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Optimization of CO_2/N_2 injection ratios in goaf by saturation adsorption capacity

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ABSTRACT

The inerting technology is a common means to prevent fires in goaf of coal mine, in which adsorption capacity is the key index to measure the inerting effect. Therefore, this paper obtained the coal spontaneous combustion (CSC) stage of Qianyingzi coal mine through programmed heating experiments, and determined the physical adsorption stage temperature (below 323.15 K) matching the actual environment. The oxidation characteristics of coal samples with different adsorption degrees were further studied by adsorption experiment and TG-DSC test. The results indicate that the combustion activation energy of coal samples follows the sequence of second-stage adsorption coal > dried coal > raw coal > first-stage adsorption coal. This implies that the CO₂ saturated adsorption can exert a specific inhibitory impact on coal combustion. Therefore, the index of the saturation adsorption capacity (SAC) was proposed to evaluate the inerting effect. We further studied the adsorption capacity of coal at different ratios of CO2/N2 by molecular simulation under different pressures (0-5 MPa). The results show that CO₂ dominates in both single-component adsorption and competitive saturated adsorption. The average of ratios (AOR) and average of differences (AOD) threshold are determined. The priority of SAC is obtained in the order of single-component (C₈), CO₂/N₂ mixture ratio at 4:6 (C_{4:6}), CO₂/N₂ mixture ratio at 2:8 (C2:8) from largest to smallest. Furthermore, a fuzzy optimization method for injection ratio of CO2/ N_2 under different pressures was established. During dynamic changes in environmental pressure, it is appropriate to inject CO₂ separately at 0.2–2.5 MPa. At 3 MPa, a mixture of CO₂/N₂ at a ratio of 2:8 is the best for prevent fires in goaf. Similarly, an inert gas with a CO₂/N₂ ratio of 4:6 is injected at 3-5 MPa.

1. Introduction

Coal spontaneous combustion (CSC) in goaf is the main disaster of coal mine, which has the characteristics of strong concealment and difficult prevention. Inerting technology is commonly used to prevent the CSC in goaf. The principle is that the inert gas is injected into the goaf to form an inerting zone around the coal. At the same time, the inert gas is adsorbed by the coal to block the coal-oxygen reaction process, thus inhibiting the CSC in the goaf (Cheng et al., 2021). Most scholars have imitated this process and studied the gas concentrations changes and microscopic mechanisms of coal oxidation at different inert gas atmospheres (Si et al., 2023) (Zhou et al., 2022) (Shao et al., 2014). There are few researches on the oxidation characteristics of pre-adsorbed coal. Zhang et al. studied the low-temperature oxidation characteristics and

functional group changes of pre-adsorbed CO_2 coal samples using a temperature-programmed experiment device (Zhang et al., 2023). The results show that the oxidation reaction of oxygen-containing functional groups was inhibited and the O_2 consumption decreased by about 4 % after the coal sample was pre-adsorbed CO_2 , which indicates that the oxidation characteristics of coal will change after the coal sample has adsorption basis. In the actual production process, the inert gas is often injected in intermittent mode, which leads to the possibility that the residual coal may have adsorbed the inert gas many times, and resulting in differences in the coal oxidation characteristics. Therefore, the oxidation characteristics of different adsorption degrees coal samples need to be further studied.

Environmental parameters such as pressure, temperature, moisture, coal metamorphism and inert gas composition will affect the coal

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Table 1

Coal sample	Weight (g)	M _{ad} (%)	A _{ad} (%)	V _{daf} (%)
QYZ	1.01	2.00	12.24	25.00

Table 2

Moisture	content	of	ov
woisture	content	OI.	UI.

