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REVIEW ARTICLE

Desorption hysteresis of coalbed methane and its controlling factors: a brief review

Weikai XU (✉)[1], Junhui LI (✉)[1], Xiang WU[2], Du LIU[1], Zhuangsen WANG[1]

1 College of Geoscience and Surveying Engineering, China University of Mining and Technology, Beijing 100083, China
2 China Coalbed Methane Co. Ltd, Beijing 100011, China

Abstract Most coal reservoirs show high gas content with relatively low desorption efficiency, which restricts the efficiency of coalbed methane (CBM) extraction and single-well productivity. This review highlights the desorption hysteresis mechanism and its controlling factors as well as methods and models to reveal desorption hysteresis and potential solutions. Methane adsorption and desorption can be recorded by both gravimetric and volumetric experiments. Although different adsorption models are used, desorption is generally considered with the Langmuir model. Desorption hysteresis is influenced by the petrophysical composition, thermal maturity, pore structure distribution of the coal, reservoir temperature, and moisture and water content. Methods for calculating desorption hysteresis include the area index, hysteresis index and introduction of a hysteresis factor and a hysteresis coefficient. Molecular dynamics simulations of methane desorption are mainly based on theories of kinetics, thermodynamics, and potential energy. The interaction forces operating among coal, water, and methane molecules can be calculated from microscopic intermolecular forces (van der Waals forces). The desorption hysteresis mechanism and desorption process still lack quantitative probe methodologies, and future research should focus on coal wettability under the constraints of liquid content, potential energy adjustment mechanism, and quantitative analysis of methane desorption rates. Further research is expected to reveal the desorption kinetics of methane through the use of the solid–liquid–gas three-phase coupling theory associated with the quantitative analysis of methane desorption hysteresis, thereby enhancing the recovery rate and efficiency of CBM wells.

Keywords desorption hysteresis, diffusion process, kinetics, multiphase coupling, coalbed methane production

1 Introduction

In recent years, two coalbed methane (CBM) industrialization bases in the Qinshui Basin and the eastern margin of the Ordos Basin have been used to accelerate production trials in the southern Junggar Basin, western Guizhou, and eastern Yunnan regions of China (Zhou et al., 2013; Li et al., 2014; Mu et al., 2015; Shao et al., 2015). By the end of 2015, the average production of CBM wells in production in China was approximately 1100 m^3/d; most of the wells were vertical wells, and the average production of vertical wells in production was only approximately 1000 m^3/d (Zheng et al., 2018; Wen et al., 2019; Wang et al., 2020). Accurate and reasonable predictions of methane desorption and production processes are important for increasing gas production rates and promoting development of the CBM industry.

Desorption, the reverse process of adsorption, is the first step in methane production (Busch et al., 2006; Zhou et al., 2013; Shi et al., 2019). Considerable CBM drainage data and adsorption–desorption experimental data show that the adsorption process and desorption process cannot be completely replicated. This is because desorption process hysteresis is the foundation of the adsorption process (Zhang and Liu, 2017; Zhou et al., 2020). The coalbed methane desorption hysteresis phenomenon refers to the phenomenon in which the desorption curve and adsorption curve for methane gas in coal seams are not completely coincident (Wang et al., 2014a). The adsorption theory of CBM has been widely discussed, and isothermal adsorption experiments are commonly used to evaluate gas content and coal adsorption capacity. Typically, the Langmuir pressure and volume (i.e., those determined by the Langmuir model) are utilized with the actual reservoir

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E-mails: xuweikai@student.cumtb.edu.cn (Weikai XU),
1149183778@qq.com (Junhui LI)

pressure and these are used to judge the critical desorption pressure and formulate the drainage and production system (Jiang et al., 2015; Lin et al., 2016; Zhang and Liu, 2017). Generally, the higher the critical desorption pressure of coal is, the higher the amount of methane desorbed under natural conditions (Busch et al., 2006; Feng et al., 2016). However, in the actual process of CBM production, many wells exhibit substantially lower production rates and are do not reach the designed recovery rate. Key issues related to this limitation include delayed or blocked methane desorption or migration processes (Jian et al., 2012; Peng et al., 2019). There are great differences in isothermal desorption curves among different coal samples, and the gas content of a well cannot be judged by the desorption pressure alone. Moreover, the larger the desorption hysteresis coefficient is, the higher the amount of residual adsorption gas. The desorption hysteresis greatly reduces the recovery and desorption efficiency of coalbed methane (Lin et al., 2016).

In this paper, the theoretical understanding of CBM adsorption and desorption is systematically summarized, and the control factors affecting CBM desorption are analyzed by reviewing recent works. This paper illustrates the results of research on the CBM desorption process for coals of different ranks subjected to different temperature, pressure, and water saturation conditions. Then, future work intended to develop a quantitative understanding of the desorption mechanism by combining molecular thermodynamics and surface physical chemistry features are discussed. It was found that the desorption efficiency of CBM directly restricts the correct evaluation of gas content resources and production efficiency under high stress and temperature conditions. This brief review is expected to enrich and inform the theoretical understanding of CBM production and coal mine safety research.

2 Material and methods for revealing desorption hysteresis

2.1 Experimental methods

The inner surfaces of many coal micropores have surface energy. When gases contact the inner surface, molecular forces cause the concentration of methane or various other gas molecules on the surface; this process is known as adsorption. This arises because the concentration of gas molecules increases gradually in an adsorption process. Accordingly, as gas molecules return to the gas phase free state, the number of gas molecules on the surface gradually decreases; this is the desorption process. Therefore, adsorption equilibrium occurs when a certain number of gas molecules are maintained on the surface, and the adsorption rate and desorption rate become equal. Two main methods exist for studying CBM desorption: gravimetric experiments and the high-pressure capacity method (Fig. 1).

