

Study on Desorption and Diffusion Characteristics of CO₂ in Cracked Coal

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Abstract

Gas migration within coal matrices is driven by concentration gradients, fundamentally representing gas diffusion and mass transfer within porous frameworks. During this process, gas molecules adsorbed on coal surfaces desorb and primarily reside in the micro-pores (<2 nm) and mesopores (2-50 nm) within the coal structure. Due to the extreme pore dimensions, gas movement is predominantly governed by intermolecular collisions and interactions with pore walls, where diffusion mechanisms dominate. To investigate the impact of CO₂ phase transition-induced fracturing shock waves on gas desorption and diffusion behavior in coal samples, this study selected three coal samples: Zhangcun (ZC), Chengzhuang (CZ), and Jiulishan (JLS). We designed and conducted isothermal natural desorption experiments for gas before and after the shock wave impact. Experimental results demonstrate a positive correlation between cumulative gas desorption capacity and initial adsorption equilibrium pressure in coal samples, indicating that the desorption capacity increases with rising initial adsorption equilibrium pressure. When initial adsorption equilibrium pressure is identical, the desorption curves of impact samples consistently outperform those of original samples. Under equivalent initial adsorption equilibrium pressure, coal samples subjected to CO₂ phase transition-induced cracking exhibit significantly higher initial gas desorption rates compared to their original counterparts, with post-impact desorption curves surpassing the original curves. For identical samples, higher initial adsorption equilibrium pressure correlates with greater early-stage gas desorption rates. This establishes a clear positive correlation between initial gas desorption rates and initial adsorption equilibrium pressure in coal samples.

Keywords

CO₂-induced phase change-induced fracturing; Gas migration; Gas desorption capacity; Gas desorption rate.

1. INTRODUCTION

Currently, various permeability enhancement techniques have been developed for high-gas, low-permeability coal seams. These include mining protection layers [1], hydraulic fracturing [2], hydraulic slotting [3], hydraulic drilling [4], deep-hole prefracturing blasting [5], CO₂ fracturing [6], acoustic vibration enhancement [7], electromagnetic field enhancement [8], and CO₂ dissolution-enhanced permeability [9]. Among these, CO₂ fracturing works by applying the physical expansion force generated during phase transition of CO₂ to coal reservoirs. This method modifies coal layer structures through shock energy, creating new pore-fracture

networks that enhance permeability. Simultaneously, CO₂'s strong adsorption capacity displaces methane from coal matrices, facilitating its entry into fractures for extraction. This dual mechanism significantly improves gas recovery efficiency. Studies [10-12] demonstrate that coal's pore structure and fracture network system serve as primary storage and migration pathways for coalbed methane. Their geometric characteristics and spatial distribution directly influence gas seepage processes. As a powerful dynamic phenomenon, CO₂ fracturing impacts coal pores and fractures through shock effects, affecting gas desorption, diffusion, and seepage stages, ultimately optimizing gas extraction [13]. This study selects three types of high-rank bituminous coals as research subjects. Through CO₂ fracturing experiments, it investigates the gas migration characteristics of coal particles before and after fracturing. This research is significant for comprehending the pore-fracture propagation mechanism of CO₂ fracturing technology, enriching and refining the permeability enhancement theory of CO₂ fracturing in coal reservoirs, and improving coalbed methane production rates.

2. EXPERIMENTAL SETUP

This study utilizes the coalbed methane adsorption-desorption experimental system independently developed by the Research Center for Coalbed Methane/Geological Engineering at Henan Polytechnic University, as shown in Figure 1.



Figure 1. Gas desorption experiment instrument

The experimental device is divided into five parts according to its function, and its responsibilities and configurations are as follows:

Gas source drive: the system is initialized with high-purity helium gas as the medium, and the sealing test of reference cylinder and sample cylinder and free volume calibration are performed.

Vacuum degassing: The system integrates a 2XZ-4 rotary vane vacuum pump, sensors, and piping. After determining the free volume, a double-cylinder vacuum is applied to completely remove residual gases, preventing methane adsorption from being affected by environmental impurities.

Gas adsorption: Composed of a methane cylinder, a high-toughness stainless steel sample cylinder, a reference cylinder, and a matching sensor, it achieves the adsorption equilibrium process. The purity of methane gas in the test is higher than 99.995%.

