Advances in
Geo-Energy Research

Vol. 16, No. 3, p. 229-243, 2025

Original article

Methane hydrate formation characteristics under different initial conditions and their impact on coal seam properties

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Keywords:
Gas disaster prevention
gas hydrate formation
hydrate saturation
gas solidification
coal seam property

Cited as:
Sun, C., Liu, S., Li, S., Wang, K., Dong, Z., Kong, S. Methane hydrate formation characteristics under different initial conditions and their impact on coal seam properties. Advances in Geo-Energy Research, 2025, 16(3): 229-243.
https://doi.org/10.46690/ager.2025.06.04

Abstract:
Due to the unique structural characteristics of hydrate, it has a potential application value in coal and gas outburst prevention in coal mines. Given the complexity of subsurface environments, it is essential to investigate the hydrate formation kinetics under varied initial conditions, as well as the subsequent impacts of hydrate formation on coal seam properties. This research mainly focuses on the hydrate formation process in coal samples with different coalification degrees under different initial pressure and water saturation conditions by using the designed hydrate formation system. The results show that gas consumption and hydrate saturation can be greatly enhanced by increasing the initial water saturation and pressure, which is favorable to reduce the coal seam gas pressure and improve the coal seam peak strength. The calculation results suggest that hydrate formation at varying saturation reduces the gas pressure by 53.05% ∼ 91.33% and increases the peak strength of coal across the tested confining pressure by 36.45% ∼ 59%. Furthermore, this study found that hydrate formation kinetics are significantly enhanced in lignite compared to that in anthracite, which may be attributed to structural variations associated with the coalification degree. The underlying mechanism requires further research in the future. The data obtained in this study regarding the effect of hydrate formation under different initial conditions on coal seam properties demonstrate the feasibility of preventing gas disasters in coal via controlling the initial conditions.

1. Introduction

Coal, oil and natural gas as the three major fossil fuels in the world provide the main source of energy for human survival (Abas et al., 2015). According to data from the National Bureau of Statistics of China, fossil fuels accounted for about 82.5% of China's energy consumption in 2022, and they still dominate in terms of energy supply (Zhang et al., 2022; Chen et al., 2023). As the world's largest energy consumer, China follows an energy structure characterized by "rich coal resources, limited oil, and low gas reserves" (Wang et al., 2016; Zeng et al., 2021). While renewable energy sources progressively occupy an increasing share of the energy, coal as one of the main energy sources still accounts for about 56.2% of the energy structure, and this situation is not expected to change quickly (Zhang et al., 2023). The mining activity of coal may be accompanied by the occurrence of gas

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Yandy Scientific Press

Received February 25, 2025; revised March 19, 2025; accepted April 11, 2025; available online April 16, 2025.

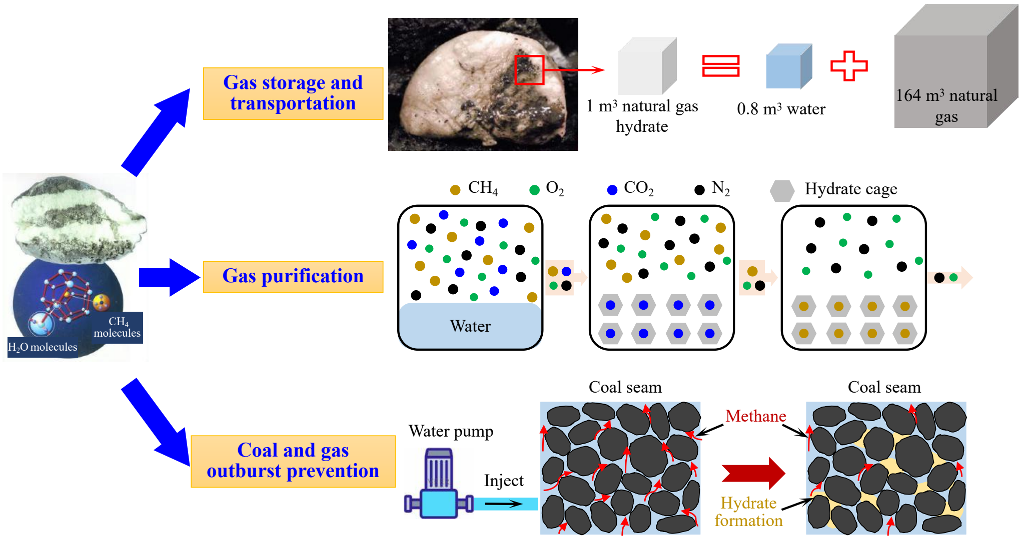

Fig. 1. The application of hydrate-based technology in many fields.

disasters. According to the National Energy Administration of China, the coalbed methane reserve buried within 2,000 m amounts to about 36.8 trillion m^3, ranking third among the global coalbed methane resources (Zhou et al., 2016). This makes China one of the countries with the most severe gas disasters; therefore, the control of gas is particularly important for mining safety.

Owing to the unique structural properties of hydrate, hydrate-based technology has fueled significant advancements in the field of purification of coal seam gas extraction, energy gas storage and transportation, and coal and gas outburst prevention (Yu et al., 2021), as shown in Fig. 1. As for the coal and gas outburst prevention based on hydrate technology, Makogon (1981) firstly proposed the hypothesis that hydrate may exist in coal seams. Later, Bustin et al. (2016) and Smirnov et al. (2016) demonstrated through experiments that the adsorbed water on the coal surface can form methane hydrate. On the basis of these studies, Wu et al. (2005) proposed the theoretical method of hydrate solidification for preventing coal and gas outburst in coal mines. They believed that for coal seams with an outburst risk, a portion of methane undergoes phase transition into hydrate within coal seam upon achieving hydrate formation conditions through high-pressure low-temperature water injection. This process leads to a substantial reduction in gas content and pore pressure, while the crystallized hydrate mechanically reinforces the coal structure by pore-filling and fracture-cementing, consequently mitigating the gas outburst risks during mining operations by delaying sudden gas desorption. For the constitutive model of hydrate-containing sediments, Yu et al. (2011) proposed a nonlinear elastic constitutive model based on the analysis of triaxial test results. Based on these results, Song et al. (2014) established a mechanical constitutive model of hydrate-containing sediments considering hydrate decomposition. These findings provide a valuable theoretical reference for subsequent research on the constitutive modeling of methane hydrate-bearing coal and the application of hydrate-based technology for coal and gas outburst prevention in mining operations.

However, due to the complex conditions of coal underground, there has been little research on the hydrate formation process under different coal seam properties, especially the effect of these properties on the hydrate formation kinetic parameters under different initial conditions and coalification degrees. Therefore, this study mainly investigated the methane hydrate formation process in coal media under different initial conditions and coalification degrees. By conducting a comprehensive analysis using both experimental observation and computational data, the influence law of initial pressure and water saturation on gas consumption, hydrate saturation, and water-hydrate conversion rate during hydrate formation in coal samples with different coalification degrees were obtained, and the relevant influencing mechanisms were also analyzed. In addition, based on the formed hydrate under different conditions, the reduction in gas pressure and the improvement in coal mechanical strength when forming hydrate with different saturations were discussed and analyzed. The relevant results can provide an important reference for the application of hydrate-based technology in gas prevention and utilization in coalbeds.

2. Materials and methods

2.1 Calculation of parameters

In the hydrate formation process, water cages formed by water molecules and hydrogen bonds will trap gas molecules, resulting in a continuous decrease in gas pressure (Aman et al., 2016). Similar to crystallization processes, hydrate formation is intrinsically exothermic, inducing temperature variations within the system. Accordingly, the hydrate formation process can be determined by monitoring the changes in system temperature and pressure, and using these data, some kinetic parameters related to hydrate formation can be calculated. In the experiment of methane hydrate formation, when injecting methane into the reactor at a certain temperature, t-

Table 1. Experimental groups for hydrate formation under different initial conditions.

