressure increased. It indicates that the adsorption is a monolayer–molecular layer adsorption. The reaction of solid–fluid and fluid–fluid interfaces is van der Waals force. Therefore, the gas molecules can be adsorbed on the solid and can also be adsorbed on the molecules. In addition, the interaction between the solid surface and the adsorbed molecules is weak, whereas the force between the adsorbed molecules is strong. In the 6–9 MPa range, the bulk density increased as CO2 pressure increased. These changes are equal to changes in the density of the adsorbed phase. Therefore, the maximum excess adsorption is obtained, and thereafter, as the pressure further increases, the adsorption decreases. In addition, it was found that the adsorption amount tends to zero, and the packing density is close to that of the adsorbed phase. The excess CO2 adsorption decreased as temperature increased (see Figure 4). The temperature during the tests was above the
CO₂ critical temperature (which is equal to 31.13 °C), especially for the tests performed at 65 and 75 °C.

Because of the CO₂ isotherm adsorption curve always using the crushing sample, in this work, we compare the isotherm adsorption curves of the plunger sample and crush sample. From the Figure 5, the average standard deviation of the isotherm adsorption curve tested by the crushing sample and plunger was equal to 19.8% and the correlation coefficient was equal to 0.91. According to the research by Pan et al., the sample sized 21 mm × 21 mm × 21 mm was determined the diffusive of shale. The result showed that the amount of gas into the shale approaches 80% at 100 min. It is indicated that most of the gas can enter the shale within a day. It indicates that gas diffusion into the shale through the plunger sample and crush sample has no obvious difference. To sum up, we believe that using the plunger sample to determine the adsorption and strain at the same time is reliable (Table 2).

Error analysis for the data shown in Figure 6 was necessary because even though the sample contents and properties were close to each other, they were not identical. The average values...
obtained using eq 1 at pressures equal to 2, 4, 6, 8, 10, 12, 14, and 16 MPa, and their corresponding errors are shown in Figure 6. The corresponding fitting parameters are listed in Table 3. The standard deviations were equal to 6.62, 3.71, 2.90, 4.27, and 5.19% for the data collected at 35, 45, 55, 65, and 75 °C, respectively. Relatively low experimental errors confirmed the similarity between our shale samples as well as experimental data reliability. Therefore, only one test was performed at rest conditions.

The maximum amounts of adsorbed CO2 were obtained at similar density values, which were equal to 361 kg/m3 at 7.88 MPa and 35 °C, 349 kg/m3 at 9.08 MPa and 45 °C, 327 kg/m3 at 10.02 MPa and 55 °C, 304 kg/m3 at 10.71 MPa and 65 °C, and 295 kg/m3 at 11.49 MPa and 75 °C (see Figure 6). These results demonstrate that bulk CO2 density is the most significant variable during CO2 adsorption at high pressure.

The adsorbed phase density values, calculated using the SDR model, shown in Table 3, were used to calculate CO2 absolute adsorption using eq 2. The results, shown in Figure 7, indicated that the CO2 uptake increased significantly as CO2 pressure was increased (below the critical CO2 pressure). However, the adsorption rate decreased as CO2 pressure was increased (see Figure 7).

### 4.2. CO2-Induced Strain

Positive strain values were used to represent swelling. Prior to each strain test, the system was allowed to reach thermal equilibrium at the target temperature, based on heating in the water bath, ensuring that any temperature-induced expansion took place. Thus, the strain observed in our shale samples at different temperatures was caused by gas behavior. The experimental data were recalculated using eq 3, and the average values (calculated

![Figure 5](image_url)  
**Figure 5.** CO2 isotherm adsorption curve at 35 °C using the plunger sample and crush sample.

![Figure 6](image_url)  
**Figure 6.** Excess CO2 adsorption by the shale sample as a function of the CO2 density and temperature.

![Figure 7](image_url)  
**Figure 7.** Total CO2 adsorbed at different temperatures as a function of CO2 pressure.

