Study of CO₂ Enhancing Shale Gas Recovery Based on Competitive Adsorption Theory

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ABSTRACT: As an indispensable part of unconventional natural gas resources, the shale reservoir is huge and widely distributed. It is of great significance to study how to enhance the shale gas recovery for improving the energy structure. In order to solve the problem of low gas production rate and long recovery period in the process of shale gas production, in this paper, the influences of pressure, temperature, moisture, and gas type on isothermal adsorption and desorption of shale gas are analyzed based on shale adsorption and desorption experiments, and the adsorption and desorption abilities of CO₂ and CH₄ in shale are compared to verify the feasibility of CO₂ enhancing shale gas recovery. Depletion production experiments and CO₂ injection experiments with different injection pressures (6 and 7 MPa), different injection rates (5, 10 and 20 mL/min), and different injection amounts are carried out. The mechanism of CO₂ enhancing shale gas recovery is proposed, and the parameters of CO₂ injection are optimized. The results show that the adsorption capacity of CH₄ increases with the increase in pressure and the decrease in temperature and moisture in a certain range. Under the same experimental conditions, the sorting of adsorption capacity is CO₂ > CH₄ > N₂, while desorption capacity is CH₄ > CO₂ > N₂. The desorption curves of the three gases lag behind the adsorption curves, in which the lag phenomenon of CO₂ is most obvious. The ultimate recovery of depletion production ranges from 66 to 73%. CO₂ injection can effectively increase the gas production rate of CH₄, and it can also keep the cumulative gas production of CH₄ growing steadily and rapidly. Within a certain range, CH₄ recovery increases with the increase in CO₂ injection pressure, the injection rate, and injection amount, but its increase range is related to the porosity and permeability of shale.

1. INTRODUCTION

Shale gas is a relatively friendly fuel compared with other fossil fuels, which has played an important role in natural gas exploration and development. Because of its extensive distribution and massive reserve in the world, shale gas has a great potential in energy supply.¹ In recent years, the development of advanced horizontal well techniques and hydraulic fracturing technology has enabled some countries to economically exploit shale gas.²,³ The United States is the first country to commercially develop shale gas, and its annual shale gas production is about 1.0 Tcf from over 40,000 shale gas wells in five primary basins,⁴ which helps America improve its energy security and depresses the natural gas prices. In the recent few years, Canada and China have also made breakthroughs in the development of shale gas,⁵–⁸ and many other nations are also pursuing the opportunity to develop shale gas.

It is known that gas shale has ultralow permeability and porosity compared with the conventional sandstone formations, which makes the flow of gas very difficult and complex⁹,¹⁰. The high production of shale gas wells heavily depends on stimulating technologies, such as horizontal wells and multistage hydraulic fracturing treatments. However, the production rate of a single shale gas well usually drops rapidly after a peak.¹¹ After reaching a certain level, the production declines slowly, and the single well produces for a few decades.¹² There is a lot of free gas stored in the fracture space after the shale hydraulically fractures, and it will form a gas flow stream with high velocity, causing a peak in the production curve. However, the gas amount in the hydraulic fracture is limited, and the production will decrease quickly when the free gas is produced. Then, the absorbed gas begins to desorb slowly and stably when the pressure declines. The practice has proved that the recovery of shale gas reservoirs is usually lower than that of the conventional natural gas reservoirs. For example, a recovery factor of 30% for Haynesville Shale in Louisiana is considered a relatively high level. There is still a
great amount of shale stored in the reservoir after depletion production.\textsuperscript{13}

As to the low recovery of shale gas reservoirs, CO\textsubscript{2} injection has a high possibility to enhance gas recovery from the experience of enhancing oil recovery by injecting CO\textsubscript{2}.\textsuperscript{14} Busch and Gensterblum et al. have proved that it is feasible to enhance coal bed methane recovery by injecting CO\textsubscript{2}.\textsuperscript{15–18} The physical properties of shale and coal display similar characteristics (naturally occurring carbonaceous organic-rich porous materials), and the shale reservoir is akin to coalbed with a distinct gas trapping mechanism of physical adsorption.\textsuperscript{19,20} Therefore, enhanced shale gas recovery (ESGR) by injecting CO\textsubscript{2} should be a possible way.