2.1.1 Gravimetric experiment

In this method, the adsorption isotherm is determined by gravity experiments on a magnetic levitation balance, which measures the mass change of solid samples during gas adsorption under conditions of controlled pressure and temperature. Therefore, the amount of gas adsorbed or desorbed can be evaluated. The mass of adsorbed gas can be monitored as a function of gas pressure or density. This method is used to estimate the adsorption capacity at equilibrium and to perform dynamic analyses as a function of time.

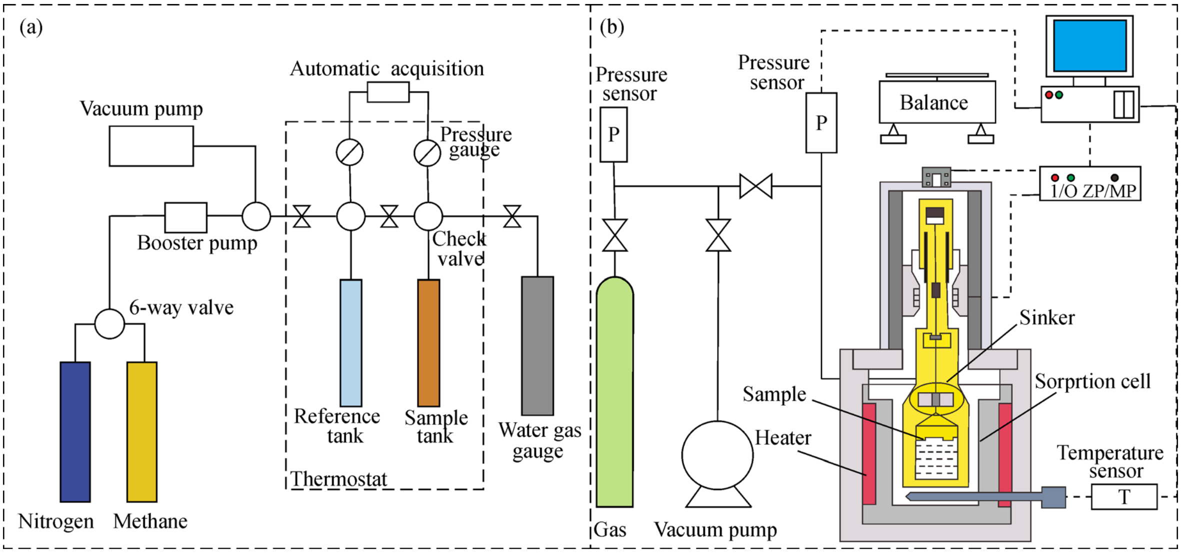


Fig. 1 Schematic diagram of the isothermal adsorption experimental system. (a) High pressure capacity experiment; (b) gravimetric experiment, from Lafortune et al. (2014) and Shi et al. (2019).

2.1.2 Volumetric experiments

In this method, processed dry coal samples are loaded into an adsorption tank. Vacuum degassing is then performed to determine the remaining volume of the adsorption tank. The pressure in the adsorption tank can be balanced by adding or releasing certain volumes of methane. Part of the gas is adsorbed, and part remains free in the remaining volume. It is known that the filled (released) methane volume minus the free volume of the remaining volume is the adsorption volume. This measurement is then repeated to obtain the equilibrium pressure and adsorption volume of each pressure segment. When the pressure is measured from low to high by adding methane gas, the adsorption isotherm is obtained. In contrast, the desorption isotherm can be obtained when the pressure is measured by reducing methane gas pressure.

2.2 Adsorption model

The isothermal adsorption experiment of coal is an effective method for estimating the amount of coalbed methane resources. The isothermal adsorption curve can be used to determine the critical pressure of adsorbed gas, estimate the maximum adsorption amount of coal and rock, and predict the gas recovery rate. A great deal of work has been done on the isothermal adsorption of methane in coal seams. The adsorption mechanism and the actual fitting of data to various adsorption models were compared. The Langmuir equation is the fitting equation adopted by most scholars. The Langmuir equation assumes that gas molecules are adsorbed on the surface of the adsorbent in the form of a monolayer. However, it is found that the Langmuir model does not fit the CH_4 isotherm of coal adsorption very well. Therefore, new fitting models have been studied, such as the Brunner-Emmet-Teller (BET) equation for adsorption of multimolecular layers (Clarkson et al., 1997), the Dubinin-Radushkevich (DR) equation (Sakurovs et al., 2007), and the Dubinin-Astakhov (DA) equation and curve-fitting equation based on micropore filling theory (Terzyk et al., 2002; Ma et al., 2011) (Table 1). Therefore, finding the most appropriate fitting equation can result in more accurate parameters to guide actual production work.

The classic form of the Langmuir model can be expressed as:

$$V_{\mathrm{ab}} = \frac{V_{\mathrm{L}} P}{P_{\mathrm{L}} + P}, \tag{1}$$

where V_{ab} is the absolute adsorption capacity, P is the equilibrium gas pressure, V_{L} is the maximum absolute adsorption capacity; and P_{L} is the gas equilibrium pressure at half V_{L}. Both V_{L} and P_{L} are Langmuir constant. According to the relationship between the excess adsorption capacity and absolute adsorption capacity, the excess adsorption capacity (V_{ex}) can be expressed as:

$$V_{\mathrm{ex}} = \left(1 - \frac{\rho_{\mathrm{b}}}{\rho_{\mathrm{a}}}\right) \frac{V_{\mathrm{L}} P}{P_{\mathrm{L}} + P}, \tag{2}$$

where ρ_{b} is the volume density of the free gas phase and ρ_{a} is the adsorption phase density. Equation (2) can be used to simulate the adsorption isotherm of coal for methane and carbon dioxide (Zhang and Liu, 2017).