Moisture c	ontent c	of QYZ.		
QYZ	Raw	Dried	First-stage adsorption	Second-stage adsorption
M _{ad} (%)	2.00	1.81	1.52	1.40

adsorption degree. Coal mines typically use CO₂ and N₂ as inert gas, which achieve the inerting of coal by displacing and occupying the adsorption site of O₂ on the coal surface (Zhu and Liu, 2012) (Yan et al., 2023). However, the difference of physicochemical properties of CO_2 and N₂ leads to the competitive adsorption of the two gases on the surface of coal, which changes the adsorption efficiency of coal (Li et al., 2019) (Liu et al., 2023) (Hao et al., 2021). Currently, molecular simulation technology is the main method to explore the competitive adsorption of gases on coal, and the current research focuses on gas injection to displace CH₄ and CO₂ storage. A few scholars have also studied the competitive adsorption capacity between inert gases and O₂. Based on the adsorption configuration of oxygen-containing coal, Ding et al. used Grand Canonical Monte Carlo (GCMC) and molecular dynamics (MD) methods to study the adsorption behavior of CO2/N2 on O2 (Ding et al., 2023). Wu et al. calculated the interaction energy and isosteric heat of inert gases adsorption on coal, finding that the competitive adsorption capacity is in the order of CO2, O2, N2 (Wu et al., 2017). Dong et al. studied the competitive adsorption relationship of CO and CO₂/O₂ on coal (Dong et al., 2023), while Wang et al. conducted similar research (Wang et al., 2022). These studies have laid a theoretical foundation for inertization mechanisms. In the actual production process, the gas injection pipeline is withdrawn with the advance of the working face, and the pressure distribution changes in the goaf. However, there is a lack of research on the optimization of CO₂/N₂ injection ratio under the change of pressure environment in goaf.

Therefore, this study employed a self-developed programmed heating device to conduct CSC experiments at room temperature to 573.15 K.



Fig. 1. Programmed heating experimental platform.



Fig. 2. CO₂ adsorption experimental platform.

Table 3

Geometric optimization parameter selection.

Setting	Parameter	References
Task	Geometry optimization	(Gao and Song, 2023)
Quality	Customized	(Ding et al., 2023) (Xi et al., 2022) (Bai
Algorithm	Smart	et al., 2021)
Energy	0.001 kcal/mol	(Xu et al., 2023)
Force	0.1 kcal/mol	
Max	50,000	(Zhu et al., 2021)
iterations		
Forcefield	Dreiding	(Gao et al., 2020)
Charge	Charge using QEq	(Meng et al., 2020)

Combined with gases adsorption equipment and TG-DSC test, the differences in oxidation characteristics of coal samples with different adsorption degrees were studied. Further, the evaluation index of adsorption effect is proposed. At different pressures (0–5 MPa), the simulation of CO_2/N_2 multi-proportion competitive adsorption on coal are conducted to study the optimal CO_2/N_2 injection ratio at the actual goaf pressure. The research results can provide theoretical parameters selection and guidance for mixed gas injection for fire prevention in goaf.

2. Methods and materials

2.1. Coal sample

The coal samples (QYZ) were obtained from the western wing of Qianyingzi coal mine. The QYZ were crushed to 0–6 mm, and part of the samples were sieved to 0.1–0.2 mm. Table 1 shows the results of the proximate analysis. We preserved the raw coal sample with moisture content of 2.00 %, dried it for 12 h to obtain the dried coal sample, and adsorbed coal samples in different adsorption degrees respectively. The moisture content is shown in Table 2.

2.2. Programmed heating experiment

Fig. 1 illustrates the programmed heating experimental platform for self-development, comprising the gas injection, heating, and gas chromatography sampling and analysis sections. In the procedure, the QYZ was placed in the heater. Attaining the set temperature, heating was halted and generated gases were analyzed for concentrations. In this experiment, varied heating parameters were set between 303.15 K-473.15 K and exceeding 473.15 K.

2.3. Adsorption experiment

Fig. 2 shows the high-pressure isothermal adsorption experimental platform. CO_2 adsorption trials were performed with 0–2.5 MPa and controlled temperature conditions (Santarosa et al., 2013). The experimental parameters were consistent with those detailed in our prior publication (Li et al., 2023). Through adsorption experiments, we obtained QYZ with different adsorption degrees, and investigated CO_2 adsorption characteristics by coal.

2.4. TG-DSC test

The oxidation characteristics of raw samples, dried samples, firststage adsorbed samples and second-stage adsorbed samples were analyzed by TG-DSC. The sample mass was 20 mg (\pm 0.5 mg), uniformly placed at the bottom of a ceramic crucible. The experiment was conducted with a flow rate of 100 mL/min. The samples were heated from environment temperature to 1073.15 K at a rate of 10 K/min in an air atmosphere.