Coal rank	Group	Design water saturation (%)	Design initial pressure (MPa)
Lignite	L1	40	15
	L2	50	15
	L3	80	15
	L4	80	12
	L5	80	18
Bituminous	B1	40	15
	B2	50	15
	B3	80	15
	B4	80	12
	B5	80	18
Anthracite	A1	80	15

he pressure will decrease continuously due to the dissolution of methane in water and the entry of methane molecules into the water cages. The hydrate formation process is considered complete when the reactor pressure stabilizes (Mech et al., 2016). The amount of methane that passes into the reactor can be determined according to the ideal gas law:

$$n_g = \frac{PV_g}{ZRT} \tag{1}$$

where n_g represents the amount of substance of gas, mol; P represents the gas pressure, MPa; V_g represents the gas volume, m^3; T represents temperature, K; Z represents the compressibility factor; R represents the gas constant with a value of 8.314 J/(mol·K). Upon hydrate nucleation, a progressive pressure reduction is observed in the reactor, and the amount of hydrate formed during this process can be obtained based on the gas consumption:

$$n_{ht} = \triangle n_{gt} = n_{g0} - n_{gt} = \frac{P_0 V_{g0}}{Z_0 R T_0} - \frac{P_t V_{gt}}{Z_t R T_t} \tag{2}$$

where n_{gt} denotes the amount of formed hydrate, mol; n_{g0} and n_{gt} respectively denote the total molar amount of methane at the beginning ($t = 0$) and end ($t = t$) of the reaction, mol. P_0 and P_t respectively denote the pressure in the reactor at the beginning and end of the reaction, MPa; V_{g0} and V_{gt} respectively denote the volume of methane at the beginning and end of the reaction, cm^3. To simplify the calculation, $V_{g0} = V_{gt}$ is often taken, and the volume change associated with hydrate-water phase transition in the reactor is considered negligible. T_0 and T_t are the temperature in the reactor at the beginning and end of the reaction, respectively, K. Since the constant temperature method is used in the experiment, the temperature in the hydrate formation process is considered stable. Z_0 and Z_t respectively represent compressibility factors corresponding to temperature and pressure at the beginning and end. In this study, the generalized compression factor diagram was used to determine the compressibility factors (Smith et al., 1949).

The amount of hydrate formed per unit volume can be calculated according to the volume of the reactor:

$$C_{ht} = \frac{n_{ht}}{V_R} \tag{3}$$

where C_{ht} is the amount of hydrate formed per unit volume, $\mathrm{mol/m}^3$; V_R denotes the volume of reactor, which is 565.5 cm^3 in this study. The formed hydrate saturation S_{ht} (expressed as a fraction) in the reactor at time t can be calculated by the following formula:

$$S_{ht} = \frac{n_{ht} V_{mh}}{V_R \varphi} \tag{4}$$

where V_{mh} represents the molar volume of hydrate, which is taken as 129.97×10^{-6} m^3/mol in this study; φ is the porosity of the sample in the reactor.

After the formation of hydrate, the water-hydrate conversion rate can be expressed as:

$$C_{wh}(\%) = \frac{\triangle n_{gt} N_h}{n_{w0}} \times 100 \tag{5}$$

where C_{wh} denotes the water-hydrate conversion rate; N_h is the hydration number, which is the number of water molecules required for the formation of hydrate. In this study, methane was used as the guest molecule, and the hydration number was 5.75 (Uchida et al., 1999). The parameter n_{w0} represents the initial molar amount of water, mol.

2.2 *Materials and apparatus*

Considering the differences in the characteristics of coal samples with different coalification degrees and the resulting differences in coal seam gas content, three kinds of coal samples (anthracite, bituminous, lignite) were selected for coalbed methane solidification experiments to study the hydrate formation process in different coal media under different initial conditions. As this study only focuses on the hydrate formation characteristics of gas within coal media of varying ranks, no detailed investigation was performed regarding the geological attribute of the coal sample source.

Before the test, coal samples were screened separately, and then coal powders with particle sizes of 60 ∼ 80 mesh were selected for the experiment. Considering the temperature and pressure conditions of hydrate phase equilibrium and the deep mining conditions, as well as the aim to improve the hydrate formation efficiency, three different initial pressures (12, 15, and 18 MPa) and initial water saturation (40%, 50%, and 80%) were set for laboratory measurements. To compare the effects of different coalification degrees and initial conditions of coal samples on the methane hydrate formation in coal media, 9 groups of experiments were designed for measurement. The specific groups are shown in Table 1.

The apparatus adopted the hydrate formation system designed by the Institute of Geology and Geophysics, Chinese Academic of Sciences (Beijing, China). The system primarily consists of five integrated components: high-pressure hydrate reactor, temperature control unit, data acquisition module, gas supply, and automated pressurization assembly. The experimental device and system schematic diagram are shown

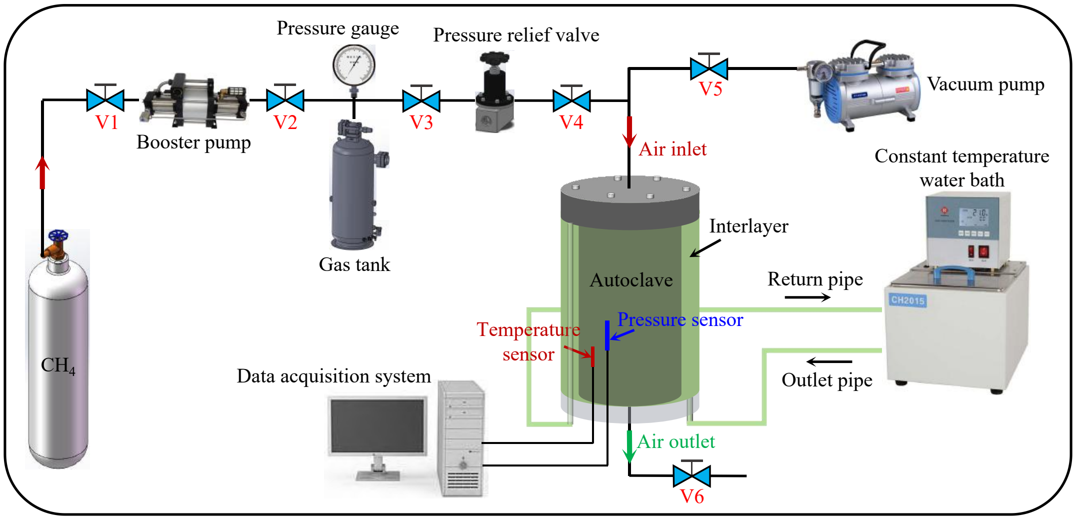

Fig. 2. Experimental apparatus and schematic diagram of the system.

in Fig. 2. The reactor comprises a cylindrical double-walled high-pressure vessel constructed with an aluminum alloy inner chamber rated for 30 MPa operation. With an effective internal geometry of 60 mm (diameter) × 200 mm (height), the system features an outer acrylic jacket enabling precise temperature regulation through circulating water bath control. A temperature sensor (PT100 type temperature sensor, effective temperature measurement range $-200 \sim +850$ °C, measurement accuracy of ± 0.1 °C) and a pressure sensor (WIKA A-10 type pressure sensor, effective measurement range $0 \sim 100$ MPa, measurement accuracy of ± 0.01 MPa) are used for continuous real-time monitoring of intra-reactor temperature and pressure dynamics. In the whole system, the methane gas source and the booster pump are connected through the pipeline, and the pressurized gas is stored in the gas tank that is connected with the reactor through the pressure relief value. The gas pressure is controlled by the pressure relief valve. During the controlled cooling and depressurization phases of the reactor's operation cycle, the data acquisition system continuously monitors and records the evolving temperature and pressure within the vessel, and the data collection is set to be performed every 20 s.