### Table 2. Mesopore and Micropore Characteristics of the Shale Samples

| sample | BET SA, m²/g | Langmuir SA, m²/g | BJH SA, m²/g | BJH volume, m³/g | average mesopore size, nm |
|--------|--------------|-------------------|--------------|-----------------|--------------------------|
| 1      | 18.3         | 25.2              | 10.0         | 0.016           | 6.2                      |
| 2      | 17.0         | 23.9              | 9.8          | 0.016           | 6.4                      |
| 3      | 18.4         | 26.3              | 10.0         | 0.015           | 6.0                      |
| 4      | 17.3         | 24.9              | 9.4          | 0.016           | 6.2                      |
| 5      | 3.38         | 3.41              | 2.40         | 2.49            | 2.27                     |

### Table 3. Experimental Data-Fitting Parameters Obtained Using the DR Model

| sample | $n_{max}$ | $D$ | $\rho_a$ | $R^2$ |
|--------|-----------|-----|----------|-------|
|        | date      | average | date | average | date | average |       |
| 35 °C  | 1         | 2.71  | 2.51    | 0.126 | 0.109 | 1460.25 | 1527.77 | 0.95  |
| 2      | 2.26      | 0.104 | 1541.24 |       |       |         |         | 0.93  |
| 3      | 2.57      | 0.097 | 1581.80 |       |       |         |         | 0.94  |
| 45 °C  | 4         | 2.26  | 2.38    | 0.097 | 0.103 | 1584.22 | 1513.20 | 0.99  |
| 5      | 2.37      | 0.110 | 1456.77 |       |       |         |         | 0.97  |
| 6      | 2.50      | 0.101 | 1498.62 |       |       |         |         | 0.98  |
| 55 °C  | 7         | 2.16  | 2.32    | 0.098 | 0.105 | 1489.06 | 1409.17 | 0.99  |
| 8      | 2.37      | 0.103 | 1389.82 |       |       |         |         | 0.98  |
| 9      | 2.44      | 0.114 | 1348.62 |       |       |         |         | 0.99  |
| 65 °C  | 10        | 2.17  | 2.25    | 0.105 | 0.102 | 1321.32 | 1330.85 | 0.99  |
| 11     | 2.37      | 0.098 | 1347.73 |       |       |         |         | 0.98  |
| 12     | 2.22      | 0.101 | 1323.50 |       |       |         |         | 0.97  |
| 75 °C  | 13        | 2.16  | 2.25    | 0.110 | 0.104 | 1229.50 | 1275.39 | 0.98  |
| 14     | 2.37      | 0.100 | 1268.63 |       |       |         |         | 0.98  |
| 15     | 2.21      | 0.103 | 1328.03 |       |       |         |         | 0.97  |
based on the results for four samples) were plotted as a function of the pressure (see Figure 8). The relative standard deviations of the data points were 7.19, 4.07, 3.77, 5.11, and 5.76% at 35, 45, 55, 65, and 75 °C, respectively. Relatively small deviations indicate minimum variations among samples and reliability of the experimental data. Therefore, only one test was performed at rest conditions (Figure 9).

![Figure 8](image1.png)  
**Figure 8.** Volumetric strain the shale samples upon CO2 injection as a function of CO2 pressure and temperature.

![Figure 9](image2.png)  
**Figure 9.** Volumetric swelling of the shale samples induced by CO2 injection at different temperatures.

The shale samples became swollen as the CO2 pressure increased. The change in surface potential energy of the shale upon CO2 adsorption was equal to the elastic energy variation.51 The swelling strain of the samples increased as the CO2 pressure increased (at values below the critical pressure) because of the increased amounts of adsorbed CO2 (see Figure 4). The adsorption capacity reached its maximum level at this period. The maximum strain values at 35, 45, 55, 65, and 75 °C were 1.55, 1.29, 1.22, 1.08, and 1.03 ‰, respectively. Because of the adsorption ability decrease, the maximum swelling of the shale gradually decreased as the CO2 temperature was increased.

However, as the CO2 pressure was increased, the shale swelling decreased in two regions. In one instance, as the pressure was increased, the shale adsorption capacity decreased (see Figure 7), and as a result, CO2-induced swelling decreased. In addition, gradually increased CO2 pressure increased the effective stress. At 16 MPa, the strain values at 35, 45, 55, 65, and 75 °C were equal to 1.28, 1.19, 1.08, 1.03, and 0.91 ‰, respectively. These strain values correspond to 82.2, 92.5, 88.9, 95.65, and 88.4% of the maximum swelling, respectively. These results agree to those reported by Pan and Connell,19 who also reported sample shrinkage decrease as the gas pressure increased.