Gas desorption: Measures gas release and average desorption rate of coal samples under different equilibrium pressures and adsorption levels, using a 500 mL graduated cylinder (2 mL precision) and associated pipelines.

Temperature control: The reference cylinder and the sample cylinder are put into the constant temperature water bath, and the two cylinders are completely immersed to accurately reproduce the temperature of the coal reservoir and ensure the constant thermodynamic conditions of the whole process of adsorption and diffusion.

3. EXPERIMENT PLAN AND STEPS

The gas adsorption-desorption experiment was conducted at a constant temperature of 25°C. The initial adsorption equilibrium was established through three pressure gradients: 0.5 MPa, 1 MPa, and 2 MPa. The detailed experimental protocol is shown in Table 1.

Table 1. Adsorption-desorption experiment scheme of original coal samples in three coal seams

Number	Tank Number	Temperature /°C	Grain Size/mm	Weight/g	Initial Equilibrium Pressure/Mpa	Recording Time /min
ZC-0	A1	25	0.18-0.25	50	0.5	120
	A2	25	0.18-0.25	50	1	120
	A3	25	0.18-0.25	50	2	120
ZC-185	A4	25	0.18-0.25	50	0.5	120
	A5	25	0.18-0.25	50	1	120
	A6	25	0.18-0.25	50	2	120
CZ-0	B1	25	0.18-0.25	50	0.5	120
	B2	25	0.18-0.25	50	1	120
	B3	25	0.18-0.25	50	2	120
CZ-185	B4	25	0.18-0.25	50	0.5	120
	B5	25	0.18-0.25	50	1	120
	B6	25	0.18-0.25	50	2	120
JLS-0	C1	25	0.18-0.25	50	0.5	120
	C2	25	0.18-0.25	50	1	120
	C3	25	0.18-0.25	50	2	120
JLS-185	C4	25	0.18-0.25	50	0.5	120
	C5	25	0.18-0.25	50	1	120
	C6	25	0.18-0.25	50	2	120

The experiment is divided into two stages: isothermal adsorption experiment and desorption experiment. The operation is as follows:

(1) Close the external valve, open the internal valve, and degas the vacuum pump for about 20 minutes until the pressure stabilizes at 0.01 MPa. Then close the internal valve and the vacuum pump.

(2) Place the coal sample tank into a 25°C constant temperature water bath. Close the external valve and open the internal valve. Open the high-purity methane cylinder inlet valve and pressure regulator valve, and continuously introduce gas for approximately 12 hours until the sample tank reaches the preset pressure. Then, close the methane inlet valve and cylinder pressure regulator valve.

(3) Record the ambient temperature and air pressure before desorption. Data recording interval: every 30 seconds during the first 30 minutes, every minute during the 30-60 minutes, and every 2 minutes during the 60-120 minutes.

(4) Before the experiment, depressurize the coal sample tank and purge the pipeline of free gas. Start the natural desorption process, measure the desorbed gas volume using a 500ml graduated cylinder (with 2ml precision) filled with water, and record the data continuously for approximately 120 minutes.

4. ORIGINAL/IMPACT SAMPLE CUMULATIVE GAS DESORPTION

Based on the integrated gas desorption experiments, this study investigates CO₂-induced gas desorption patterns in coal before and after thermal shock. Table 2 presents the cumulative gas desorption values (120 min) for Zhangcun (ZC), Chengzhuang (CZ), and Jiulishan (JLS) coal samples under different initial adsorption equilibrium pressures, with corresponding 120min desorption curves shown in Figure 2.

Table 2. Cumulative desorption of coal samples under different pressures

Number	Equilibrium Pressure (MPa)	Q1(cm ³ /g)	Q3(cm ³ /g)	Q10 (cm ³ /g)	Q120(cm ³ /g)
ZC-0	0.50	0.73	1.21	1.96	4.34
	1.00	1.17	1.95	3.15	6.96
	2.00	1.61	2.68	5.11	10.10
ZC-185	0.50	1.33	2.23	3.23	5.72
	1.00	1.78	2.80	4.71	9.32
	2.00	2.43	4.06	7.00	13.01
CZ-0	0.50	0.71	1.23	2.05	4.68
	1.00	1.13	1.93	3.22	7.37
	2.00	1.81	3.37	5.18	11.03
CZ-185	0.50	0.95	1.59	3.02	5.98
	1.00	1.84	2.96	4.71	9.55
	2.00	2.10	3.52	6.69	13.32
JLS-0	0.50	0.70	1.20	3.39	4.54
	1.00	1.19	2.21	2.71	7.22
	2.00	1.72	2.95	4.92	11.24
JLS-185	0.50	1.13	1.93	3.07	6.22
	1.00	2.26	3.77	5.38	9.76
	2.00	3.16	5.27	7.76	13.65