CO\textsubscript{2} is the main greenhouse gas, and CO\textsubscript{2} emission has continued to increase over the past few years. One way of solving the problem is the geologic storage of CO\textsubscript{2} in gas shale.\textsuperscript{21,22} There are three advantages for ideal CO\textsubscript{2} storage in gas shale: (1) CO\textsubscript{2} can enhance the recovery of shale gas; (2) the storage capacity is huge; (3) there is no leak of CO\textsubscript{2}. Gas shale contains a lot of nanopores, and it can adsorb CO\textsubscript{2} strongly, which is propitious to CO\textsubscript{2} storage.

It has been proved that gas shale has a stronger affinity to CO\textsubscript{2} than to CH\textsubscript{4} which means the gas shale will absorb more CO\textsubscript{2} when they exist at the same time. Many studies about CO\textsubscript{2} injection to enhance shale gas recovery have been performed by numerical simulations and experimental studies. Khan et al.\textsuperscript{26} studied the feasibility and economic benefits of shale gas produced by CO\textsubscript{2} based on numerical simulation. Moinfar et al.\textsuperscript{27} established a complex fracture model to simulate the improvement of shale gas recovery by injecting CO\textsubscript{2}. Kim et al.\textsuperscript{28} concluded that compared with the no-injection scenario, CO\textsubscript{2} flooding, and CO\textsubscript{2} huff and puff flooding increase CH\textsubscript{4} production by 24 and 6\%, respectively. Moreover, at the end of mining, the injected CO\textsubscript{2} can be stored in the shale. Liu et al.\textsuperscript{29} presented a novel methodology based on nuclear magnetic resonance (NMR). It can be used to measure the enhanced gas recovery (EGR) efficiency caused by CO\textsubscript{2} injection. Sun et al.\textsuperscript{30} have proved that CO\textsubscript{2} sequestration with enhanced natural gas recovery can achieve CO\textsubscript{2} sequestration and enhance CH\textsubscript{4} recovery in shale gas reservoirs, and the injection pressure has a huge impact on CO\textsubscript{2} storage and natural gas production rate. Li and Elsworth\textsuperscript{31} have proved that injecting CO\textsubscript{2} into shale gas reservoirs is beneficial to increase the permeability of fracture. Bacon et al.\textsuperscript{32} developed simulations of methane production and supercritical carbon dioxide injection, and they found that CH\textsubscript{4} desorption from clays is greater than that from organic matter after injecting CO\textsubscript{2}. Liu et al.\textsuperscript{33} have proved that CO\textsubscript{2} storage in shale reservoirs is feasible; over 95\% of the injected CO\textsubscript{2} is effectively sequestered instantaneously, with gas adsorption being the dominant storage mechanism. Sang et al.\textsuperscript{34} have proved that pressure is an important factor affecting the ultimate recovery of shale gas, and a pressure depletion scheme can affect the process of gas production in shale deeply.

However, the optimal injection parameters and the underlying mechanisms of enhanced CH\textsubscript{4} recovery by injecting CO\textsubscript{2} are still not well-understood. Therefore, it is meaningful to perform an experimental investigation to analyze the behaviors and mechanisms of ESGR by CO\textsubscript{2} injection. In this study, the influence of pressure, temperature, moisture, and gas type on isothermal adsorption and desorption of shale gas is analyzed based on shale adsorption and desorption experiments, and the adsorption and desorption abilities of CO\textsubscript{2} and CH\textsubscript{4} in shale are compared. The ultimate recovery of depletion production and CO\textsubscript{2} injection production are compared, and the feasibility of CO\textsubscript{2} enhancing shale gas recovery is proved. The mechanism of CO\textsubscript{2} enhancing shale gas recovery is studied, and the optimal CO\textsubscript{2} injection parameters are investigated. The research results lay a solid foundation for a better understanding of the CO\textsubscript{2} displacement process and provide a guide for optimizing the designs of CO\textsubscript{2} injection composition and injection strategy in field applications.