The maximum swelling strain decreased as the temperature was increased, which can be explained by two phenomena. First is sample swelling strain dependence on its adsorption ability. At the highest adsorbed CO2 amount, the maximum strain resulting from adsorption at high temperatures was lower than at low temperatures (see Figure 7). Second is similar values of the confinement pressures on the shale samples at high and low temperatures. The gas pressure- and adsorption-induced strains are discussed in Sections 4.4 and 4.3, respectively.

4.3. Gas Pressure-Induced Strain. Figure 10 shows the average values of the linear strain induced by He injection for the three shale samples as well as the error bars. The relative standard deviations of the perpendicular and parallel data were 7.5 and 9.6%, respectively, indicating the high reliability of the data. Because helium has no adsorption ability, there is no creep without deviator stress.52 Thus, the measured deformation was caused only by the pressure caused by the injected He gas.

![Figure 10](image3.png)  
**Figure 10.** Strain induced by gas injected at different pressures.

The shale samples exhibited compressive deformation affected by the gas pressure (Figure 10). Below 8 MPa, compressive strain increased linearly with pressure. At the same time, a significant shrink strain nonlinear increase was also observed. According to Ma and Zoback,42 the Biot coefficient does not significantly increase at low pore pressure. As the pore pressure increases, the Biot coefficient decreases. Thus, as He pressure increased, the effective stress would also increase linearly at low pressure, whereas at high pressures, the stress would increase nonlinearly. Experimental data fitting showed a linear relationship between the gas pressure and the linear strain of the shale. The perpendicular and parallel strain slopes were 0.02465 and 0.0172, respectively (see Figure 10). By comparing the Hooke equation to the fitting curve,53 one can see that the slope is inversely proportional to the shale bulk modulus. The vertical and radial elastic moduli obtained from the fitting were equal to 40 and 58 GPa, respectively.

4.4. Strain Caused by Gas Adsorption. A model used to describe coal formation swelling showed that the strain was proportional to the amount of CO2 absorbed by coal.19 The shale strain caused by CO2 injection ($\varepsilon_p$) and the adsorption-induced swelling ($\varepsilon_a$) effects

$$
\varepsilon = \varepsilon_p + \varepsilon_a
$$

(6)

The swelling strain caused by the adsorption increased with pressure (see Figure 11). Adsorption-induced strain was similar to the strain induced by CO2 injection in the 0–4
CO₂ was slowly adsorbed, and the sample volume increased as the surface layer thickness increased during CO₂ penetration into the pores and cracks. In this region, the pressure effect on the shale strain was not noticeable. The ratio between the adsorption-induced strain and CO₂-induced strain was equal to 1.27 ‰ at 2 MPa. However, the difference between the adsorption-induced strain and the CO₂-induced strain was evident as the pressure was increased. In this region, the strain effect caused by pressure was visible, and the ratio between the average strain caused by gas adsorption and CO₂-induced strain was 1.79 ‰ at 16 MPa.

Additionally, at higher pressures, the CO₂-induced strain became negative because of the pressure effect, which agrees with the results shown by Pan and Connell19 using the coal (Tables 4 and 5).

To assess practical applications of this approach, we plotted volumetric strain data as a function of the amount of adsorbed CO₂ (see Figure 12). According to the results shown by Day et al.,22 the volumetric strain caused by adsorption in coal linearly correlated with the amount of adsorbed gas. Therefore, we also fitted our data using linear approximation (see Figure 12).

The volumetric strain caused by the shale adsorption of CO₂ indeed linearly correlated with the amount of adsorbed CO₂ (see Figure 12). However, the correlation coefficients for the data collected at 35 and 55 °C were somewhat low (0.80 and 0.94, respectively), which might indicate that the strain and CO₂ adsorption amounts might not be in a linear relationship at these temperatures. The first explanation is that the value of the adsorbed phase density was constant and independent of the temperature. However, in some cases, the test temperature was above the critical temperature of CO₂; thus, the liquid CO₂ could not evaporate. Thus, if the density of the adsorbed phase was different at different pressures and temperatures, at this time, it cannot be taken into account because of insufficient data currently available. The second explanation is that even though different shale samples showed similar pressure-induced strain data, the samples might still have different mechanical properties.