2.3 Experimental scheme

According to the hydrate formation system described above, the specific experimental scheme was as follows: Firstly, the reactor was filled with the prepared coal samples and the quality was recorded. The reactor was sealed, followed by the preparation of coal samples with precisely controlled water saturation according to the experimental design. The specific method is shown in Fig. 3. Before the test, the reactor was evacuated with a vacuum pump, and at the same time, the temperature was raised by the temperature control system to ensure that no hydrate formed during the initial pressurization stage. Upon stabilization of the reactor's internal temperature and pressure, the pressure reduction valve was systematically regulated to introduce gas and achieve gradual pressurization. After reaching the predetermined pressure setpoint, the temperature control system was activated to progressively cool the system to 10 °C for hydrate formation. Throughout this process, the reactor's internal temperature and pressure were continuously monitored and recorded by the data acquisition system. Hydrate formation was considered complete when the system pressure remained stable for a minimum duration of 4 h or longer.

According to the experimental schematic, following the preparation of coal samples with designed water saturation, the reactor was connected to the gas supply system, then evacuated, and subsequently pressurized through controlled gas injection. To simplify the operation and reduce the issues of airtightness caused by the disassembly and assembly of the device, the only changed parameter in the experiment was the initial pressure of the measurement group affected by different initial pressures under the same water saturation conditions, as long as it was ensured that the hydrate was fully decomposed and left at room temperature for a long time. Due to the memory effect of hydrate and to ensure the accuracy of the obtained data, the influence of different initial conditions on the rate of hydrate formation in different experimental groups was ignored.

3. Results and analysis

Following the experimental design, this investigation systematically examined the methane hydrate formation characteristics within coal media of varying ranks under controlled initial conditions. Certain kinetic parameters were obtained, such as gas consumption, hydrate saturation, and water-hydrate conversion rate in the hydrate formation process based on the acquired data. The detailed data are shown in Table 2.

3.1 Water saturation-dependent hydrate formation dynamics

Consistent with the experimental design, the methane hydrate formation process in two different coal media (lignite

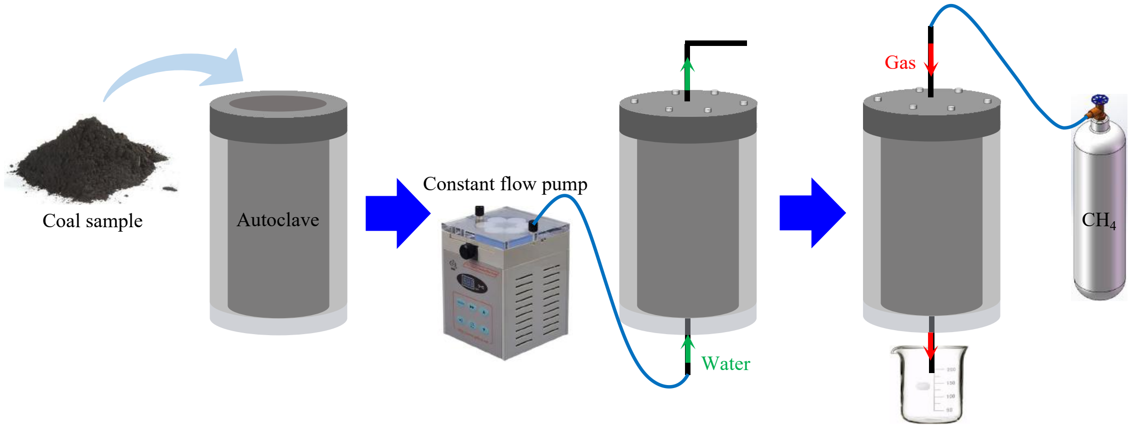

Fig. 3. Preparation of experimental samples with the designed water saturations.

Table 2. Parameters of methane hydrate formation in coal under different conditions.

Group	Temperature (°C)	Water saturation (%)	Initial pressure (MPa)	End pressure (MPa)	Gas consumption (mol)	Hydrate saturation (%)	Conversion rate (%)
L1	9.8	42	15.60	9.60	0.9056	45.80	86.79
L2	9.8	52	15.30	9.10	0.9327	47.33	72.58
L3	10.1	82	15.83	8.67	1.0715	54.19	52.81
L4	10.1	81	12.58	7.44	0.7880	39.59	38.84
L5	10.0	80	18.13	10.03	1.1616	58.45	58.36
B1	9.9	41	15.20	10.12	0.7303	38.83	75.59
B2	10.0	51	15.10	9.13	0.8685	46.78	72.79
B3	9.7	81	15.15	8.82	0.9204	48.63	47.63
B4	9.8	79	12.55	7.38	0.7561	39.70	39.93
B5	10.3	81	18.10	10.54	1.0246	54.13	53.02
A1	10.1	81	15.23	9.29	0.8460	45.44	44.90

and bituminous) was mainly measured under initial water saturations of about 40%, 50% and 80%. The monitoring and calculation data of some parameters are shown for groups L1-L3 and B1-B3 in Table 2. Fig. 4 presents the pressure change curves with time during the methane hydrate formation in lignite (a) and bituminous (b) under different initial water saturation conditions when the initial pressure is 15 MPa and the formation temperature is about 10 °C. It can be seen that the pressure drops rapidly after hydrate formation under different initial water saturation conditions, and the pressure reduction rate gradually slows down as time progresses, which means that hydrate will form rapidly in the initial stage of formation when the temperature and pressure are appropriate, and there is a short induction time. In the later stage of hydrate formation, the driving force decreases due to the decrease in pressure. The formed hydrate film hinders the contact and migration of gas and water, so the formation rate gradually decreases until the end of the hydrate formation stage. For these two kinds of coal samples, the final pressure after hydrate formation becomes lower with the increase in the initial water saturation under the same initial pressure and temperature, which means that water saturation is closely related to gas consumption under the forming conditions of gas saturation. Therefore, it is necessary to quantitatively analyze the influence of initial water saturation on some relevant kinetic parameters of hydrate formation.

Next, the variations in gas consumption, hydrate saturation, and water-hydrate conversion rate with water saturation during methane hydrate formation in lignite and bituminous were analyzed. As shown in Fig. 5(a), gas consumption increases with the increase in water saturation in the two coal media, while gas consumption is higher in lignite under each water saturation condition compared with bituminous. Fig. 5(b) presents the correlation between initial water saturation and the resultant hydrate saturation. Hydrate saturation is mainly affected by the gas consumption and the void volume in the reactor. In both coal media, hydrate saturation demonstrates trends analogous to gas consumption, exhibiting progressive enhancement with increasing water saturation. However, Fig. 5(c) reveals an inverse relationship between water saturation

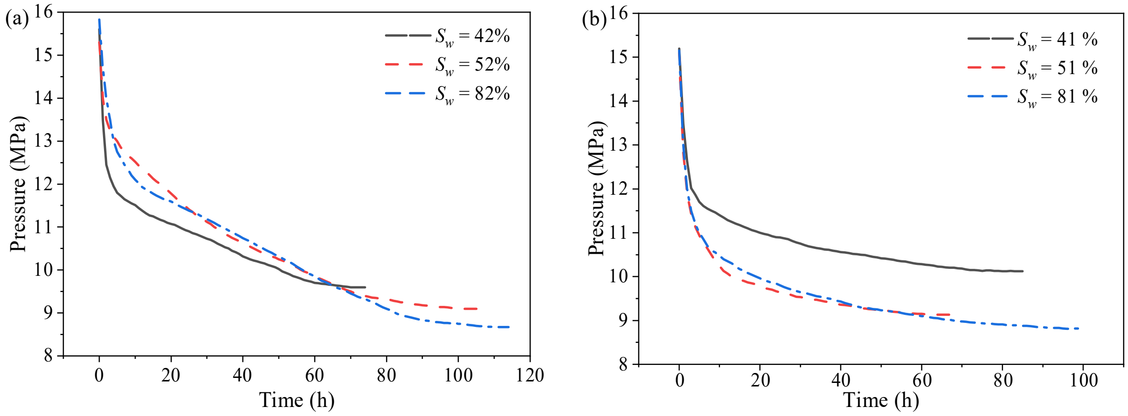

Fig. 4. Pressure change curves with time during methane hydrate formation under different initial water saturations (S_w) at an initial pressure of 15 MPa: (a) Lignite and (b) bituminous.