2.3 Desorption model

Revisiting the derivation of the Langmuir model, the adsorption rate (r_{ad}) of gas on a planar surface can be expressed as:

$$r_{\mathrm{ad}} = \alpha \theta \mu, \tag{3}$$

where α is the proportion of the total surface that can interact with the gas molecules; θ is the proportion of the effective surface on which adsorption of gas molecules has not occurred; and μ is the total rate of adsorption of gas

Table 1 Adsorption mechanism of different adsorption models

Adsorption model	Equation	Notation	Sources
Langmuir	$V = \frac{V_{\mathrm{L}} P}{P_{\mathrm{L}} + P}$	V: adsorption quantity; V_{L}: Langmuir volume constant, cm^3/g; P: gas pressure, MPa; P_{L}: Langmuir pressure constant, 1/MPa	Langmuir (1917)
DR	$V = V_0 \exp[-D \ln^2 (P^0/P)]$	V_0: coal micropore volume, cm^3/g; P^0: saturated vapor pressure, MPa	Sakurovs et al. (2007)
DA	$V = V_0 \exp[-D \ln^n (P^0/P)]$	n: temperature and coal pore distribution of model parameters	Terzyk et al. (2002)
BET	$V = \frac{V_{\mathrm{m}} Cp}{(P^0 - P)[1 + (C - 1)(P/P^0)]}$	V_{m}: BET equation of monolayer adsorption capacity, cm^3/g; C: adsorption heat correlation constant	Clarkson et al. (1997)
Curve fitting	Quadratic equation: $V = b_0 + b_1 P + b_2 P^2$; Cubic equation: $V = b_0 + b_1 P + b_2 P^2 + b_3 P^3$ Logarithmic equation: $V = b_0 + b_1 \ln P$	b_0: constant term; b_1: coefficient; b_2: quadratic coefficient; b_3: cubic term coefficient	Ma et al. (2011)

molecules on the surface. For the adsorption process, the desorption rate ($r_{\mathrm{de}}^{\mathrm{ad}}$) of the gas from the plane surface can be expressed as:

$$r_{\mathrm{de}}^{\mathrm{ad}} = \varphi v, \tag{4}$$

where φ is the part of the usable surface on which adsorption of gas molecules has occurred, and v is the total rate of the gas molecules that will be dissociated from the surface. During desorption, the rate of desorption of a gas from a flat surface ($r_{\mathrm{de}}^{\mathrm{de}}$) comes from only one portion (r_{de}^{ad}).

Owing to the influence of many factors, some gas adsorption surfaces may be unavailable during desorption (Busch et al., 2003; Bae et al., 2009; Battistutta et al., 2010). Only a part of the available adsorption process can be used to express the amount of desorbed gas, as follows:

$$r_{\mathrm{de}}^{\mathrm{de}} = \beta \times r_{\mathrm{de}}^{\mathrm{ad}} = \beta \varphi v, \tag{5}$$

where β is the hysteresis parameter representing the difference in desorption level relative to adsorption and is between 0 and 1. When β is 0, there are no adsorption sites available for desorption (Zhang and Liu, 2017), and when β is 1, all adsorption sites can be desorbed. The sum of the fractions of exposed surface and the gas adsorbed surface must be equal to 1:

$$\theta + \varphi = 1. \tag{6}$$

When the gas is in equilibrium, r_{ad} is equal to $r_{\mathrm{de}}^{\mathrm{ad}}$:

$$\alpha \theta \mu = \beta \varphi v. \tag{7}$$

Combining Eqs. (6) and (7):

$$\varphi = \frac{\alpha \mu}{\beta v + \alpha \mu}. \tag{8}$$

and $\alpha/v = \sigma$ and $\varphi = n/n_{\infty}$. Then, Eq. (8) can be rewritten as:

$$\frac{n}{n_{\infty}} = \frac{\sigma \mu}{\beta + \sigma \mu}, \tag{9}$$

where n is the number of molecules of adsorbed gas on the surface per unit area compared to the maximum number of adsorbed gas molecules; n_{∞} refers to the same area; and σ is the ratio of the total effective surface area (α) to the total desorption level (v), representing the desorption availability of surface adsorption sites. The isothermal desorption model can be expressed as:

$$q = \frac{abP}{\beta + bP}, \tag{10}$$

where P is the gas equilibrium pressure, q is the adsorption capacity under pressure, a is a constant related to the maximum adsorption capacity, and b is a constant related to the efficiency of gas desorption. For absolute adsorption and excess adsorption, the classical form of the Langmuir desorption model can be expressed as:

$$V_{\mathrm{ab}} = \frac{V_{\mathrm{L}} P}{\beta P_{L} + P}, \tag{11}$$

$$V_{\mathrm{ex}} = \left(1 - \frac{\rho_{\mathrm{b}}}{\rho_{\mathrm{a}}}\right) \frac{V_{\mathrm{L}} P}{\beta P_{\mathrm{L}} + P}, \tag{12}$$

where $V_{\mathrm{ab}} = q$; $V_{\mathrm{L}} = a$; and $P_{\mathrm{L}} = 1/b$. Equation (12) is used to simulate the isotherm for excessive desorption of methane and carbon dioxide from coal (Zhang and Liu, 2017).

Zhao et al. (2017) gave the adsorption and desorption curves of 24 coal samples when they studied the control of adsorption and desorption of coal to coal (Fig. 2). This provides an example for our research, and the results showed a hysteresis phenomenon. In the adsorption-desorption curves of the 24 coal samples, the adsorption curve and desorption curve were not coincident, and the desorption curve was higher than the adsorption curve. Although the coal facies play a controlling role, this was not enough to reveal the factors influencing desorption hysteresis.