2.5. GCMC simulation

The QYZ coal sample is a young bituminous with a carbon content of 82–83 %, which is basically consistent with the properties of the coal molecular model proposed by W.H. Wiser. The molecular formula is $C_{192}H_{166}N_4O_{19}S_9$. We constructed the model and optimized the force field configuration, followed by annealing. Table 3 shows the parameters selected for geometric optimization.

Table 4 presents the comparison of the carbon molecule energy levels before and after optimization. The total energy decreased significantly, enhancing the stability of the molecular structure. The final optimized coal molecule model is depicted in Fig. 3. The optimized parameters of the coal structure model were obtained with the lattice constants of A = B = C = 16.3 Å and the interaxial angles of $\alpha = \beta = \gamma = 90^{\circ}$. The mass of a coal cell molecule is 5.197 $\times 10^{-21}$ g.

To investigate the single-component adsorption of CO_2 and N_2 on coal, the crystalline model of coal molecules was imported into the Fixed Pressure task of the Sorption module. The Metropolis method with medium accuracy was selected for the simulations. The system temperature ranged from 303.15 K to 323.15 K, and pressure was converted to fugacity inputs in 0.5 MPa increments at 0–5 MPa. CO_2 and N_2 were then mixed and the CO_2 was increased by 10 % step by step for simulation. The temperature is set to 303.15 K, and other parameters are consistent with those set for the single component. The results of competitive adsorption and single-component adsorption were compared to optimize the inerting adsorption parameters.

3. Results and discussion

3.1. CSC stages analysis

Fig. 4 shows the trend of gas concentration changes during the QYZ heating process. At low-temperature stage (323.15 K-333.15 K), coal initiates the chemical adsorption of O2, resulting in a decrease in O2 concentration. Then, in the high-temperature stage (around 353.15 K), the active functional groups on the coal interact with oxygen atoms, leading to increased concentrations of CO and CO₂. Similarly, Wang et al. also noted heightened levels of CO and CO₂ during coal heating processes (Wang et al., 2022). As the temperature increases, the oxidation of coal produces C_2H_6 (at 403.15 K), C_2H_4 (at 423.15 K), and C₃H₆CO₂ (at 443.15 K). It indicates that the coal oxidation reaction enters the accelerated stage and begins to enter the self-heating stage. Beyond 473.15 K, the O₂ concentration decreases from 18.39 % to 14.27 % in 473.15 K-513.15 K. Wang et al.'s investigation also confirming the fluctuation in O2 levels during coal thermal treatment (Wang et al., 2022). The concentrations of the three alkene gases exhibit a more significant increase after 493.15 K. They continue to rise with

 Table 4

 Energy comparison before and after coal molecule optimization.

	TE (kJ/mol)		VEE (kJ/mol)				NBE (kJ/mol)	
		BSE	BAE	TSE	ISE	HBE	VDW	CE
Initial	10831.90	2608.73	69.80	113.05	5.13	0	8057.50	-22.31
Final	639.76	88.23	79.73	97.20	2.37	0	408.55	-36.34



Fig. 3. QYZ coal molecules optimized by annealing.



Fig. 4. Concentration variation of CSC indicator gases.

Table 5	
CSC stages	of QYZ.

Stage	Temperature range (K)	Extreme temperature (K)	Adsorption Stage
Latent	< 323.15	323.15	Physical adsorption
	323.15-353.15	353.15	Chemical
Composite	353.15-393.15	393.15	adsorption
Pyrolysis	393.15-493.15	493.15	
Combustion	> 533.15	533.15	

temperature until 533.15 K, indicating that the coal is about to enter the combustion stage, suggesting the imminent shift towards combustion. Consistently, Ma et al. investigated the alkene gas production during coal heating processes and found similar trends (Ma et al., 2023).