### 5. CONCLUSIONS

Strains of shale samples collected from the Longmaxi Formation of lower Silurian in Yibin City, Sichuan Province, in the Sichuan Basin were studied. The adsorption capacities of shale samples, as well as their CO₂-induced swelling and He-

### Table 4. Parameters Obtained Using the SDR Fitting Model

| temperature (°C) | test number | data | average | data | average | data | average | R² |
|------------------|-------------|------|---------|------|---------|------|---------|----|
| 35 °C            | 1           | 2.21 | 2.00    | 0.056| 0.055   | 1.27×10⁻⁵| 0.000867| 0.99|
|                  | 2           | 2.02 |         | 0.046|         | 8.52×10⁻⁴|         | 0.99|
|                  | 3           | 1.78 |         | 0.064|         | 4.79×10⁻⁴|         | 0.98|
| 45 °C            | 4           | 1.63 | 1.63    | 0.074| 0.078   | 5.99×10⁻³| 7.45×10⁻⁵| 0.98|
|                  | 5           | 1.50 |         | 0.077|         | 6.49×10⁻³|         | 0.98|
|                  | 6           | 1.78 |         | 0.083|         | 9.88×10⁻³|         | 0.97|
| 55 °C            | 7           | 1.54 | 1.63    | 0.082| 0.084   | 1.04×10⁻⁴| 0.000107| 0.98|
|                  | 8           | 1.66 |         | 0.080|         | 1.09×10⁻⁴|         | 0.98|
|                  | 9           | 1.68 |         | 0.090|         | 1.08×10⁻⁴|         | 0.98|
| 65 °C            | 10          | 1.21 | 1.38    | 0.075| 0.077   | 2.14×10⁻⁴| 0.000142| 0.98|
|                  | 11          | 1.53 |         | 0.082|         | 1.11×10⁻⁴|         | 0.99|
|                  | 12          | 1.41 |         | 0.075|         | 9.99×10⁻⁵|         | 0.99|
| 75 °C            | 13          | 1.40 | 1.73    | 0.101| 0.123   | 2.78×10⁻⁴| 0.000268| 0.99|
|                  | 14          | 2.39 |         | 0.177|         | 3.88×10⁻⁴|         | 0.99|
|                  | 15          | 1.41 |         | 0.090|         | 1.38×10⁻⁴|         | 0.06|

### Figure 12. Adsorption-induced shale strain as a function of the adsorbed gas. Data points represent the test data, while the curves represent the fitting.
induced strain, were analyzed at 35–75 °C and 0–16 MPa. The following conclusions were made based on the experimental results collected in this work:

1. The maximum excess adsorption at different temperatures correlated with the bulk phase density: as the CO₂ temperature increased, the density of the maximum adsorption of CO₂ excess decreased.

2. The density of the adsorbed phase was obtained by fitting the excess CO₂ adsorption data by the DR model.

3. At low pressure, the shale strain caused by injected CO₂ was mostly related to the adsorbed CO₂, whereas at high CO₂ pressures, the shale strain was caused by CO₂ pressure.

4. The amount of uptake adsorbed CO₂ linearly correlated with the adsorption-induced strain.

## REFERENCES

(1) Khan, S.; Peng, Z.; Li, Y. Energy consumption, environmental degradation, economic growth and financial development in globe: Dynamic simultaneous equations panel analysis. Energy Rep. 2019, 5, 1089–1102.

(2) Cooper, J.; Stamford, L.; Azapagic, A. Economic viability of UK shale gas and potential impacts on the energy market up to 2030. Appl. Energy 2018, 215, 577–590.

(3) Mewawala, C.; Jiang, Y.; Bhattacharyya, D. Techno-economic optimization of shale gas to dimethyl ether production processes via direct and indirect synthesis routes. Appl. Energy 2019, 238, 119–134.

(4) Myers, T. Potential Contaminant Pathways from Hydraulically Fractured Shale to Aquifers. Groundwater 2012, 50, 872–882.

(5) Buono, R. M.; Mayor, B.; López-Gunn, E. A comparative study of water-related issues in the context of hydraulic fracturing in Texas and Spain. Environ. Sci. Pol. 2018, 90, 193–202.

(6) Wang, Y.; Dong, D. Z.; Li, J.; Wang, S. Reservoir characteristics of shale gas in Longmaxi Formation of the Lower Silurian, southern Sichuan. Acta Pet. Sin. 2012, 33, 551–561.