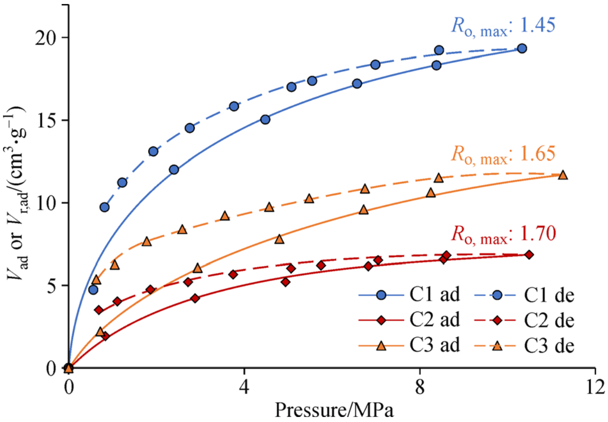


Fig. 2 Adsorption and desorption isotherms of studied coal samples. Note: ad, adsorption; de, desorption; V_{ad}, adsorbed gas content; $V_{\mathrm{r,ad}}$, residual gas content; C1, C2, C3, Coal sample number (Referenced from Zhao et al., 2017).

3 Factors influencing desorption hysteresis

Extensive research has been conducted on the CBM adsorption mechanism by considering the desorption mechanism, the adsorption theoretical models of single-component and multi-component gases, and the similarities/differences between different adsorption models. Herein, the main factors affecting CBM adsorption are evaluated (Table 2), including temperature, pressure, water content, coal quality, and coal rank (John et al., 1997; Crosdale et al., 1998; Li et al., 2010; Zhang et al., 2010; Feng et al., 2016; Tang et al., 2020; Li et al., 2020a).

Desorption is the reverse process of adsorption, yet there are essential differences between adsorption conditions and adsorption processes of underground methane during CBM production (Day et al., 2008a; Jian et al., 2012; Zhou et al., 2013). Adsorption–desorption experiments of CH_4, CO_2, N_2, and other single-component and multi-component gases show that the desorption process typically features reversibility and hysteresis. The occurrence of hysteresis is mainly due to the expansion of the coal matrix caused by methane adsorption, which narrows the pore roar channel (Wang et al., 2014a; Lin et al., 2016). The influencing factors include coal rank, organic content of the coal, temperature, pressure, particle size, water content, minerals, and pore structures (Fig. 3) (Krooss et al., 2002; Busch et al., 2004; Pan et al., 2010; Han et al., 2013; Li et al., 2019; Zou et al., 2020). In addition, recent studies have shown that thermal and mechanical effects of external fields (such as sound and electric fields) affect the pore structure of coal. Furthermore, the surface potential energy of coal is changed to affect the adsorption and desorption performance (Chen et al., 2017).

3.1 Petrophysics composition, thermal maturity and microcrystal structure

Vitrinite has specific surface area and adsorption capacity larger than those of inertinite (Moore, 2012). As the pressure is reduced to allow for desorption, the desorption rate of methane in high-rank coal is lower than that in low-rank coals, while desorption hysteresis is more obvious (Zhu et al., 2019; Yan et al., 2021). However, some studies have shown that long-flame coal shows obvious hysteresis in the desorption curve, yet there is good coincidence in coking coal samples.

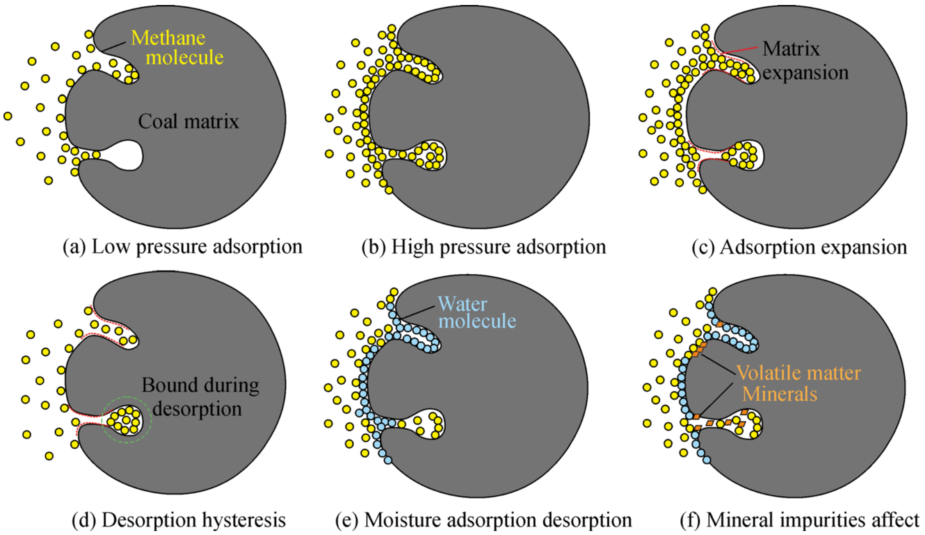
From a microscopic view, the adsorption of methane by coal is mainly the result of the interaction between the macromolecular structure of coal and gas molecules. Through experimental study, it was found that oxygen-containing functional groups in coal can impede the adsorption of methane, while fatty side chains can increase the adsorption of methane. The adsorption and desorption of methane can be explained by changes in the microcrystalline structure that occur during the process of coalification. With an increase in the metamorphic degree, some energetic oxygen-containing groups in the alkane side chain break off. Then, the recombination polarities of soot aromatic structures increase, and the number of nanoscale pores increases; this is more conducive to methane adsorption and storage, which further affects the desorption process (Bustin and Clarkson, 1998). In coal sample experiments with different deformation structures, an increase in the degree of destruction of the coal sample led to decreases in the particle sizes of the coal sample and increases in the irreversibility of desorption (Busch et al., 2006). The desorption of CBM requires a limited particle size, and when the particle sizes in the coal sample exceed that particle size limit, desorption strength decreases with the increase in particle size (6 mm), which is not obvious. With decreasing coal particle size, the influence of temperature on the desorption rate gradually weakens.