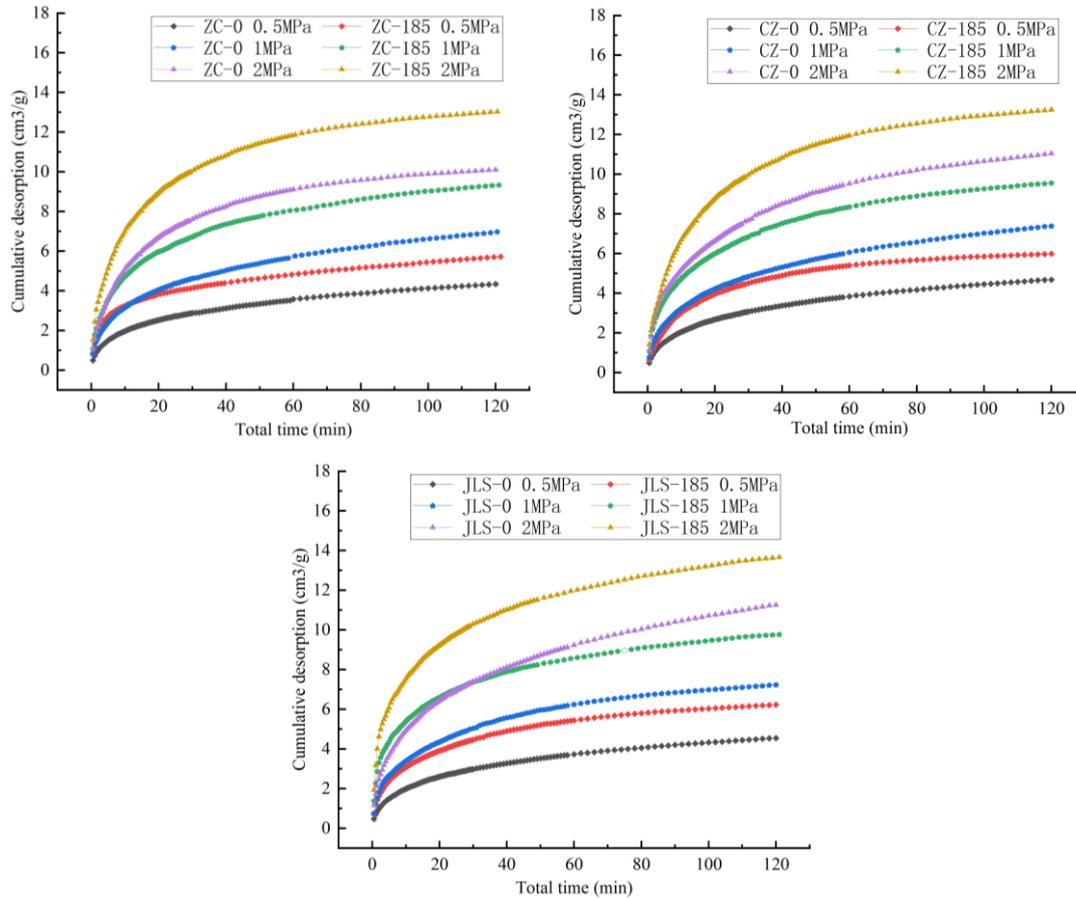


Figure 2. Gas desorption curve

As can be seen from Table 2 and Figure 2:

The gas desorption curves of three coal samples exhibited similar patterns before and after the shock. The desorption volume gradually increased over time, with the initial curve showing a steep slope and rapid upward trend, indicating a swift desorption rate. Subsequently, the desorption curve gradually flattened, the upward trend of desorption volume slowed down, and the desorption rate progressively decreased.

The cumulative desorption of gas in coal samples is positively correlated with the initial adsorption equilibrium pressure, that is, the cumulative desorption of gas in coal samples increases with the increase of the initial adsorption equilibrium pressure.