2. RESULTS AND DISCUSSION

2.1. Isothermal Adsorption and Desorption. 2.1.1. Effect of Temperature and Pressure. The CH\textsubscript{4} amount adsorbed and desorption amount is measured with different temperatures and pressures. The results are shown in Figure 1.

According to Figure 1, it is obvious that CH\textsubscript{4} adsorption capacity on the samples is affected by temperature and pressure, and the adsorption amount increases with increasing pressure and decreases with increasing temperature. The adsorption amount of three core samples is different at the same temperature and pressure, and the adsorption capacity of SK\textsubscript{1} is strongest and that of SK\textsubscript{3} is weakest. The reason for this is that the total organic content (TOC) of SK\textsubscript{1} is the highest, which indicates that the adsorption capacity has a positive relationship with the TOC. Furthermore, the adsorption isotherm and desorption isotherm are not coincident, and there is a misalignment hoop between the two curves. The hoop is caused by many factors, including the deformation of the micropores in the samples, the gas condensate, or phase transition. The hysteresis of desorption means that the recoverable reserves are lower than the theoretical reserves.

2.1.2. Effect of Moisture. The powder of sample SK\textsubscript{1} is used in the study of moisture. The content of water for the four powder samples is 0, 1.51, 3.42, and 5.78\%, respectively. The adsorption and desorption isotherm are measured at 40 °C, and the gas type is CH\textsubscript{4}. The results are shown in Figure 2.
The decrease in ΔH can explain the difference in shale adsorption capacity for different gases. The greater the heat of gas molecules, the stronger its adsorption capacity in shale. Therefore, it is feasible to improve shale gas recovery by injecting CO₂. In the competitive adsorption process of CO₂ and CH₄, CO₂ is easy to be absorbed, and it is not easy to desorb in the production process, which can promote the desorption of CH₄ and enhance the recovery of CH₄. At the same time, it is conducive to CO₂ storage.

Table 1. CH₄ Recovery of the Shale Samples

| shale sample | gas production/mL/g | recovery/% |
|--------------|---------------------|------------|
| SK₁          | 1.399               | 72.86      |
| SK₂          | 1.082               | 69.81      |
| SK₃          | 0.5287              | 66.09      |

It can be seen that under the same conditions, the adsorption curves and analytical curves of the three gases have different trajectories. There is a lag between the analytical curves and the adsorption curves. The lag phenomenon of CO₂ on shale is the most obvious, followed by CH₄ and finally by N₂. It can be inferred that the adsorption capacity of CO₂ is greater than that of CH₄ and N₂. This is because adsorption is accompanied by a change in heat. On the one hand, it is manifested as a decrease in Gibbs free energy (ΔG). On the other hand, it shows the loss of degrees of freedom and entropy (ΔS) decreases. Therefore, the free enthalpy (ΔH) can be expressed as

\[
ΔH = ΔG + T \cdot ΔS
\]  

(1)

2.3. CO₂ Injection Experiments. 2.3.1. Effect of CO₂ Injection Pressure. As shown in Figure 5, after CO₂ injection at different injection pressures, CH₄ gas recovery rate increases rapidly with time, then remains stable, and finally decreases to zero. Compared with depletion production, the CH₄ production rate does not decrease rapidly in the medium-term stage but remains stable for a period of time. The adsorption site of CH₄ is mainly the center of the six-membered oxygen ring. The main adsorption site of CO₂ is the position of the oxygen atom in the six-membered oxygen ring, and the adsorption site around the ion has a stronger adsorption capacity. Therefore, when CO₂ is injected into shale reservoirs, CO₂ molecules will compete with CH₄. Compared with CH₄ molecules, CO₂ is easier to absorb and more difficult to desorb, so CO₂ molecules can occupy the short time and depletion production not only takes a long time but also has a low ultimate recovery, which ranges from 66 to 73%. There is still a lot of CH₄ adsorbed on shale samples that have not been resolved. It is necessary to take effective measures to displace the residual adsorbed CH₄ to improve the recovery of shale gas.