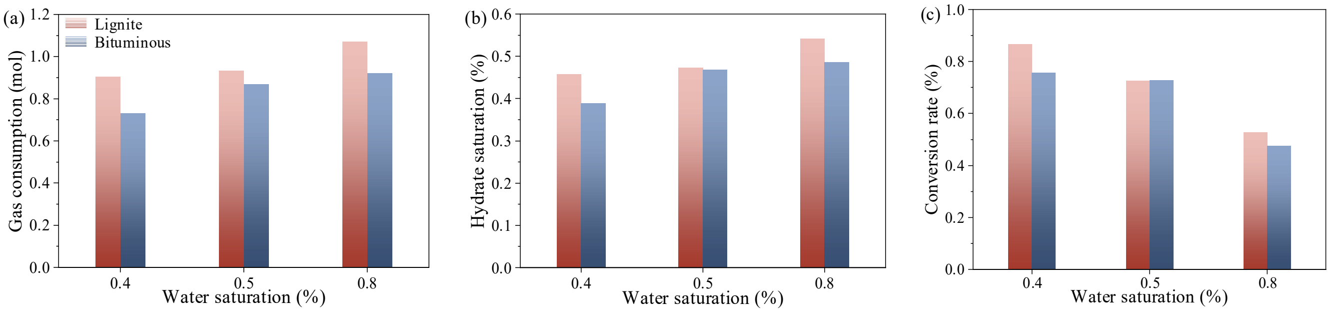

Fig. 5. Effect of water saturation on the change in the related parameters of hydrate formation in lignite and bituminous at an initial pressure of 15 MPa: (a) Gas consumption, (b) hydrate saturation and (c) water-hydrate conversion rate.

and the water-hydrate conversion rate in two coal media, that is, the greater the water saturation, the lower the water utilization efficiency, although more gas may be consumed and more hydrate may be formed in this scenario. Elevated water saturation enhances both gas consumption and hydrate saturation, yet it concomitantly reduces the water-hydrate conversion rate, suggesting the incomplete phase transformation of pore water into hydrate.

Under relatively low water saturation conditions, the majority of water exists in adsorbed states on coal particles surfaces (Wang et al., 2020). When the temperature and pressure are appropriate, methane and water will preferentially form hydrate on the coal surface, instead of slowly diffusing into the water. Therefore, hydrate will also have a faster formation rate under relatively low water saturation conditions. In this study, a water saturation of 40% ∼ 50% was more conducive to the full formation of hydrate. Gas consumption, hydrate saturation and water-hydrate conversion rate have similar law changes with water saturation in the two coal media. At the same time, hydrate formed in lignite has higher values for gas consumption under the measured three water saturation conditions, hydrate saturation and water-hydrate conversion rates, indicating that lignite may be more conductive to hydrate formation.

The increase in water saturation provides more water molecules for hydrate formation, and the uniform distribution of water in the reactor allows for a larger contact area between methane and water molecules (Xia et al., 2024). From the perspective of gas and water migration, most water is adsorbed on the coal medium surface at a relatively low water saturation, resulting in partial pore cavitation and thus a higher water-hydrate conversion rate under the gas saturation condition. However, elevated water saturation adversely affects the uniformity of water distribution in the void, leading to localized water accumulation. The formation of hydrate film on coal particle surfaces progressively expands the gas-water contact barrier through lateral growth, reducing the available space for subsequent hydrate formation. Meanwhile, the growth along the vertical thickness will hinder the migration and contact between gas molecules and water molecules in the solution, interrupting the hydrate formation process and reducing the conversion rate of hydrate (Li et al., 2010; Ge et al., 2019). This effect is represented in Fig. 6. Therefore, if the increase in water saturation is controlled and the distribution of water in the medium is uniform, the kinetic process of hydrate formation can be enhanced through controlled increases in water saturation. When the water saturation reaches a certain level, the uniform water distribution in the medium is affected. Although the gas consumption and the amount of hydrate will be increased to a certain extent, the formation of hydrate

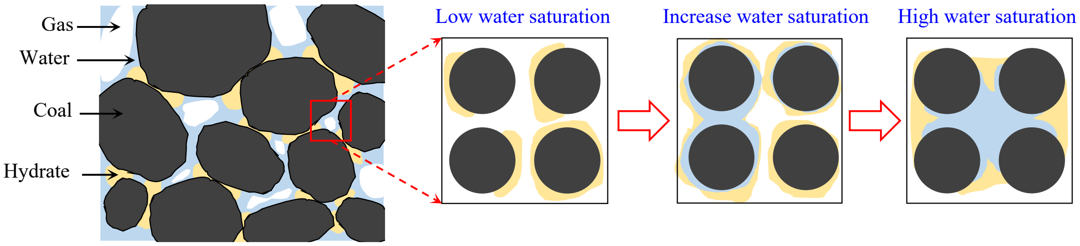

Fig. 6. Description of the hydrate formation process under different water saturation conditions, illustrating that the formed hydrate may hinder further contact between gas and water when the water saturation increases to a certain extent.

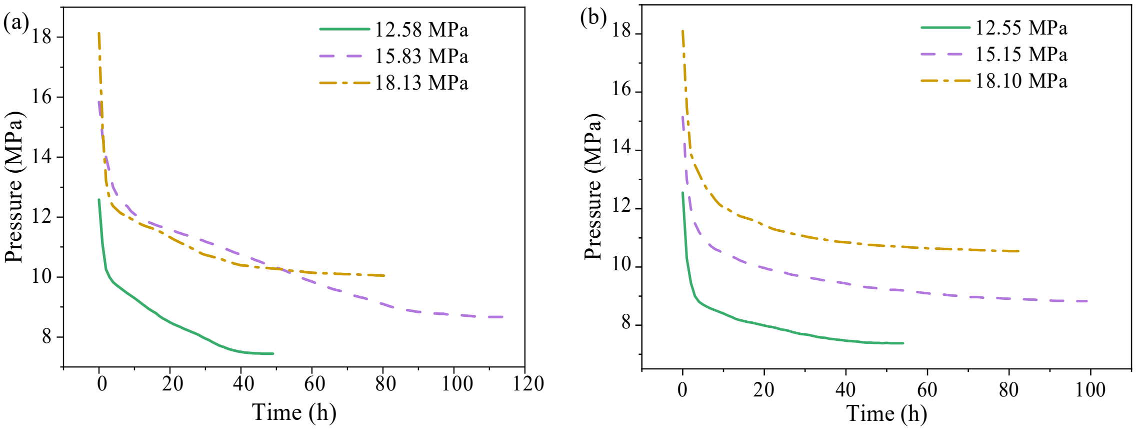

Fig. 7. Pressure change curves with time during methane hydrate formation under different initial pressures at an initial water saturation of 80% for (a) Lignite and (b) bituminous.

film between particles will hinder the further contact between gas and water, resulting in a decrease in the water-hydrate conversion rate.

3.2 Pressure-dependent hydrate formation dynamics

The methane hydrate formation process was systematically investigated in both lignite and bituminous coal media under controlled initial pressures of 12, 15 and 18 MPa. The monitoring and calculation data of some parameters are shown for groups L3-L5 and B3-B5 in Table 2. Fig. 7 presents the pressure change curves with time during the methane hydrate formation in lignite (a) and bituminous (b) under different initial pressure conditions at a water saturation of 80% and formation temperature of about 10 °C. It can be seen that the pressure rapidly decreases after hydrate formed in two coal media in the early stage of the reaction, and this decreasing trend slows down gradually with time. The experimental results demonstrate that the maximum pressure drop during hydrate formation occurs under higher initial pressure conditions, indicating that there is a greater driving force in the initial stage for hydrate formation, resulting in a rapid hydrate formation and pressure decrease. The observed pressure reduction deceleration during the later reaction stages primarily results from the hydrate-induced obstruction of interparticle gas and water diffusion pathways. Concurrently, progressive gas depletion diminishes the driving force for both gas diffusion and subsequent hydrate formation.