The desorption curves of the impact samples consistently outperformed those of the original samples under identical initial adsorption equilibrium pressures. In the 120-minute experiment, the cumulative desorption capacities increased as follows: ZC from 4.34 cm³/g to 5.72 cm³/g, CZ from 4.68 cm³/g to 5.98 cm³/g, and JLS from 4.54 cm³/g to 6.22 cm³/g at 0.5 MPa. When the initial pressure was raised to 1 MPa, the capacities rose to 9.32 cm³/g for ZC, 9.55 cm³/g for CZ, and 9.76 cm³/g for JLS. At 2 MPa, the values increased further to 13.01 cm³/g for ZC, 13.32 cm³/g for CZ, and 13.65 cm³/g for JLS. These results demonstrate that the CO₂ phase transition-induced fracturing at 185 MPa pressure caused a consistent increase in the cumulative desorption capacities of all three coal samples.

5. ORIGINAL/IMPACT SAMPLE GAS DESORPTION RATE

The coal-like gas desorption rate refers to the amount of gas released per unit time, reflecting the speed of gas release. In order to more intuitively analyze the desorption capacity of the three

coal samples before and after impact, Figure 3 shows the desorption rates of three coal samples within 600s.

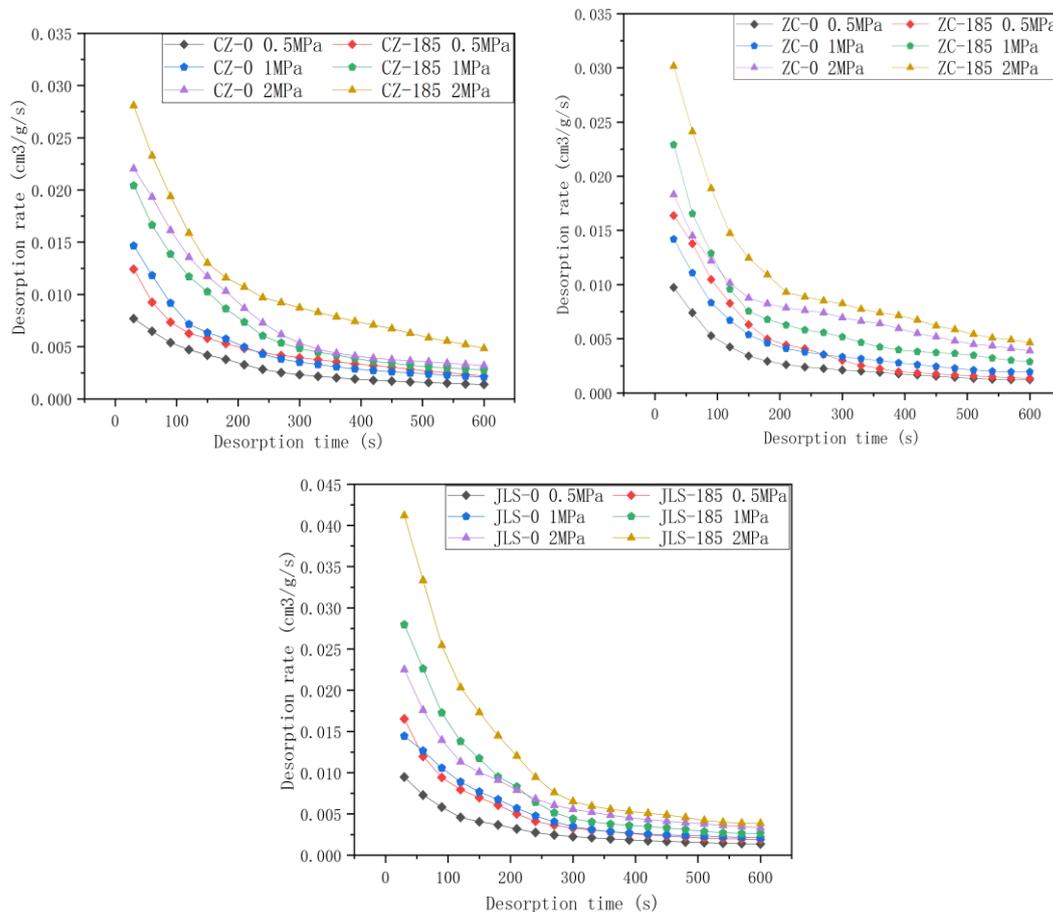


Figure 3. 600s gas desorption rate

As shown in Figure 3, the desorption rate curves and cumulative desorption curves of the original and shock samples from the three regions exhibit opposite trends within 10 minutes. During the initial gas desorption phase, the desorption rate is extremely rapid, but gradually slows down over time, eventually approaching zero.