3.2 Pore structure

The adsorption capacity of coal for methane has a positive correlation with the pore specific surface area and

Table 2 Factors influencing coalbed methane desorption

Factors	Main conclusions	Sources
Temperature	Adsorption capacity α (1/temperature) CH_4 isotherm maximum for lowest rank at highest temperature Temperature affects Langmuir pressure constant P Nonlinear change in adsorption capacity and temperature	Krooss et al. (2002); Li et al. (2010)
Pressure	Adsorption capacity α pressure Saturation pressure is a key factor	Chattaraj et al. (2016)
Petrographic composition	Vitrinite-rich groups show stronger adsorption capacity than inert groups Adsorption capacity α vitrinite content Vitrinite of higher surface area	Crosdale et al. (1998); Bustin and Clarkson (1998)
Rank	Gas sorption increases with the rank Coal structure changes due to sorption to attain a stable thermodynamic system	Levy et al. (1997); Czerw (1997)
Moisture	Water entering coal pores reduces gas diffusivity, porosity, and permeability Methane adsorption capacity increases nonlinearly with the decrease in moisture content Gas diffusion rate α (1/moisture)	Busch et al. (2004); Crosdale et al. (2008)
Mineral matter	Mineral matter has a negative impact on gas sorption on coal Pore adsorption capacity increases with the increase of minerals Adsorption capacity α (1/mineral matter)	Faiz et al. (2007)
Pore structure	Desorbed gas gathers in the micropore spaces in the coal matrix Adsorption-desorption only occurred in small pores and micropores Followed the Langmuir equation	Clarkson and Bustin (1999b)



(a) Low pressure adsorption (b) High pressure adsorption (c) Adsorption expansion
(d) Desorption hysteresis (e) Moisture adsorption desorption (f) Mineral impurities affect

Fig. 3 Diagram showing methane adsorption and desorption hysteresis under different influencing factors (Moore, 2012).

micropore volume but has no obvious relationship with the total pore volume. The adsorption capacity of coal increases with an increase in vitriol content and decreases with an increase in inert content, indicating that the adsorption of methane mainly occurs in the micropores of the coal matrix (Crosdale et al., 1998). With increasing coal seam depth, the proportions of macroscopic pores (> 1000 nm) and mesopores (100–1000 nm) decrease obviously (Li et al., 2017). The specific pore surface area is mainly determined by micropores and ultramicropores (Mianowski and Marecka, 1998).

With an increase in the metamorphic degree of coal, the volume proportions of micropores and small pores in coal increase. The higher the coal rank is, the smaller the average pore radius, the more complex the pore increase, and the higher the adsorption capacity of methane in the pore area (Li et al., 2017; Li et al., 2020b). Correspondingly, the theoretical desorption capacity of methane increases, and the desorption rate also increases (Sakurovs et al., 2016). The micropores and small pores of the coal samples affect the desorption stage, desorption volume, and desorption rate, among which micropores have the greatest influence (Zelenka, 2016). At the same time, if the methane molecules in the pores cannot be diffused effectively and the concentration cannot be reduced in time, methane can be readsorbed. Due to skeletal deformation and the decrease in pore throat diameter in the process of adsorption–desorption, the amount of gas involved in the desorption process decreases at the same equilibrium pressure, resulting in hysteresis (Figs. 3(c) and 3(d)). The structure of coal changes due to adsorption and the presence of water vapor in pore surfaces; this will reduce gas diffusivity and coal porosity, which exhibit a nonlinear relationship (Busch et al., 2004; Faiz et al., 2007).

3.3 Reservoir temperature

Temperature has a great influence on the adsorption and desorption of methane. There is a nonlinear relationship between the adsorption capacity and temperature; this causes adsorption capacity to decrease with increasing temperature, which affects the Langmuir pressure constant (Krooss et al., 2002; Bustin and Clarkson, 1998). The adsorption capacity increases with increasing pressure, and saturation pressure is the key factor. Moreover, the adsorption capacity of mixed gases is weaker than that of pure gases (Jiang et al., 2015). Adsorption and desorption experiments at different temperatures showed that desorption hysteresis became less obvious with increasing temperature (from 20°C to 40°C) (Ma et al., 2011). However, experimental results have also shown that desorption hysteresis was more obvious with increasing temperature (from 30°C to 50°C) (Yang et al., 2013). Moreover, experimental results at low temperatures (0°C and below) show that reducing the temperature can inhibit gas desorption from coal, and the lower the temperature is, the more obvious the desorption hysteresis (Wang et al., 2014b).

3.4 Moisture and water content

Experimental results for dry coal, balanced water coal, and water-injected coal samples showed that the adsorption capacity of coal decreases with an increase in water content. However, moisture content had little effect on the ultimate adsorption capacity of high-rank coal samples (Day et al., 2008b). Water injection experiments on coal samples with different particle sizes showed that water has an obvious inhibitory effect on methane adsorption (Wang and Jiang, 2016). Saline water inhibits methane desorption to a greater extent than distilled water. Some scholars hold the opposite view for different coal ranks, believing that water can improve the desorption rate of CBM in low-rank coal (Crosdale et al., 2008). However, some results have shown that added water promotes the desorption of methane in medium- and high-rank coals and inhibits the desorption of methane in low-rank coal. In addition, the influence of moisture content on lump coal was also investigated, and this showed results different from those of pulverized coal.