On the basis of the above analysis, some kinetic parameters of hydrate formation were quantitatively evaluated across varying initial pressure conditions. Fig. 8 presents the obtained pressure-dependent relationship for gas consumption, hydrate saturation and water-hydrate conversion rate in both coal media, suggesting that there is a consistent positive correlation between initial pressure and all measured parameters in both lignite and bituminous. Both the hydrate yield and conversion efficiency remain comparatively low, consistent with prior investigations examining the effects of pressure on hydrate formation in porous media (Stern et al., 1996; Zhang et al., 2019). The comparison results also show that the formation of hydrate in the two coal media has similar kinetic parameters at a relatively low initial pressure (12 MPa), and the influence of pressure on the hydrate formation is less affected by the difference in coal sample properties. As the initial pressure increases, the effect of pressure on the kinetic parameters becomes apparent depending on the coal sample. Hydrate formation in lignite has a higher kinetic process than that in bituminous. This is because compared with bituminous, lignite contains more water and relative carbon content, and the abundant oxygen-containing groups on its surface (such as carboxyl groups and phenolic hydroxyl groups, etc.) make it more hydrophilic (Liu et al., 2020). Under the same water saturation condition, more water is adsorbed on the surface of

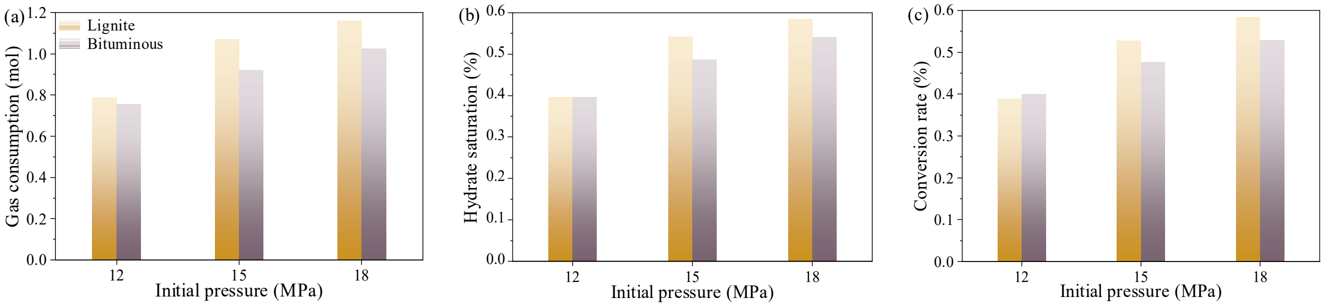

Fig. 8. Effect of initial pressure on the change in the related parameters of hydrate formation in lignite and bituminous at an initial water saturation of 80%: (a) Gas consumption, (b) hydrate saturation and (c) water-hydrate conversion rate.

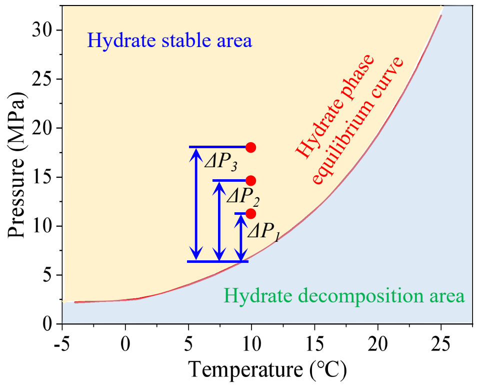

Fig. 9. Pressure difference leading to hydrate formation under different driving forces.

coal particles, reducing the adsorption of methane molecules on the coal surface, as well as increasing the dissolution of gas in water (Wang et al., 2020), thus promoting the formation of hydrate.

The hydrate formation rate and some related kinetic parameters are proportional to the driving force when the water saturation is determined under constant temperature, which is mainly controlled by the pressure difference $\triangle P$ between the initial pressure and the equilibrium pressure (Ribeiro Jr and Lage, 2008). An increased pressure differential indicates greater deviation from the phase equilibrium boundary, thereby enhancing the driving force for hydrate formation, as shown in Fig. 9. Since hydrate formation is a process where guest molecules are encapsulated within hydrogen-bonded water cages, the increase in driving force can improve the formation probability of water cages along with the binding ability of guest molecules and water cages, thus promoting the formation of hydrate crystals (Guo et al., 2009).

Hydrate is formed mainly in the spaces between sediment particles. In a sediment medium with relatively uniform water distribution, the particles not only provide spaces for the adsorption of gas and water but also nucleation sites for the hydrate. Under suitable pressure and temperature conditions, the heterogeneous nucleation mechanism governs the preferential formation of hydrate crystals on the particle surfaces (Sosso et al., 2016; Khurana et al., 2017). When the water saturation in the sediment reaches a certain degree, the surface of particles may be covered by a certain thickness of water. In this case, the hydrate film is first formed on the gas-liquid surface, and then gradually increases in thickness through longitudinal growth (Zhang et al., 2021). When the initial pressure is small, this lower pressure cannot provide enough driving force for the gas molecules to penetrate the formed hydrate film and react with the water molecules inside. The subsequent increase in initial pressure enhances the ability of gas to penetrate the hydrate film, thereby changing the formed hydrate saturation and conversion rate of hydrate. When the particles cannot be fully covered by water to form a water film, they will connect with each other by a liquid bridge due to the action of capillary force (Xia et al., 2023). At this time, water between the particle spaces is surrounded by hydrate film formed by liquid bridge. If the initial pressure is small or the hydrate film is thickened to a certain extent, the water in the void cannot contact with the gas anymore to form hydrate. Fig. 10 illustrates the promoting effect of increasing initial pressure on hydrate formation under different water saturation conditions. Meanwhile, from an energy perspective, the increase in initial pressure decreases the molar Gibbs free energy of the gas-liquid system, raises the collision frequency between gas molecules and water molecules at the liquid surface, improves the nucleation probability, and accelerates the formation rate of hydrate crystals (Sayani et al., 2021; Kvamme, 2022).

3.3 Coal rank-dependent hydrate formation dynamics

The preceding analysis has revealed distinct variations in the hydrate formation kinetics across different water saturations and initial pressures within the coal media, demonstrating the significant influence of coal matrix properties on the hydrate formation dynamics. Therefore, this study further compared the hydrate formation process in three coal media with different coalification degrees under the same water saturation (80%) and initial pressure (15 MPa). From the analysis of the obtained temperature and pressure data during hydrate formation, some relevant kinetic parameters were acquired, as shown in groups L3, B3 and A1 in Table 2. Fig. 11 presents the pressure change curves with time during the methane hydrate formation in the three coal media under the initial pressure of

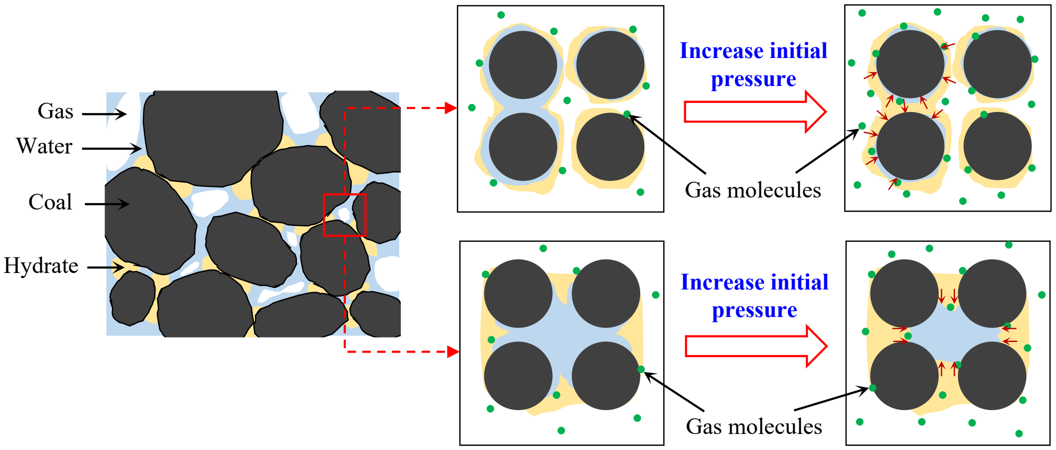

Fig. 10. Description of the hydrate formation process with the increase in initial pressure under low and high water saturation conditions.