Table 5 presents the classification system for CSC. In the latent adsorption process, physical adsorption dominates below 323.15 K which is consistent with the mine environment. Chemical adsorption occurs above 323.15 K. This is continued with the composite temperature stage, where the concentrations of CO and CO₂ rise at 353.15 K. The pyrolysis stage at 393.15 K leads to the generation of hydrocarbon gases as the temperature increases. Finally, during the combustion stage, the concentrations of CO and CO₂ increase rapidly when the temperature exceeds 533.15 K.



Fig. 5. CO_2 adsorption capacity on QYZ (Santarosa et al., 2013) (Dong et al., 2023) (Yu et al., 2023).



Fig. 7. Adsorption equilibrium time at various pressure.

3.2. CO_2 adsorption on coal

Fig. 5 shows the results of previous CO_2 adsorption tests. At 0–5 MPa (308.15 K), excess CO_2 adsorption studies were conducted on subbituminous coal. The growth of adsorption capacity slowed down at 0.5 MPa and tended to level off at 1.4 MPa (Santarosa et al., 2013). Similarly, investigation on bituminous coal at 0–5 MPa and 303.15 K revealed a gradual stabilization of adsorption capacity at 3 MPa (Dong et al., 2023). Analyzing the single-component adsorption of CO, CO_2 ,

Table 6						
QYZ mass change	before and	after	different	degrees	adsor	otion.

Stages	Initial mass (g)	Final mass (g)	Mass increment (g)
First-stage adsorption	516.12	517.62	1.5
Second-stage adsorption	506.86	508.98	2.12



Adsorption time (min)

Fig. 6. Comparison of adsorption equilibrium time at various pressure.





Fig. 9. Activation energy of QYZ combustion.

 Table 7

 Linear fitting results of QYZ combustion activation energy.

QYZ	<i>-E</i> /R	R ²	E (kJ/mol)
Raw	-8490.70	1.00	70.59
Dried	-9698.23	0.99	80.63
First-stage adsorption	-7669.43	1.00	63.76
Second-stage adsorption	-9741.86	0.99	80.99

and O_2 on bituminous coal at 0–16 MPa and 303.15 K, it was observed that CO_2 reached saturation adsorption first (Yu et al., 2023). Combined with the results of our investigation, all indicate that the adsorption/ desorption of CO_2 on coal will gradually reach equilibrium, and the

adsorption rate will decrease as the adsorption progresses. When the adsorption/desorption of CO₂ reach equilibrium, the CO₂ adsorption of coal is close to saturation. The adsorption capacity of CO₂ at this time is called the saturation adsorption capacity (SAC), which is the most intuitive indicator to investigate the adsorption of CO₂/N₂ on coal.

3.2.1. Adsorption characteristics

Based on the CSC stages and the actual underground environment, CO_2 adsorption on coal was carried out under physical adsorption conditions (303.15 K). Fig. 6 shows the adsorption capacity of CO_2 on coal at different adsorption degrees. Consistent with the previous investigation, the adsorption capacity increases with pressure, but the growth gradually slows down (Yu et al., 2022). The second-stage



Fig. 10. Adsorption mechanism of multiple inert gases on coal.

adsorption capacity of QYZ for CO_2 is lower than that of the first stage at each pressure point, ranging from -0.0056 to 0.07103 mmol/g. This indicates that CO_2 remains partially adsorbed on coal even after the first stage. In the second-stage adsorption, coal is partly saturated with CO_2 , leading to a decline in adsorption capacity. In the first-stage adsorption, capacity increases over time until the onset of second-stage adsorption, where the growth rate decreases and ultimately stabilizes. Therefore, we believe that the two stages CO_2 adsorption on coal is a process in which the adsorption capacity tends to saturate and reaches the SAC.

Fig. 7 shows the adsorption saturation time at different pressure. The time required to reach adsorption equilibrium and the adsorption capacity show a positive correlation at identical pressure conditions (Jiang et al., 2020). With increasing pressure, the adsorption saturation time decreases.

Table 6 shows the mass variations of QYZ before and after different degrees adsorption. The mass increment following the second-stage surpasses that of the first-stage, indicating incomplete saturation after the initial adsorption phase. The subsequent gas injection allows the coal to approach saturation adsorption. This demonstrates the importance of preventing CSC in goaf through multiple injections of inert gas.