(7) Zhang, L.; Wang, Y.; Miao, X.; Gan, M.; Li, X. Geochemistry in geologic CO₂ utilization and storage: A brief review. Adv. Geo-Energy Res. 2019, 3, 304–313.

(8) Liu, F.; Ellett, K.; Xiao, Y.; Rupp, J. A. Assessing the feasibility of CO₂ storage in the New Albany Shale (Devonian-Mississippian) with potential enhanced gas recovery using reservoir simulation. Int. J. Greenhouse Gas Control 2013, 17, 111–126.

(9) Mohagheghian, E.; Hassanzadeh, H.; Chen, Z. CO₂ sequestration coupled with enhanced gas recovery in shale gas reservoirs. J. CO₂ Util. 2019, 34, 646–655.

(10) Zhang, X.; Lu, Y.; Tang, J.; Zhou, Z.; Liao, Y. Experimental study on fracture initiation and propagation in shale gas using supercritical carbon dioxide fracturing. Fuel 2017, 190, 370–378.

(11) Huang, J. W.; Jin, T. Y.; Barrufet, M.; Killoough, J. Evaluation of CO₂ injection into shale gas reservoirs considering dispersed distribution of kergen. Appl. Energy 2020, 260, 114–285.

(12) Yan, F.; Xu, J.; Peng, S.; Zou, Q.; Li, Q.; Long, K.; Zhao, Z. Effect of capacitance on physicochemical evolution characteristics of bituminous coal treated by high-voltage electric pulses. Powder Technol. 2020, 367, 47–55.

(13) Yan, F.; Xu, J.; Peng, S.; Zou, Q.; Zhou, B.; Long, K.; Zhao, Z. Breakdown process and fragmentation characteristics of anthracite subjected to high-voltage electrical pulses treatment. Fuel 2020, 275, 1179296.

(14) Liu, Y.; Zhang, J.; Wei, J.; Liu, X. Optimum structure of a Laval nozzle for an abrasive air jet based on nozzle pressure ratio. Powder Technol. 2020, 364, 343–362.

(15) Ranjit, P. G.; Liu, Y.; Wei, J.; Liu, X. Effect of abrasive mass flow on the abrasive acceleration and erosion rates of abrasive gas jets. Rock Mech. 2019, 52, 3085–3102.

(16) Day, S.; Fry, R.; Sakurovs, R. Swelling of Australian coals in supercritical CO₂. Int. J. Coal Geol. 2008, 74, 41–52.

(17) Anggara, F.; Kyuro, S.; Sandra, R.; Sugai, Y. The effect of megascoposic texture on swelling of a low rank coal in supercritical carbon dioxide. Int. J. Coal Geol. 2014, 125, 45–56.

(18) Chen, T.; Peng, X. T.; Pan, Z. J. Experimental study of swelling of organic rich shale in methane. Int. J. Coal Geol. 2005, 59, 64–73.

(19) Pan, Z.; Connell, L. D. A theoretical model for gas adsorption-induced coal swelling. Int. J. Coal Geol. 2007, 69, 243–252.

(20) Pan, Z.; Connell, L. D. Modelling permeability for coal reservoirs: A review of analytical models and testing data. Int. J. Coal Geol. 2012, 92, 1–44.

(21) Charoeosuppanimit, P.; Sayeed, A. M.; Robert, L. High-pressure adsorption of gases on shales: measurements and modeling. Int. J. Coal Geol. 2012, 95, 34–46.

(22) Day, S.; Fry, R.; Sakurovs, R.; Weir, S. Swelling of coals by supercritical gases and its relationship to sorption. Energy Fuels 2010, 24, 2777–2783.
(23) Ao, X.; Lu, Y.; Tang, J.; Chen, Y.; Li, H. Investigation on the physics structure and chemical properties of the shale treated by supercritical CO₂. J. CO₂ Util. 2017, 20, 274–281.

(24) Zhou, S.; Ning, Y.; Wang, H.; Liu, H.; Xue, H. Investigation of methane adsorption mechanism on Longmaxi shale by combining the micropore filling and monolayer coverage theories. Adv. Geo-Energy Rev. 2018, 2, 269–281.

(25) Chareonsuppanimit, P.; Mohammad, S. A.; Robinson, R. L.; Jr.; Gasem, K. A. M. High-pressure adsorption of gases on shales: Measurements and modeling. Int. J. Coal Geol. 2012, 95, 34–46.