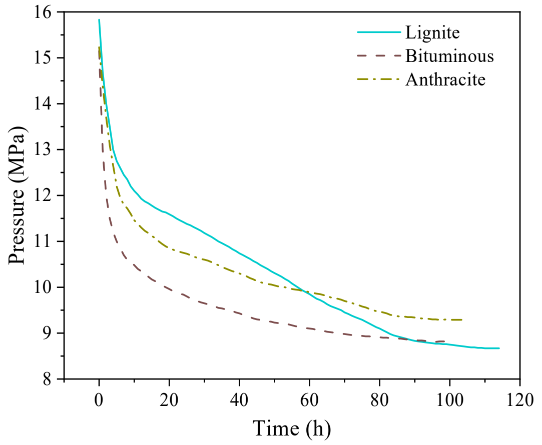

Fig. 11. Pressure change curves with time during methane hydrate formation under the initial pressure of 15 MPa and initial water saturation of 80%.

15 MPa and initial water saturation of 80% at the formation temperature of about 10 °C. It can be seen that the hydrate formation rate in the three coal media is relatively high at the initial stage, but the final pressure after hydrate formation is quite different under the same driving force and gas-water content. Compared with hydrate formation in bituminous and anthracite, the final pressure in lignite is lower, which means that lignite may be more conducive to hydrate formation under the tested conditions.

To quantitatively evaluate the differential kinetics of methane hydrate formation in distinct coal media, this study conducted the calculations and analysis of some parameters in three coal media. The variation trends in gas consumption, hydrate saturation and water-hydrate conversion rate with respect to the degree of coalification during hydrate formation are depicted in Fig. 12. It is evident that as the coalification degree increases, there is a corresponding decrease in gas consumption, hydrate saturation and the water-hydrate conversion rate during hydrate formation. This suggests that hydrate formed in lignite exhibits the highest kinetic process, followed by that in bituminous, while that in anthracite displays the lowest. During the initial formation stage of coal, a myriad of physical and chemical processes lead to the significant differences in the composition of coal with varying degrees of coalification. As coal evolves from lignite to anthracite, the influence of high temperature and pressure underground results in a decrease in moisture and volatile components, accompanied by a relative increase in carbon content (Ahamed et al., 2019). When methane hydrate forms in different coal samples at set water saturation and pressure conditions, the decrease in intrinsic moisture and change in oxygen-containing functional groups on the coal surface may be the main reasons influencing the variation in some kinetic parameters of this hydrate. According to the different structures of coal, its macromolecules can be divided into different "basic structural units". These different structural units are connected by bridge bonds and have different alkyl side chains and oxygen-containing functional groups on their surfaces (Xie, 2015; Xia et al., 2020). The structural units of different kinds of coal are shown in Fig. 13.

From a microscopic viewpoint, the mechanism governing hydrate formation is predominantly dictated by the binding ability between gas molecules and water molecules. Under isothermal-isobaric conditions, when external perturbations induce the aggregation of water molecules, the intermolecular interactions are enhanced, promoting the formation of water cages. This structural reorganization significantly improves the host-guest binding affinity between water cages and gas molecules, thus increasing both the yield and conversion efficiency of hydrate formation. Taking the basic structural unit types of coal with different metamorphism degrees as bases, it is known that the variations in elemental compositions and the presence of oxygen-containing functional groups on the coal surface exert a significant influence on the distribution pattern of water molecules (Liu et al., 2021; Ren et al., 2023). Lignite exhibits pronounced hydrophilic characteristics owing to its abundant oxygen-containing functional groups, particularly hydroxyl and carboxyl groups. Serving as effective hydrogen

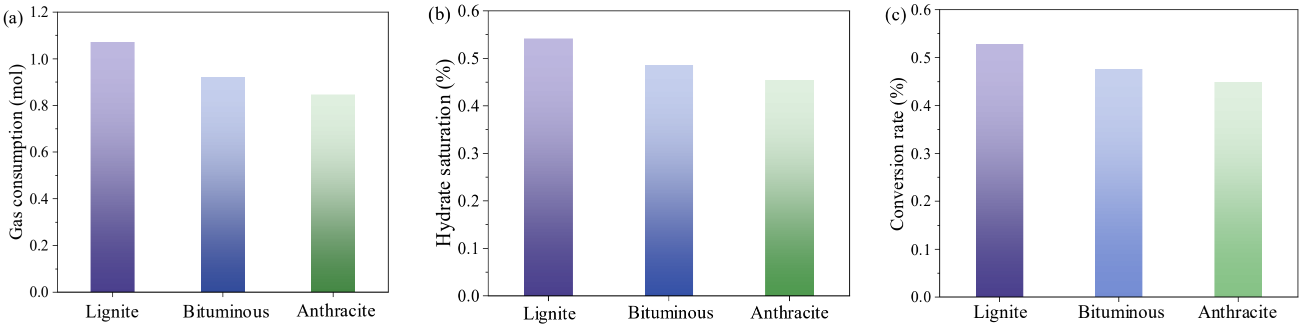

Fig. 12. ffect of coalification degree on the change in related parameters of hydrate formation at an initial pressure of 15 MPa and water saturation of 80%: (a) Gas consumption, (b) hydrate saturation and (c) water-hydrate conversion rate.

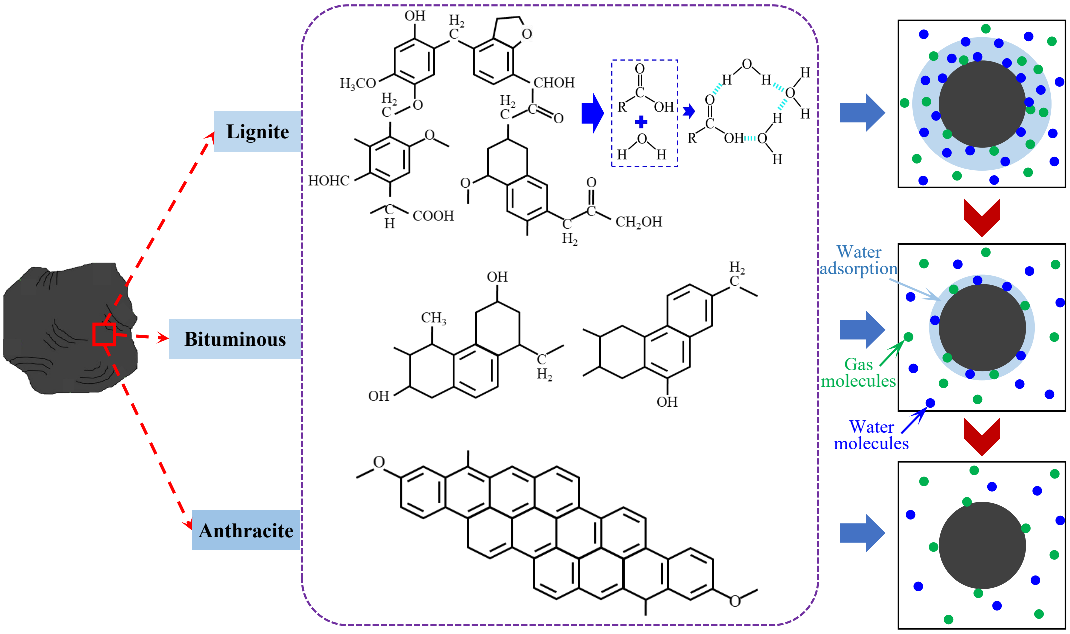

Fig. 13. Basic structural unit model of coal media with different coalification degrees and the adhesion states of water molecules on the surface.

bond acceptors, these hydroxyl groups can readily establish hydrogen bonding networks with water molecules (Medhekar et al., 2010). This molecular interaction significantly accelerates the nucleation and growth of hydrate cages. Under identical formation driving forces, the accelerated development of hydrate cages significantly reduces the nucleation induction time. Concurrently, oxygen-containing functional groups facilitate the generation of a greater number of molecular clusters with critical nucleus sizes, thereby enhancing the overall hydrate formation kinetics. The substantial adsorption of water molecules on the coal surface results in an enlarged contact area with gas, thereby fostering a more favorable environment for the formation and transformation of hydrate. The limited presence of hydrophilic functional groups on anthracite surfaces results in minimal water molecule adsorption. Consequently, water and gas molecules maintain a relatively homogeneous distribution, leading to significantly slower hydrate formation kinetics compared to lignite under identical conditions. The principle of adsorption states of gas and water molecules on coal surfaces with different coalification degrees is shown in Fig. 13.