From the above, it can be seen that there are a large number of experimental results and analyses of the factors influencing CBM desorption; however, the main limitations arise from qualitative analyses and the lack of quantitative characterization. In addition, the combined effect of temperature and water content on the desorption of different coal rank samples remains controversial.

3.5 Desorption hysteresis mechanism

Desorption hysteresis of coalbed methane is controlled by multiple factors, which complicates further exploration and research. In the processes of adsorption and desorption, changes in pore structure lead to decreases in desorption capacity, which is the key factor affecting desorption. Desorption hysteresis becomes more obvious with increasing temperature. High water content promotes the desorption of medium- and high-rank coal and inhibits the desorption of low-rank coal. However, mineral composition, coal structure and maturity exert little influence.

In summary, the hysteresis phenomenon seen with coalbed methane desorption is mainly caused by the expansion of the coal matrix as a result of methane adsorption, which narrows the pore throat. This process is affected by coal rank, coal organic matter content, temperature, pressure, particle size, water content, and mineral and pore structure. Of course, it can also be affected by an external field and coal surface potential energy. The mechanism of desorption hysteresis should be explained from two perspectives: desorption blockade and migration blockade. The material composition of coal determines adsorption, the pore system is the channel for migration, and both are the material causes of desorption hysteresis; methane desorption and migration are driven by energy changes. The components in the material system and energy system interact with each other, resulting in desorption hysteresis.

4 Methods to calculate desorption hysteresis rate

At present, the analysis of desorption lag is mainly based on qualitative descriptions. However, in studies of porous media such as soil, polymer and organic materials, scholars have carried out in-depth studies on the desorption hysteresis coefficient and proposed many empirical formulas, which can be used to quantitatively describe the degree of desorption hysteresis. According to different classification standards, these empirical formulas can be divided into four categories: Freundlich index (Ding and Rice, 2011), equilibrium concentration in the solid phase (Ran et al., 2004), slope index (Braida et al., 2003; Wu and Sun, 2010) and area index (Zhu and Selim, 2000). The Freundlich index can be applied to monolayer adsorption of porous media and can also be applied to adsorption on nonuniform surfaces, and the index is more suitable for low concentration adsorption. The equilibrium concentration index and slope index in the solid phase can accurately describe the degree of hysteresis at a single point (Wang et al., 2014a). The area index can simulate the hysteresis trend from a completely reversible state to an irreversible state in the desorption process.

However, these four formulas are based on desorption hysteresis coefficients of other porous media, which are not completely applicable to the quantitative analysis of CBM desorption hysteresis. For example, the Freundlich index depends on a specific isotherm model (Freundlich equation), which is not often used to fit the gas adsorption isotherm of coal, and its applicability is limited due to low concentrations. The solid equilibrium concentration index and slope index describe the lag degree of different single points but not the whole isotherm. If there is residual adsorption, the hysteresis coefficient will become infinite, which does not accord with the actual situation of coal reservoirs (Wang et al., 2014a).

On this basis, some scholars have used the area index method for reference and proposed a method to calculate a hysteresis coefficient suitable for methane desorption. This includes the method of calculation with reference to the area index (Zhu and Selim, 2000; Wang et al., 2014a), the introduction of the hysteresis factor (Qi et al., 2016) and use of the ratio of the critical desorption pressures calculated from adsorption and desorption curves to determine the hysteresis coefficient (Lin et al., 2016) (Table 3).

The method of drawing lessons from the area index mainly uses the Langmuir model to fit the desorption experimental data, but we can also use a curve fitting method, such as cubic polynomial, quartic polynomial, logarithmic function, exponential function, comprehensive model, Weibull function and so on to fit the desorption curve. However, the method of drawing lessons from the area index also has the following main problems: 1) the fitting equation does not reflect the adsorption-desorption mechanism in the sense of model parameters and does not fully reflect the thermodynamics and molecular dynamics of motion in the desorption process; 2) the current model basically considers coal and rock as a unified whole and does not take into account the influence of different pore size shapes on the desorption hysteresis; and 3) the

Table 3 Calculation method of the hysteresis coefficient of methane desorption

Calculation method	Equation	Notation	Sources
Area index	$HI = 100\left(\frac{A_{\mathrm{de}} - A_{\mathrm{ad}}}{A_{\mathrm{ad}}}\right)$	A_{de}: area under the adsorption isotherm; A_{ad}: area under the desorption isotherm	Zhu and Selim (2000)
Hysteresis index	$HI = \frac{A_{\mathrm{de}} - A_{\mathrm{ad}}}{A_{\mathrm{sf}} - A_{\mathrm{ad}}} \times 100\%$	A_{de}: area under the adsorption isotherm; A_{ad}: area under the desorption isotherm; A_{sf}: measure hysteresis area	Wang et al. (2014a)
Introducing hysteresis factor	$P_1 = \alpha P$; $Q = \frac{Q_{\mathrm{m}} b P_1}{1 + bP_1}$	α: hysteresis factor; P: adsorption equilibrium pressure; P_1: desorption equilibrium pressure; Q: molality of the adsorbed gas during desorption; Q_{m}: saturation adsorption capacity of single molecule; b: adsorption constant	Qi et al. (2016)
Hysteresis coefficient	$H_{\mathrm{c}} = \frac{P_{\mathrm{dcd}}}{P_{\mathrm{acd}}}$	P_{dcd}: isothermal desorption curve critical desorption pressure; P_{acd}: isothermal adsorption curve critical desorption pressure	Lin et al. (2016)