3.2.2. Combustion characteristics

(a) Curve analysis

Fig. 8 depicts the TG-DSC curve of QYZ. In contrast to the dried coal, both the raw and adsorbed coal exhibit heightened peak heat flow, attributed to moisture content in the raw coal. Equally, Zhao et al. demonstrated a similar impact of moisture content on peak heat flow in coal samples (Zhao et al., 2015). In addition, at elevated temperatures, a small amount of CO_2 in the adsorbed coal is reduced to CO and continues to participate in the combustion reactions.

At the combustion of QYZ, the weight loss process initiates at 603.15 K for the dried coal, whereas in raw coal samples, it commences at 607.15 K. In addition, the sharp weight loss temperatures of the different degrees adsorbed coal are 591.15 K and 598.15 K, respectively, both lower than the dried coal. Combined with the moisture content of each coal in Table 2, the adsorption of CO_2 reduces the moisture content. As a result, the coal enters the combustion stage faster. Aligning with this phenomenon, Wu et al. underscored CO_2 adsorption's role in decreasing moisture content and accelerated the coal's progression to combustion (Wu et al., 2020).

(b) Activation energy analysis

Fig. 9 shows the ignition activation energy of different coal samples.



Fig. 11. Single-component adsorption capacity of CO2 and N2 on QYZ.

Table 8	
Fitting results of adsorption capacity of CO2 and N2 on Q	YZ.

Gas	Temperature(K)	а	b	R ²	Gas	Temperature(K)	а	b	R ²
CO_2	303.15	2.11	3.71	0.94	N ₂	303.15	0.85	0.25	0.96
	313.15	1.99	4.06	0.92		313.15	0.87	0.21	0.97
	323.15	1.94	3.92	0.93		323.15	1.11	0.12	0.97

Based on the results shown in Table 7, it can be observed that the ignition activation energy decreases after the first-stage adsorption. Subsequently, it increases after the second-stage adsorption and exceeds that of the dried coal. This indicates that a small amount of adsorption does not inhibit the CSC, but can actually promote the self-ignition of coal oxidation. When the coal approaching the SAC of CO_2 can prevent coal oxidation autoignition.

3.3. SAC for CO₂, N₂

Fig. 10 shows the CO_2/N_2 adsorption mechanism on coal. O_2 is displaced in the adsorption process of CO_2 and N_2 on coal. In addition, there is a certain amount of interaction among the CO_2/N_2 . Due to differences in factors such as SAC, various gases compete for adsorption under actual conditions in mining areas (Jin et al., 2017). Excavation of the face results in inert gas pipeline replacement, altering pipeline distances from specific points in goaf. This will affect the pressure at that point. Therefore, the SAC is used as an indicator parameter to investigate the competitive adsorption patterns of CO_2/N_2 in coal molecules. We compare the single gas adsorption and competitive adsorption behavior of CO_2 and N_2 at different pressures.

3.3.1. SAC of single-component

Fig. 11 shows the fluctuation of SAC for CO_2 and N_2 on coal at different temperatures within 0–5 MPa. During the increase of the adsorption capacity (0–2 MPa), the gases on coal are continuously transformed. As the pressure increases, the density of the free phase gas increases, forcing it to enter the adsorption phase. Due to the smaller kinetic diameter of CO_2 (3.3 Å) compared to N_2 (3.64 Å), it can enter more pore structures, hence offering a higher adsorption capacity compared to N_2 . At 2–5 MPa, the CO_2 adsorption capacity escalates by 0.03 mmol/g, nearing saturation, consistent with the capacity observed at the same temperature and pressure.

The temperature dependence of coal adsorption for CO_2 decreases with increasing temperature (Mustafa et al., 2020), which is consistent with previous investigations. The SAC decreases with temperature for both gases. However, a greater decrease is observed for CO_2 compared to N_2 which indicates that CO_2 adsorption on coal is more affected by temperature. At the same temperature/pressure, the SAC of CO_2 is higher.

After applying the Langmuir model for fitting, the parameters derived are shown in Table 8. The adsorption capacity $a_{(CO2)} > a_{(N2)}$ at the same temperature, indicating higher SAC of coal for CO₂. The adsorption equilibrium constant $b_{(CO2)} > b_{(N2)}$, indicating that the CO₂ adsorption rate on coal is significantly higher than N₂ at 0–2 MPa. As the pressure increases to 2 MPa, the increase in CO₂ adsorption slows and gradually approaches saturation, while N₂ adsorption continues to rise.