4. Discussion

Research on the hydrate formation process can provide valuable references for the application of hydrate-based technology for many fields. In this study, the effect of initial conditions on certain kinetic parameters of hydrate formation under different coal samples was analyzed, and the results obtained will provide ideas for the solidification of coalbed methane. The dissociation of hydrate constitutes an endothermic process. Considering the low thermal conductivity of hydrate, it is difficult to transfer heat from the surroundings to achieve the condition of continuous decomposition of hydrate in a short time (Cai et al., 2020). Therefore, during the mining

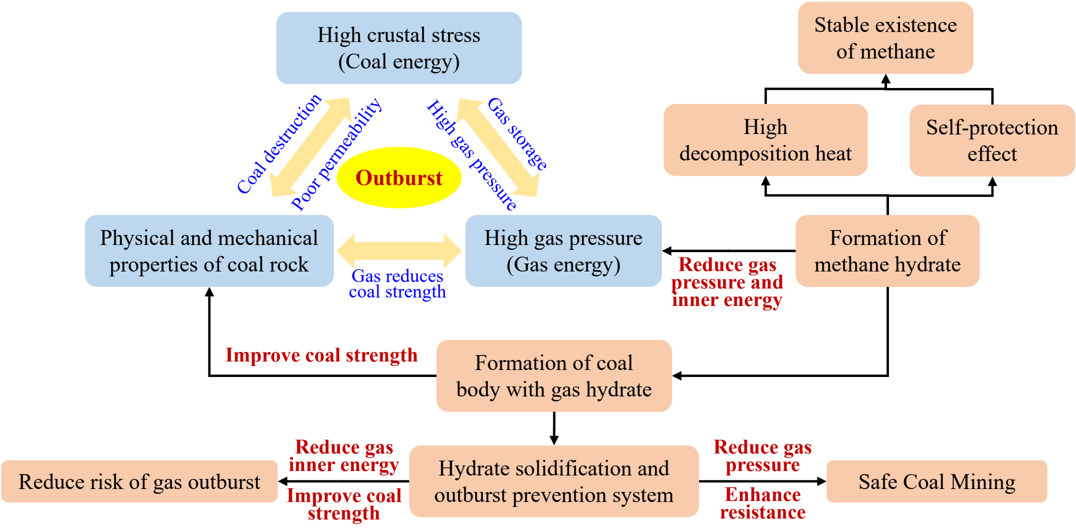

Fig. 14. Process of using hydrate-based technology for gas solidification to prevent coal and gas outbursts in coal mining (Wu and Zhang, 2024).

operation in coal and gas outburst mines, although the crushing of coal will destroy the hydrate equilibrium conditions, it will not cause coal and gas outburst accidents. When applying hydrate-based technology for coal seam gas solidification, the crux of the matter lies in determining whether the formation of hydrate with varying saturations can effectively mitigate gas pressure/content within the coal seam or substantially augment the strength of the coal. This assessment is pivotal in ascertaining the viability and efficacy of hydrate-based technology for coal seam gas solidification. According to the research conducted by Wu and Zhang (2024), the process of using hydrate-based technology for gas solidification to prevent coal and gas outbursts in coal mining can be represented in Fig. 14.

Reducing the gas content and pressure in coal seams can effectively lower the occurrence of coal and gas outburst disasters. In order to analyze the application effect of hydrate-based technology in coal gas consolidation and outburst prevention, this study mainly focuses on the influence of hydrate with different saturations formed in coal media under different conditions on gas pressure and coal mechanical properties. Based on previous studies (Wu and Zhang, 2024), the following assumptions were made: 1) The gas in the coal seams is approximately a standard gas, of which the free gas satisfies the ideal gas law. 2) The porosity of coal is about 10% $\sim$ 40% (mainly referring to experimental coal). The gas content per cubic meter of coal is about 6 $\sim$ 20 m^3, with the proportion of free gas being about 15%. 3) The volume of pores per cubic meter of coal is 0.1 m^3 when the porosity of coal is 10%. Therefore, the gas pressure for different free gas contents per cubic meter of coal can be gained based on the above assumptions and the ideal gas law (Wu and Zhang, 2024):

$$P=\frac{nRT}{V}=\frac{\rho vRT}{MV} \tag{6}$$

where M represents the molar mass of methane, 16 g/mol; ρ represents the methane density at room temperature and pressure, 0.7174 kg/m^3; v represents the volume of methane, m^3; n denotes the amount of methane substance, mol; V is the volume of pores per cubic meter of coal, m^3.

According to the assumptions, the gas content per cubic meter of hydrate is 164 m^3 when methane molecules completely occupy the hydrate cages and hydrate is formed in 0.1 m^3 pore space per cubic meter of coal. At this time, the solidified gas content can be obtained based on the formed hydrates characterized by different saturations.

Currently, there is no consistent conclusion on the proportion of adsorbed and free gas consumed during the formation of methane hydrate in porous media. However, it can be confirmed that hydrate nucleation preferentially occurs on the surface of solid particles, as these regions act as primary nucleation sites for hydrate formation (Warrier et al., 2016; Ke et al., 2019; Nguyen et al., 2020). Due to the adsorption of water molecules on the coal surface, adsorbed gas in non-water saturated coal media may be consumed preferentially during hydrate formation, while only a portion of free gas is consumed. Therefore, when analyzing the effect of hydrate formation on gas pressure in coal seams, assuming that only 25% of the solidified gas comes from free gas during hydrate formation, the pressure change of coal seam after hydrate formation can be obtained according to Eq. (6). Considering that the hydrate formed by the adsorbed gas in the coal pores will occupy the pore spaces, the influence of the dynamic changes between free gas and adsorbed gas resulting from the consumption of adsorbed gas caused by hydrate formation involved in the calculation was ignored. Table 3 shows the theoretical values of coal gas pressure before and after the formation of hydrate with different saturations in bituminous and anthracite. The initial gas content is assumed based on the gas content per cubic meter of coal.

It can be seen from Table 3 that the formation of hydrate with different saturations has a significant effect on the redu-

Table 3. Theoretical values of gas pressure before and after methane hydrate formation in coal under different conditions.

Group	Initial gas (m^3)	Pressure before (MPa)	Hydrate saturation (%)	Consolidated gas (m^3)	Pressure after (MPa)	Pressure reduction rate (%)
B5	4.47	0.73	31.04	1.63	0.29	60.60
B5	5.11	0.84	31.04	1.63	0.39	53.03
B2	4.49	0.74	38.83	2.04	0.18	75.81
B2	5.14	0.84	38.83	2.04	0.28	66.33
B3	4.54	0.74	46.78	2.49	0.06	91.33
B3	5.19	0.85	46.78	2.49	0.17	79.92
A1	5.82	0.95	52.15	2.77	0.20	79.19
A1	7.12	1.17	52.15	2.77	0.41	64.79

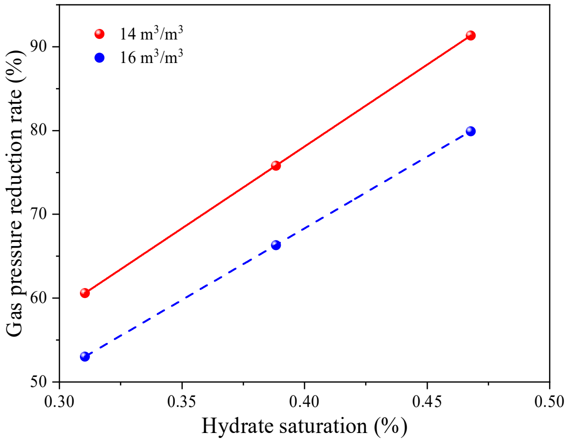

Fig. 15. Effect of different hydrate saturations on the gas pressure reduction in bituminous media when the coal gas contents are 14 and 16 m^3/m^3.