Figure 4. Relationship between methane production rate and time.
adsorption sites of CH$_4$ molecules, which promotes desorption of CH$_4$. Therefore, because of the preferential adsorption of CO$_2$, CH$_4$ adsorbed is gradually replaced and exploited. Although the contribution of CH$_4$-free gas production to total production decreases gradually in the stable production stage, the desorbed CH$_4$ gas compensates for the decrease of CH$_4$-free gas production and keeps the gas production rate of shale gas stable. At the same time, the desorbed gas of shale gas accounts for an increasing proportion of total gas production. Therefore, we can see that CO$_2$ injection at different pressures can effectively prolong the stable production time of CH$_4$ and keep the cumulative gas production of CH$_4$ growing steadily and rapidly.

Table 2 shows that the recovery of SK$_1$, SK$_2$, and SK$_3$ increases significantly after injecting CO$_2$. Among them, the recovery increase of SK$_3$ is much higher after injecting CO$_2$ (7 MPa). The shale reservoir is a high stress-sensitive medium. With the exploitation of shale gas, the pore pressure of the shale reservoir decreases, and the shale fracture closes, which reduces the permeability of the shale. The injection of CO$_2$ can alleviate the decrease of pore pressure, improve the permeability of shale, and improve the core with low permeability significantly. Therefore, CO$_2$ injection can effectively improve the final recovery of CH$_4$ and within a certain range, it is significant to improve the CH$_4$ recovery by enhancing the injection pressure of CO$_2$ for the low permeability formation.

**Table 2. Recovery Comparison of Different Injection Pressures**

| number | recovery of depletion production (%) | recovery of different injection pressures (6 MPa) (%) | recovery of different injection pressures (7 MPa) (%) | growth margin |
|--------|-------------------------------------|-----------------------------------------------------|-----------------------------------------------------|--------------|
| SK$_1$ | 72.86                               | 93.66                                               | 98.09                                               | 28.55        |
| SK$_2$ | 69.81                               | 87.74                                               | 94.84                                               | 23.89        |
| SK$_3$ | 66.09                               | 81.88                                               | 94.13                                               | 35.85        |

The increased range of SK$_3$ and SK$_3$ is significantly higher than that of SK$_1$. Therefore, the effect of changing the CO$_2$ injection rate on the recovery of low porosity cores is more significant. This is because the rapid injection of CO$_2$ can make CO$_2$ gas enter into some nanopores and micropores, which are not affected by depletion production, improving CH$_4$ desorption in the pores and further improving shale gas recovery.

**2.3.3. Effect of the CO$_2$ Injection Amount.** It can be seen from Figure 7 that the ultimate recovery increases with increase in the amount of injection CO$_2$. This is because shale reservoirs are strongly stressed by sensitive media. With the exploitation of shale gas, the pore pressure of the shale reservoir decreases, and the shale fracture closes, causing the shale permeability to decrease. Injecting CO$_2$ can alleviate the reduction of shale pore pressure and help maintain the permeability of shale. However, the increasing rate at different ratios is different. There is a fast rate when the ratio is less than 2.5, and the increasing degree becomes flat when the ratio is higher than that. There is competitive adsorption and displacement when CO$_2$ is injected into a shale formation, and the CH$_4$ will be replaced and displaced more fully when CO$_2$ is injected. However, when the amount of carbon dioxide is saturated, it is useless to inject more carbon dioxide. The rise of CH$_4$ recovery obviously becomes slow after 2.5 ratios of CO$_2$ injection. Therefore, the optimal CO$_2$ injection ratio is 2.5.

**3. CONCLUSIONS**

In this study, laboratory experiments are conducted to investigate the effects of pressure, temperature, and moisture on adsorption and desorption in shale. By comparing CO$_2$ injection with depletion production, the mechanism and optimal injection parameters are analyzed. Major conclusions of this study are as follows:

1. The pressure, temperature, and moisture have a relatively strong effect on the isothermal adsorption of shale gas.

2. Compared with CH$_4$, CO$_2$ is easier to be adsorbed and is more difficult to desorb. Injecting CO$_2$ can promote desorption of CH$_4$. Also, it is conducive to the geological burial of CO$_2$, which can slow down the greenhouse effect.