Under identical initial adsorption equilibrium pressure, the coal sample exhibited significantly higher initial desorption rates of methane gas after undergoing CO₂-induced phase transition-induced cracking impact compared to the original sample. The desorption rate curve of the impacted coal sample consistently outperformed that of the original sample. The maximum rate difference between the two samples was observed during the initial desorption phase, with this gap gradually diminishing as the experiment progressed. This indicates that the methane desorption rate in the impacted coal sample decays more rapidly than in the original sample. Using coal samples from Zhangcun Mine as a case study: At an initial adsorption equilibrium pressure of 0.5 MPa, the desorption rate for the shock sample was 0.0164 cm³/(g·s) at 30 seconds, compared to 0.0097 cm³/(g·s) for the original sample (difference: 0.0067). By 600 seconds, the shock sample's desorption rate decreased to 0.0014 cm³/(g·s) versus 0.0012 cm³/(g·s) for the original sample, with the difference narrowing to 0.0002. Under 1 MPa initial adsorption equilibrium pressure, the shock sample showed 0.0230 cm³/(g·s) desorption at 30 seconds versus 0.0142 cm³/(g·s) for the original sample (difference: 0.0088). By 600 seconds, the shock sample's rate dropped to 0.0029 cm³/(g·s) compared to 0.0019 cm³/(g·s) for the original sample, with the difference reduced to 0.0002. At 2 MPa initial adsorption equilibrium pressure, the shock sample exhibited 0.0301 cm³/(g·s) desorption at 30 seconds versus 0.0183

$\text{cm}^3/(\text{g}\cdot\text{s})$ for the original sample (difference: 0.0118). By 600 seconds, the shock sample's desorption rate decreased to $0.0047 \text{ cm}^3/(\text{g}\cdot\text{s})$ compared to $0.0039 \text{ cm}^3/(\text{g}\cdot\text{s})$ for the original sample, with the difference narrowing to 0.0008.

In the gas desorption process of coal samples from three regions within 600 seconds, both original samples and those subjected to CO₂ phase change-induced fracturing impact showed a clear positive correlation between initial adsorption equilibrium pressure and early gas desorption rate. For identical samples, the maximum rate difference occurred during the initial desorption phase, gradually decreasing as the experiment progressed, indicating faster rate decay with higher initial adsorption pressure. Taking the Julishan impact sample as an example: at 30 seconds, the gas desorption rates corresponding to 2.0 Mpa, 1.0Mpa, 0.5Mpa initial adsorption equilibrium pressure were $0.0412 \text{ cm}^3/(\text{g}\cdot\text{s})$, $0.0279 \text{ cm}^3/(\text{g}\cdot\text{s})$, and $0.0165 \text{ cm}^3/(\text{g}\cdot\text{s})$, showing differences of 0.0133 and 0.0114. At 600 seconds, the rates decreased to $0.0039 \text{ cm}^3/(\text{g}\cdot\text{s})$, $0.0026 \text{ cm}^3/(\text{g}\cdot\text{s})$, and $0.0019 \text{ cm}^3/(\text{g}\cdot\text{s})$, with the difference narrowing to 0.0013 and 0.0007 respectively.

6. CONCLUSION

The migration of coal matrix methane is driven by concentration gradients, fundamentally representing gas diffusion and mass transfer within porous frameworks. During this process, desorbed methane molecules primarily occupy micro-pores (<2 nm) and mesopores (2-50 nm) within the coal structure. Due to their microscopic dimensions, gas movement in these pores is predominantly governed by intermolecular collisions and interactions with pore walls, where diffusion mechanisms dominate. Experimental data demonstrate a positive correlation between cumulative methane desorption from coal samples and initial adsorption equilibrium pressure: both values increase with rising initial adsorption pressure. When initial adsorption pressures are identical, desorption curves of impact samples consistently exceed those of original samples. Under equivalent initial conditions, coal samples subjected to CO₂-induced phase transition fracture exhibit significantly higher initial methane desorption rates compared to their original counterparts, with post-impact desorption curves surpassing the original curves. For identical specimens, higher initial adsorption pressure correlates directly with enhanced early-stage methane desorption rates, establishing a clear positive correlation between initial adsorption pressure and early desorption efficiency.

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