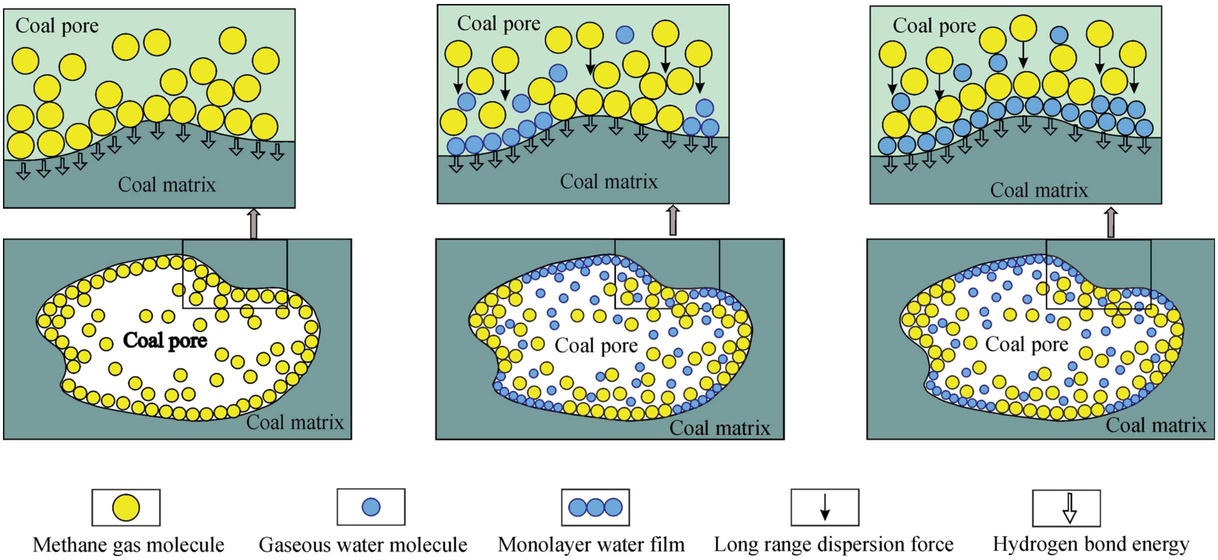


Fig. 4 Stress analysis of methane adsorption on the coal matrix under different water content conditions.

maximum adsorption pressures of isothermal adsorption and desorption experiments are generally 10 MPa, which is derived from the previous design. Now, the maximum adsorption pressure is also designed by considering the depth, and it can exceed 10 MPa.

5 Molecular dynamics associated with methane desorption

An underground coal reservoir is composed of solid (coal matrix), liquid (mainly coal seam water), and gaseous (CBM) materials. The interaction between coal and methane is mainly one of physical adsorption, while the presence of water molecules complicates the interaction between coal and methane (Suuberg et al., 1993; Zhuravlev and Porokhnov, 2019). Methane molecules have no polarity, and there is no electrostatic force operating between them and coal macromolecules (Charrière and Behra, 2010). However, a dipole is induced by the polarization of the coal molecule, and a dispersion force is generated by the change in the adjacent electric field, which constitutes the main force between the coal matrix and methane molecules (Zhou et al., 2016).

However, water molecules are more easily adsorbed on the surface of coal than methane, mainly due to hydrogen bonding between the coal molecules and water molecules (Fig. 4). This is because no strict conditions are required for the formation of hydrogen bonds; thus, hydrogen bonds are often formed in solids, liquids, and gases, making water molecules more advantageous than methane molecules for adsorption on the coal surface. By considering the influence of these water molecules, researchers have carried out water injection experiments on coal samples. The experimental results showed that water overcame the interfacial tension and wetted the pore surfaces of the coal matrix, thus reducing the surface polarity and dispersion force for methane adsorption. Although the force exerted by the water film on methane molecules is relatively small, the film provides more adsorption sites, and its effect on the adsorption performance of coal samples of different ranks is still controversial.

The essence of dynamic change in the adsorption–desorption of methane is the variation in adsorption heat. Theoretically, adsorption and desorption processes are reversible dynamic equilibrium processes; thus, the gas content involved in the adsorption process should be equal to that in the desorption process. However, according to calculated results of adsorption heat, the caloric value of the equivalent heat in the adsorption process is always less than that in the desorption process. In other words, the caloric value released during the adsorption process cannot match the caloric value required in the desorption process; hence, to a certain extent, desorption cannot be carried out thoroughly, resulting in hysteresis for CBM. This process shows that the smaller the difference between the heat of the adsorption process and that of the desorption process is, the easier the desorption with an increase in temperature.

Based on this, many researchers have discussed the adsorption model and theory for coal and methane from the standpoint of theories of kinetics, thermodynamics, and potential energy (Chattaraj et al., 2016). There are mainly Langmuir models for the adsorption of single molecular layers on solid surfaces, Dubinin-Radushkevich (DR) models, and Dubinin-Astakhov (DA) models based on adsorption potential theory (Clarkson et al., 1997). The Brunner-Emmet-Teller (BET) equation, which involves multilayer adsorption and capillary condensation, is fitted with an empirical formula based on experimental data. The comprehensive adsorption model considers thermodynamics (Collins, 1991), adsorption potential, etc. Some scholars have compared the applicability and simulation accuracy of different models, including the ordering of the DA, DR, BET, and Langmuir equations (Clarkson and Bustin, 1999a). The difference between the Langmuir and Freundlich isothermal equations and the applicability of the Langmuir and DA equations for coal rocks with different degrees of metamorphism were also considered. The experimental phenomenon of the solid–liquid–gas phase was explained at the physicochemical level by calculating the molecular interactions between coal, water, and methane.