3. All the desorption curves of CO$_2$, CH$_4$, and N$_2$ lag behind their adsorption curves. The lag phenomenon of CO$_2$ is the most obvious, followed by CH$_4$ and N$_2$. The delayed desorption of shale indicates that the recoverable reserves of shale are smaller than the theoretical reserves.
4 Increasing the CO₂ injection pressure and rate can effectively increase the gas production rate and recovery efficiency of shale gas. The increase in CO₂ injection pressure has a more obvious effect on the samples with lower permeability, and when the CO₂ injection rate is greater than 5 mL/min, continuing to increase the injection rate has a more obvious effect on samples with lower porosity.

4. EXPERIMENTAL SECTION

4.1. Sample Collection and Characterization. Three shale core samples from the Cen Gong shale reservoir of China are used in the experiments, including SK₁, SK₂, and SK₃. The permeability of samples is measured by helium, and the mineral compositions, TOC, and maturity of organic matter (Ro) are measured. The results are in Table 4.

Table 4 shows that the porosity range of shale core is 3.685–7.671%, and the permeability range of the shale sample is 0.0537 × 10⁻³–0.4872 × 10⁻³ μm². The porosity and permeability of shale sample are low. The compositions of samples mainly include clasolite, clay mineral, and authigenic brittle minerals. Clasolite minerals are mainly composed of quartz and feldspar. For all samples, illite is the major clay mineral. However, the content of kaolinite and chlorite is relatively low. The TOC of samples is relatively high and Ro is all higher than 2.5%. According to the evaluation criteria of shale reservoirs, the shale formations have great potential for production.

4.2. Equipment. 4.2.1. Adsorption and Desorption Experimental System. The experimental device for adsorption and desorption is designed to study the adsorption capacities of core samples, and the influence of pressure, temperature, moisture, and gas type on adsorption and desorption of gas is analyzed (shown in Figure 8).

The adsorption capacities of gas are calculated based on the gas state equation and mass conservation equation. The isotherm adsorption curves are measured by raising the pressure value in the standard room and then making the system consisting of a sample room and standard room balanced. The isotherm desorption curves are measured by reducing the pressure value in the standard room. The system temperature is controlled by the constant temperature water bath.

4.2.2. Shale Gas Exploitation Experimental System. The experimental setup is shown in Figure 9. The experimental system consists of five parts: the power system, model system, data collection system, back pressure system, and vacuum pumping system. The standard room is connected to a high-pressure cylinder or booster pump in the left and a core holder in the right. A pump is used to provide confining pressure to the core holder. The core holder pressure is the formation pressure, and the confining pressure is overburden pressure. A backpressure regulator (BPR) is used to design different pressure decline rates. The volume of production gas is measured by the volume of discharged water. The device realizes automatic continuous measurement and control of temperature and pressure of the system and ensures the accuracy of data monitoring and measurement.

5. EXPERIMENTAL METHODS AND PROCEDURES

5.1. Free Space Volume Calibration. As an inert gas, the adsorption of helium in rock samples can be neglected. Therefore, helium is chosen as the calibration gas, and the free space volume of rock samples is calibrated by the gas expansion method using the real gas equation of state. The calculation methods are shown in Formulas 2 and 3.

\[ P_a V_a Z_a + P_b V_b Z_b = P_0 (V_a + V_i) \]  
\[ V_i = V_s Z_a Z_b - P_0 Z_a Z_b \]  

where \( P_a \) is the initial absolute pressure of standard chamber A, MPa; \( P_b \) is the initial absolute pressure of sample chamber B, MPa; \( P_0 \) is the absolute pressure after equilibrium, MPa; \( V_s \) is the volume of free space in sample chamber B, m³; \( V_a \) is the volume of standard chamber A, m³; \( Z_a \) is the gas compression coefficient when pressure is \( P_a \); \( Z_b \) is the gas compression coefficient when pressure is \( P_b \).