3.3.2. SAC of multi-component

In previous works, scholars have compared the adsorption capacities of sub-bituminous coal for various gas mixtures, including 100 % CO₂, 90 % CO₂ + 10 % N₂, 70 % CO₂ + 30 % N₂, 30 % CO₂ + 70 % N₂, 10 % CO₂ + 90 % N₂ and 100 % N₂. The findings indicated that CO₂ predominantly influences the coal inerting process (Yu et al., 2023). In addition, another investigation was conducted to investigate the pyrolysis combustion rate and thermodynamic properties of coal at 18 % O₂ concentration with different CO₂/N₂ ratios (10:0, 8:2, 6:4, 4:6, 2:8, and 0:10). A CO₂/N₂ ratio of 4:6 was found to have the best inhibitory effect on coal pyrolysis combustion (Wu et al., 2023). Thus, our investigation focuses on the investigation of the SAC of coal using CO₂/N₂ mixtures



Fig. 12. CO₂/N₂ competitive adsorption capacity on QYZ.



Fig. 13. CO₂/N₂ competitive adsorption selectivity on QYZ.

with ratios of 1:9, 2:8, 3:7, and 4:6 to offer insights into the coal inerting process.

Fig. 12 shows the variation of the competing SAC of coal for CO_2 and N_2 . Aligning with previous analyses, CO_2 plays a dominant role in the variation of total gas adsorption when examining CO_2/N_2 coalbed methane replacement technology (Sun et al., 2022). With an increment in the CO_2 content within the mixture, the curves of multi-component adsorption capacity align closer to that of CO_2 . The maximum SAC is observed at a CO_2 concentration of 40 %. It ranges from 0 to 1.909 mmol/g. The N_2 maximum adsorption capacity of 0–0.0895 mmol/g is observed only when the CO_2 concentration reaches 10 %. It is followed



Fig. 14. Priority of maximum saturated adsorption capacity.

 Table 9

 The AOR and AOD calculated results.

Threshold	C _S C _{4:6}	C _S C _{2:8}	C4:6 C2:8		
AOR	1.21	1.70	1.37		
AOD	0.25	0.59	0.34		

by a slow decrease with further increase of CO_2 concentration. In comparison, the variation range of N_2 adsorption capacity under singlecomponent conditions (0–5 MPa, 30 °C) is between 0–0.4338 mmol/g. N_2 is more affected by CO_2 during competitive adsorption.

Fig. 13 shows the adsorption selectivity of coal for CO_2 and N_2 . Adsorption capacity can provide a qualitative assessment of the relative strength of adsorption between two gases. However, for evaluating the magnitude of adsorption capacity, adsorption selectivity is more intuitive. The adsorption selectivity range of CO_2 competitively adsorbing N_2 is 99.55–302.7, significantly exceeding 1. Below 0.5 MPa, a higher CO_2 concentration gives better adsorption selectivity for N_2 . In contrast, at 1–5 MPa, a CO_2/N_2 ratio of 2:8 demonstrates superior adsorption advantages.

3.4. Optimization CO_2/N_2 ratio for SAC

Comparing the results of single-component and competitive adsorption of CO₂, it was observed that at each pressure, the SAC of single-component adsorption was larger than that of competitive adsorption. Long et al. similarly studied the analogous cases of adsorption capacities (Long et al., 2021). In the competitive adsorption, the maximum SAC was achieved when $CO_2/N_2 = 4:6$, reaching 1.909 mmol/g. Observe the adsorption selectivity, $CO_2/N_2 = 2:8$ was found to be the most favorable for coal adsorption of CO2 under most pressure conditions. Thus, we established a priority (shown in Fig. 14) based on the SAC at different pressures as follows: the maximum SAC of the single-component (C_S) > the SAC of $CO_2/N_2 = 4.6$ (C_{4:6}) > the SAC of $CO_2/N_2=2{:}8$ (C_{2:8}). Based on this, we developed a fuzzy optimization method for selecting the CO2/N2 proportion, using the absolute difference as the primary threshold and relative relations as the auxiliary threshold. Yan et al. used similar methods to propose effective prediction strategies for coal intensity changes due to carbon dioxide adsorption (Yan et al., 2020).