ction rate of coal seam gas pressure in bituminous and anthracite; the reduction rate reaches 53.05% ∼ 91.33%. Comparative analysis reveals that there is a notable gas pressure reduction in coal seam. The gas pressure in the two coal media decreases from 0.73 ∼ 1.17 MPa prior to consolidation to merely 0.41 MPa afterwards. This post-consolidation pressure is below the critical pressure of 0.74 MPa associated with coal and gas outburst. Compared with the gas pressure prior to hydrate formation, the generation of hydrate with different saturations leads to a substantial decrease in gas content within the coal, which effectively lowers the risk of coal and gas outburst. On the basis of the influence of hydrate formation on the decrease in gas pressure in coal, the relationship between hydrate saturation and pressure decline rate in bituminous was obtained through curve fitting, as shown in Fig. 15. It can be seen that the gas pressure reduction rate in coal shows a linear relationship with hydrate saturation under different gas contents in coal, suggesting that higher hydrate saturation can lead to a lower gas pressure in coal, hence a diminished risk of coal and gas outburst.

At the same time, for the areas with high gas pressure, the coal body has high elastic energy and low strength. Mining operations induce the structural degradation of coal seams, significantly altering the physical and mechanical characteristics of the coal body. When the coal seam gas convers into hydrate, the reduction in gas content is conductive to reducing the gas internal energy, improving the strength of coal, thus reducing the occurrence of outburst accidents. Gao et al. (2018) studied the changes in the peak strength of coal under different confining pressure conditions under different hydrate saturations in coal by a three-axis experimental device, and proved that the formation of hydrate enhances the ability of coal to resist external forces. The relationship between the peak strength of coal and confining pressure under different hydrate saturation conditions is shown in Fig. 16(a). From the above relationship in the sample, the variation law of peak strength with hydrate saturation under different confining pressure conditions can be obtained through fitting. In this study, it was assumed that the peak strength of coal with different hydrate saturations formed in bituminous also exhibits a similar variation law with confining pressure as in the Taoshan Coal Mine above. Therefore, taking the relationship between the peak strength of Taoshan coal samples with hydrate saturation under different confining pressure conditions determined by the above fitting as a basis, combined with the saturation data of hydrate formed in bituminous coal obtained in this study, the variation law of peak strength of bituminous with hydrate saturation under different confining pressures could be obtained, as shown in Fig. 16(b). It can be seen that the formed hydrate in bituminous can significantly improve the peak strength of coal, which increases with rising hydrate saturation. Compared with low confining pressure, hydrate saturation exerts a more pronounced enhancement on coal peak strength under elevated confining pressures relative to low-pressure conditions. When the confining pressure is 4 MPa, the peak strength of coal containing hydrate only increases from 4.15 to 6.53 MPa when the hydrate saturation increases from 31% to 59%, corresponding to an increase rate of 36.45%. However, when the confining pressure is 6 MPa, the peak strength increases from 4.88 to 11.24 MPa, equivalent to an increase rate of 56.58%. The observed correlation between coal peak strength and hydrate saturation across varying confining pressures

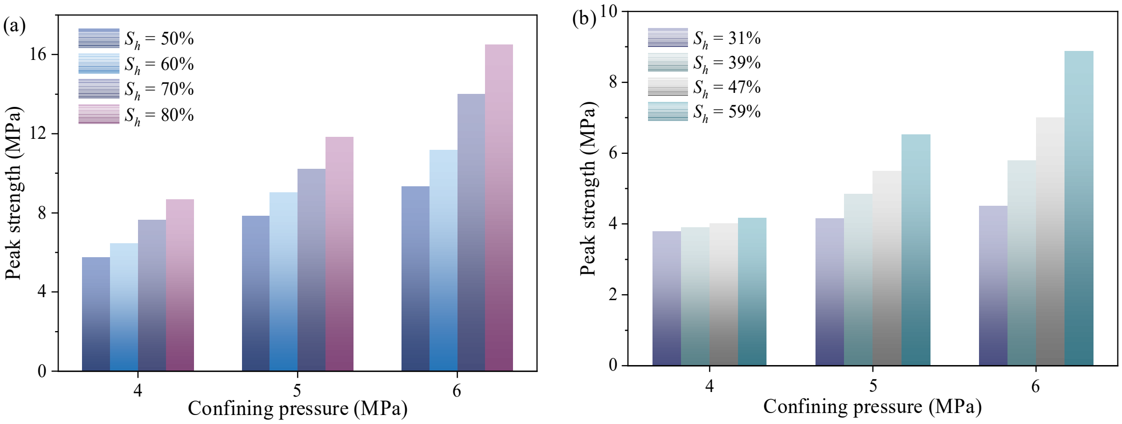

Fig. 16. Relationship between the peak strength and confining pressure of (a) Taoshan coal mine and (b) measured bituminous under different hydrate saturations.

demonstrates that hydrate formation substantially enhances the deformation resistance of coal, with this reinforcing effect exhibiting positive saturation dependence.

Coal is a medium with pores and fractures, two of the important factors affecting its strength (Meng et al., 2015). When hydrate is formed in coal, the solid hydrate will fill the pores and cracks, providing support and by the particles in coal more tightly bound together, and reducing the porosity and fracture space of the coal, thus improving its strength and stability.

5. Conclusions

This study mainly investigated the methane hydrate formation process in lignite, bituminous and anthracite media under different initial conditions through experiments. According to the analysis of some kinetic parameters in the experiment, the influence of different initial water saturations, initial pressures and coalification degrees of coal sample on the methane hydrate formation process was obtained. At the same time, on the basis of the experimental and computational data, the effect of hydrate formation with different saturations in bituminous and anthracite samples on the coal seam gas pressure and coal mechanical properties were discussed and analyzed. The main conclusions can be drawn as follows:

1) When hydrate is formed in different coal media, the increase in the initial water saturation boosts gas consumption and hydrate saturation. However, the formation of hydrate film on the surface of coal particles will hinder the migration of gas molecules and their contact with water molecules, thereby reducing the water-hydrate conversion rate, while the increase in initial pressure will lead to an increase in gas consumption, hydrate saturation, and the water-hydrate conversion rate. The initial pressure predominantly affects the driving force of hydrate formation. Elevated pressure enhances the collision frequency between gas and water molecules, thereby increasing the probability of gas molecule entrapment within developing water cages, ultimately accelerating the overall hydrate formation kinetics.
2) The kinetic parameters of hydrate formation exhibit a decreasing trend along with the increase in coal rank across various initial conditions. This suggests that lignite-hosted methane hydrate systems have significantly higher kinetic parameter values under the experimental conditions examined. Considering the different physical and chemical processes taking place during coal formation, it is believed that the influence of coal rank on the hydrate formation is mainly related to the coal properties, manifesting in the types and quantities of functional groups contained in coal, which in turn affect the distribution of water molecules on the surface of coal particles. Regarding the influencing mechanism, further research will be conducted in our future work.
3) Taking the theory of gas solidification and outburst prevention by hydrate-based technology as a basis, this study discussed and analyzed the effects of hydrate formation with different hydrate saturations on the gas pressure and mechanical properties of coal samples. The experimental results demonstrated that hydrate formation significantly reduces coal seam gas pressure while simultaneously enhancing both the peak strength and deformation resistance of coal matrices. These findings suggest that in-situ hydrate generation could serve as an effective mitigation strategy against coal and gas outburst hazards.

Acknowledgements

This work was supported by the Specialty Fund of Zhejiang Institute of Tianjin University (No. ZITJU2024-ZYHY003).

Conflict of interest

The authors declare no competing interest.

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