(26) Chalmers, G. R.; Bustin, R. M. The organic matter distribution and methane capacity of the Lower Cretaceous strata of Northeastern British Columbia, Canada. Int. J. Coal Geol. 2007, 70, 223–239.

(27) Scherer, G. W. Dilatation of Porous Glass. J. Am. Ceram. Soc. 1986, 69, 473–480.

(28) Busch, A.; Alles, S.; Gensterblum, Y.; Prinz, D.; Dewhurst, D.; Raven, M.; Stanjek, H.; Krooss, B. Carbon dioxide storage potential of shales. Int. J. Greenhouse Gas Control 2008, 2, 297–308.

(29) Kumar, H.; Elewther, D.; Marone, C. J. Permeability evolution of shale and coal under differential sorption of He, CH₄ and CO₂. Presented at the 2010 Fall Meeting of the American Geophysical Union, 2010.

(30) Lahann, R.; Maria, M.; Rupp, J.; Agnieszka, D. Influence of CO₂ on New Albany Shale composition and pore structure. Int. J. Coal Geol. 2011, 108, 2–9.

(31) Dai, X.; Wang, M.; Wei, C.; Zhang, J.; Wang, X.; Zou, M. Factors affecting shale microscopic pore structure variation during interaction with supercritical CO₂. J. CO₂ Util. 2020, 38, 194–211.

(32) Shi, X.; Jiang, S.; Wang, Z.; Bai, B.; Xiao, D.; Tang, M. Application of nanoindentation technology for characterizing the mechanical properties of shale before and after supercritical CO₂ fluid treatment. J. CO₂ Util. 2020, 37, 158–172.

(33) Reiser, T. F. T.; Benham, M. J.; Aplin, A. C.; Thomas, K. M. Methane adsorption on shale under simulated geological temperature and pressure conditions. Energy Fuels 2013, 27, 3099–3109.

(34) Bi, H.; Jiang, Z.; Li, J.; Li, P.; Chen, L.; Pan, Q.; Wu, Y. The Ono-Kondo model and an experimental study on supercritical adsorption of shale gas: a case study on Longmaxi shale in southeastern Chongqing, China. J. Nat. Gas Sci. Eng. 2016, 35, 114–121.

(35) Sakurovs, R.; Day, S.; Weir, S.; Duffy, G. Application of a Modified Dubinin–Radushkevich Equation to Adsorption of Gases by Coals under Supercritical Conditions. Energy Fuels 2007, 21, 992–997.

(36) Day, S.; Sakurovs, R.; Weir, S. Supercritical gas sorption on moist coals. Int. J. Coal Geol. 2008, 74, 203–214.

(37) Zhou, S.; Xue, H. Q.; Ning, Y.; Guo, W.; Zhang, Q. Experimental study of supercritical methane adsorption in Longmaxi shale: Insights into the density of adsorbed methane. Fuel 2008, 211, 140–148.

(38) Terasaki, K.; Peck, R. B.; Mesarig, G. Soil mechanics in engineering practice, 3rd ed.; John Wiley & Sons: New York, 1996

(39) Nur, A.; Byerlee, J. D. An exact effective stress law for elastic deformation of rock with fluids. J. Geophys. Res. 1971, 76, 6414–6419.

(40) Warpsinski, N. R.; Teufel, L. W. Determination of the effective stress law for permeability and deformation in low-permeability rocks. SPE Formation Evaluation, 1992. No. 20572, pp 123–131.

(41) Franquet, J. A.; Abass, H. H. Experimental evaluation of Biot’s poroelastic parameter—three different methods. Rock Mechanics for Industry: Proceedings of the 37th U.S. Symposium on Rock Mechanics; Balkema: Rotterdam, 1999.

(42) Ma, X. D.; Zoback, M. D. Laboratory investigation on effective stress in Middle Bakken: implications on poroelastic stress changes due to depletion and injection. 50th U.S. Rock Mechanics Geomechanics Symposium; ARMA Houston Conference: USA Texas, 2016.

(43) Zhang, W.; Guo, M.; Jiang, Z. Parameters and Method for Shale Gas Reservoir Evaluation. Nat. Gas Geosci. 2011, 22, 1093–1099.