To examine the relative relationships between the values, we introduced the average of ratios (AOR) as an auxiliary threshold, which is represented by Eq. (1). The average of differences (AOD) as the primary threshold was then proposed to investigate the absolute differences between the values, as shown in Eq. (2).

$$AOR = \frac{\sum_{n=1}^{11} (a/b)_n}{11}$$
(1)

Table 10	
Optimization of CO_2/N_2 ratio (AOR & AOD).	

Pressure	SAC (mmol/g)		AOR ₁ 1.21	AOR ₂ 1.70	AOR ₃ 1.37	AOR Selection	AOD ₁ 0.25	AOD ₂ 0.59	AOD ₃ 0.34	AOD Selection	
	Cs	C4:6	C _{2:8}	Cs/C4:6	Cs/C2:8	C4:6/C2:8		Cs-C4:6	Cs-C2:8	C4:6-C2:8	
0.2	1.05	0.64	0.30	1.61	3.47	2.15	4:6	0.40	0.74	0.35	CO_2
0.5	1.30	0.94	0.59	1.38	2.19	1.59	CO_2	0.35	0.71	0.35	CO_2
1	1.52	1.19	0.87	1.28	1.76	1.37	CO_2	0.34	0.66	0.32	CO_2
1.5	1.76	1.37	1.08	1.28	1.62	1.26	CO_2	0.38	0.67	0.29	CO_2
2	1.86	1.49	1.24	1.25	1.51	1.21	CO_2	0.37	0.63	0.26	CO_2
2.5	1.98	1.63	1.31	1.21	1.51	1.24	CO_2	0.35	0.67	0.32	CO_2
3	1.92	1.69	1.44	1.14	1.33	1.17	2:8	0.23	0.48	0.25	2:8
3.5	1.89	1.84	1.49	1.03	1.27	1.23	2:8	0.05	0.40	0.35	4:6
4	2.01	1.91	1.51	1.05	1.33	1.26	2:8	0.10	0.50	0.40	4:6
4.5	2.11	1.93	1.51	1.09	1.40	1.28	4:6	0.18	0.60	0.42	4:6
5	2.00	1.94	1.51	1.03	1.32	1.28	2:8	0.06	0.49	0.42	4:6

$$AOD = \frac{\sum_{n=1}^{11} (a - b)_n}{11}$$
(2)

where *n* is the number of pressure stages, *a* is C_S or $C_{4:6}$, and *b* is $C_{4:6}$ or $C_{2:8}$.

Table 9 shows the calculated results. When the SAC is less than the corresponding threshold, the difference in coal adsorption characteristics between the two components is ignored and the subsequent priority is selected. CO_2/N_2 mixture ratio at 2:8 is selected if $C_S C_{4:6}$, $C_S C_{2:8}$, and $C_{4:6} C_{2:8}$ are all less than their respective threshold; CO_2/N_2 mixture ratio at 4:6 is selected if $C_S C_{4:6}$ and $C_S C_{2:8}$ are both less than their respective threshold; otherwise, CO_2 is selected.

Table 10 shows the optimum choice of CO_2/N_2 ratio based on AOR and AOD. There is a similar law between $C_S-C_{4:6}$ is below AOD₁ and $C_S/C_{4:6}$ is below AOR₁ at 3–5 MPa. $C_S/C_{2:8}$ is below AOR₂ at 1.5–5 MPa, and $C_S/C_{2:8}$ is below AOR₃ at 1.5–5 MPa. From the SAC, single-component CO₂ has the best effect at 0.2–2.5 MPa, while CO_2/N_2 mixture ratio at 4:6 is selected at 3.5–5 MPa owing to $C_S-C_{4:6}$ is below AOD₁. At 3 MPa $C_{4:6}-C_{2:8}$ is lower than AOD₃, so CO_2/N_2 mixture ratio at 2:8 is selected using adsorption selectivity as a reference.