Table 4. Basic Parameters of Shale Core Samples

| clasolite/% | illite/% | kaolinite/% | chlorite/% | authigenic brittle/% | solid volume (\( V_s \)) cm³ | porosity (\( \phi \)) % | permeability (K) md | TOC/% | Ro/% |
|------------|---------|------------|-----------|--------------------|----------------------------|------------------------|---------------------|-------|------|
| SK₁        | 46.2    | 29.1       | 1.7       | 0.4                | 18.720                     | 2.11                   | 0.1773              | 6.14  | 2.71 |
| SK₂        | 56.7    | 24.8       | 1.4       | 0.6                | 17.033                     | 3.14                   | 0.2560              | 5.61  | 2.58 |
| SK₃        | 71.2    | 18.9       | 0.7       | 0.2                | 18.536                     | 3.97                   | 0.2819              | 4.98  | 2.61 |
The pressure in the sample room before balance; \( P_{\text{room}} \) to get higher equilibrium pressures. The adsorption and the equilibrium pressure is recorded as \( P \).

A part of the shale sample is pulverized to a powder, which is heated until the mass keeps constant. Then, 60 to 80 mesh powders are utilized to do the isothermal adsorption. The system is first vacuumed, airtightness is tested, and then, first vacuumed by a vacuum pump again, and airtightness is tested, and then, the sample room is opened, and time is recorded by the drainage method and stopwatch. The volume of methane adsorbed by shale sample is \( V_0 \).

\[
V_0 = \frac{P_1 V_h}{Z_1 P_{\text{sc}}} - \frac{P_2 V_h}{Z_2 P_{\text{sc}}} - \frac{P_2 V_p}{Z_2 P_{\text{sc}}}
\]  

5.3. Depletion Production Experiment. The depletion production experiment is carried out on the basis of the shale adsorption experiment. First, shale samples are isothermally adsorbed and saturated with methane gas to simulate real shale reservoir conditions. When the adsorption process of shale sample reaches the equilibrium state (equilibrium pressure \( P_2 \)), the volume of methane adsorbed by shale sample is \( V_0 \).

\[
V_0 = \frac{P_1 V_h}{Z_1 P_{\text{sc}}} - \frac{P_2 V_h}{Z_2 P_{\text{sc}}} - \frac{P_2 V_p}{Z_2 P_{\text{sc}}}
\]

The total adsorption capacity at \( P_1 \) is

\[
n_i = \sum \Delta n_i
\]

5.4. \( \text{CO}_2 \) Injection Experiments. In this part, three factors that may affect the ultimate recovery have been investigated: (1) the pressure of injection \( \text{CO}_2 \), (2) the rate of injection \( \text{CO}_2 \), and (3) the volume of injection of \( \text{CO}_2 \). In order to separate the \( \text{CH}_4 \) and \( \text{CO}_2 \) in the outlet, the \( \text{NaOH} \) solution is used to absorb \( \text{CO}_2 \). The discharged water is used to calculate the pressure gas cylinders, 6 — pressure relief valve, 8 — valve, 15 — pressure transducer, 16 — constant temperature water bath, 17 — data acquisition system.
the volume of production CH₄. The experimental system is vacuumed by the vacuum pump at the beginning.

As to corresponding conditions (1), the displacement experiments of CO₂ under different injection pressures are carried out on the basis of depletion production experiments. The placement experiments of SK₁, SK₂, and SK₃ are carried out at 30 °C. The adsorption equilibrium pressures of SK₁, SK₂, and SK₃ are 4.5 MPa. During the experiment, CO₂ gas is injected into the sample chamber at a high-pressure CO₂ cylinder at constant pressure (6 and 7 MPa), and the decline rate of BPR is 0.1 MPa/min. The mixed gases of CO₂ and CH₄ are produced through NaOH solution and distilled water in turn, and the CH₄ gas production at a certain time is recorded by the stopwatch.

As to corresponding conditions (2), the displacement experiments of shale samples SK₁, SK₂, and SK₃ are carried out with an adsorption equilibrium pressure of 4.5 MPa and temperature of 30. During the experiment, CO₂ gas is injected into the sample chamber by a high-pressure CO₂ injection CO₂, the CO₂ is stored in the standard room after the decline of CH₄ and CH₄ is saturated with CH₄ after saturating CH₄. The injection amount is calculated by the pressure difference of the standard room. The ratio of the CO₂ injection amount to the total amount of CH₄ in the sample room is calculated. The pressure of the sample room is 4.5 MPa after saturating CH₄.

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Notes

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