4. Application of CO₂/N₂ ratio optimization method

Inerting technology encompasses the injection of CO_2/N_2 into the goaf through three methods: pipeline, buried pipeline, and borehole injection (Liang and Luo, 2008). This can be used to inert the coal at specific zone of goaf. However, as the working face advances, the distance between the injection pipeline and the target zone increases, as shown in Fig. 10. This leads to a redistribution of pressure at the zone. The injection process at the target zone can be seen as multiple-adsorption of CO_2/N_2 on coal. Investigation demonstrates that true effectiveness in inertization and fire prevention is achieved only when CO_2/N_2 adsorption nears saturation within the coal. This emphasizes the significance of optimizing inerting methods to maintain safe working conditions in coal mine.

In practical field applications, the fuzzy optimization method needs to accommodate the pressure of the CO_2/N_2 injection. For example, at 5 MPa, an optimal injection ratio of CO_2/N_2 mixture ratio at 4:6 can be selected. When the injection point moves backward, the pressure drops to 2.5 MPa, single-component injection of CO_2 becomes viable. This method facilitates the saturation adsorption of inerting gases on coal, leading to enhanced inerting efficiency and cost savings through reduced injection volume.

5. Conclusions

In this paper, different oxidation stages of QYZ and the influence of different CO_2 adsorption degree on CSC were studied through a series of experiments, and the SAC index was proposed. The adsorption

characteristics of CO_2/N_2 single-component and four multi-components under different pressures were studied using molecular simulation methods. Finally, the optimization method of CO_2/N_2 injection ratio based on SAC is proposed to provide theoretical parameter selection and guidance for mixed gas injection fire prevention in goaf. The main conclusions are as follows:

(1) In the program heating experiment, the physical adsorption stage temperature of QYZ is below 323.15 K. After pretreatment of QYZ with different CO₂ adsorption degree, the combustion activation energy of coal samples follows the sequence of second-stage adsorption coal > dried coal > raw coal > first-stage adsorption coal, which indicates that CO₂ saturated adsorption plays a crucial role in inhibiting CSC.

(2) Below 303.15 K, QYZ exhibits initial growth and gradual saturation in two CO_2 adsorption stages. The residual CO_2 from the first-stage adsorption affects the second-stage adsorption. Compared with previous studies, it is found that in the coal physical adsorption stage (303.15 K), the adsorption of CO_2 on coal gradually reaches a balance between adsorption and desorption with the increase of pressure, which is considered as the adsorption saturation of coal. Therefore, we propose the concept of Saturation Adsorption Capacity (SAC).

(3) The SAC of CO₂ is greater than that of N₂, and the SAC of CO₂/N₂ is mainly affected by the CO₂, which indicate that CO₂ has absolute superiority in single-component and competitive saturation adsorption. In this case, the average of ratios (AOR) and average of differences (AOD) threshold are determined. The priority of SAC is obtained in the order of single-component (C_S), CO₂/N₂ mixture ratio at 4:6 (C_{4:6}), CO₂/N₂ mixture ratio at 2:8 (C_{2:8}) from largest to smallest.

(4) A fuzzy optimization method of CO_2/N_2 injection ratio at different pressure is established according to the dynamic change of the actual goaf pressure, and the optimal CO_2/N_2 injection ratio was determined to achieve saturated adsorption of inert gas in coal. In actual production, the single-component CO_2 injection is selected between 0.2 to 2.5 MPa. At 3 MPa, a mixture of CO_2/N_2 at a ratio of 2:8 is the best for prevent fires in goaf. Similarly, an inert gas with a CO_2/N_2 ratio of 4:6 is injected at 3–5 MPa.

CRediT authorship contribution statement

Junhong Si: Funding acquisition, Investigation, Methodology, Project administration, Resources, Writing – review & editing. Zihao Zhao: Conceptualization, Visualization, Writing – original draft, Writing – review & editing. Lin Li: Investigation, Methodology, Resources, Writing – review & editing. Genyin Cheng: Funding acquisition, Project administration, Resources, Supervision. Junchao Chen: Investigation, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial

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interests or personal relationships that could have appeared to influence the work reported in this paper.

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