Additionally, to better analyze the internal mechanism of action, some scholars have used an empirical potential function to simulate the interaction between methane and graphite (Mosher et al., 2013). Other scholars have used quantum chemistry to calculate aspects of the relationship between the coal surface and methane. Molecular kinematics were also used to analyze methane molecular motion under the influence of temperature and pressure (Chen et al., 2017), and molecular simulation was used to study methane adsorption potential energy.

Many experimental studies of methane adsorption and desorption have been carried out; theoretical discussions and molecular simulations have also been carried out gradually, and the forces operating between coal, water, and methane molecules have essentially been clarified. However, it has been established that the physical properties of the coal matrix surface do change under different wetting conditions. This, in turn, changes the molecular forces operating between coal, water, and methane, which have not yet been clarified, and includes differences in the molecular forces of coal at different scales. At present, research is focused on either the mechanism of desorption or the fitting of the desorption equation, ignoring the lack of synchronization and the phenomenon of hysteresis seen the processes of adsorption and desorption, that is, the process of gas diffusion.

6 Potential topics for further research

In previous experiments and studies of field drainage processes, the adsorption isotherm has typically been used to determine CBM production parameters such as “CBM desorption rate,” “critical desorption pressure,” and “theoretical recovery.” However, an increasing body of evidence shows that the desorption curve is different from the adsorption curve, yet the desorption process is still rather poorly understood (Fig. 5).

Previous studies have been carried out on the factors influencing adsorption and desorption of methane and the reasons for desorption hysteresis. At the same time, substantial work has been done on the microscopic mechanism of molecular action inside methane reservoirs, and certain interesting research results have been obtained. Overall, an underground coal reservoir is a three-phase coupled system comprising coal–gas–water, and the phase transition of methane is affected by reservoir temperature, pressure and pore structure. Therefore, it is necessary to systematically summarize various factors restricting the desorption of methane and establish an accurate mathematical model to guide predictions and establish the development potential of CBM.

6.1 The influence of water on methane desorption

In the process of CBM exploitation, there is initially no free gas in the fracture system, and only the aqueous phase can flow in open coal seams. When the coal seam begins to drain and depressurizes, the pressure of the water phase in the coal seam continues to decrease. At this time, the curvature of the gas–liquid interface reduces, and the capillary pressure decreases. When the pressure of the aqueous phase is further reduced, the gas–liquid interface is convex relative to the fracture system, owing to dynamic wetting hysteresis, and the capillary pressure points to the matrix system. The fluid tension at the gas–liquid interface

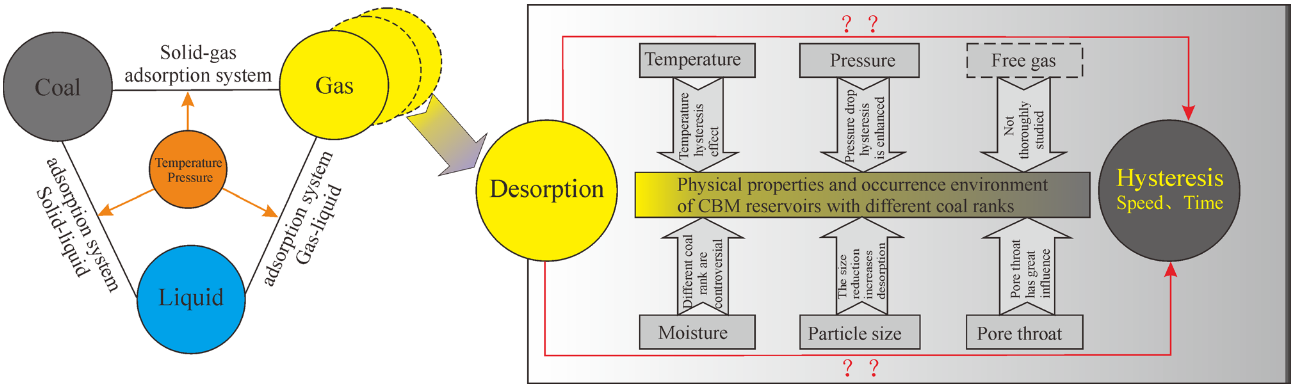


Fig. 5 Schematic diagram of factors influencing coalbed methane desorption.

is then not sufficient to maintain the liquid surface deformation; thus, methane bursts into the fracture system from the matrix, and the gas well begins to produce gas. In this case, the methane pressure is greater than the water phase pressure, and the gas phase pressure is equal to the sum of the water phase pressure and capillary pressure (Fig. 6). Therefore, the hydrodynamic sealing mechanism can explain the critical desorption of methane (Li and Horne, 2007).

6.2 Thermodynamic variation during adsorption and desorption

The heat of adsorption is the heat released by gas molecules when they move to the solid surface. The adsorption heat is used to analyze the change law for adsorption and desorption of CBM from a molecular point of view. The heat difference between adsorption and desorption is the thermodynamic cause of desorption hysteresis, and the heat difference is also different under the influence of different temperatures and pressures, different wetting degrees, and different pore structures. Thus, the interactions between methane molecules, water molecules, and coal macromolecules are analyzed using the method of controlled variables, and the extent of influence for each variable is studied. Furthermore, the internal cause of desorption hysteresis is intuitively analyzed from the knowledge of thermodynamics, and the mechanism of adsorption heat generation in the process of coalbed gas desorption is explained.

6.3 Quantitative analysis of desorption hysteresis

At present, most analyses of the hysteresis effect are still in the qualitative analysis stage, and most of preliminary quantitative analyses are based on the area index, which does not reflect the real conditions of the coal reservoir. To carry out a quantitative study of methane desorption, it is necessary to clearly understand the relationships among desorption, diffusion, and percolation. By fitting the adsorption–desorption experimental data, the three-phase interaction force was determined from the change law of

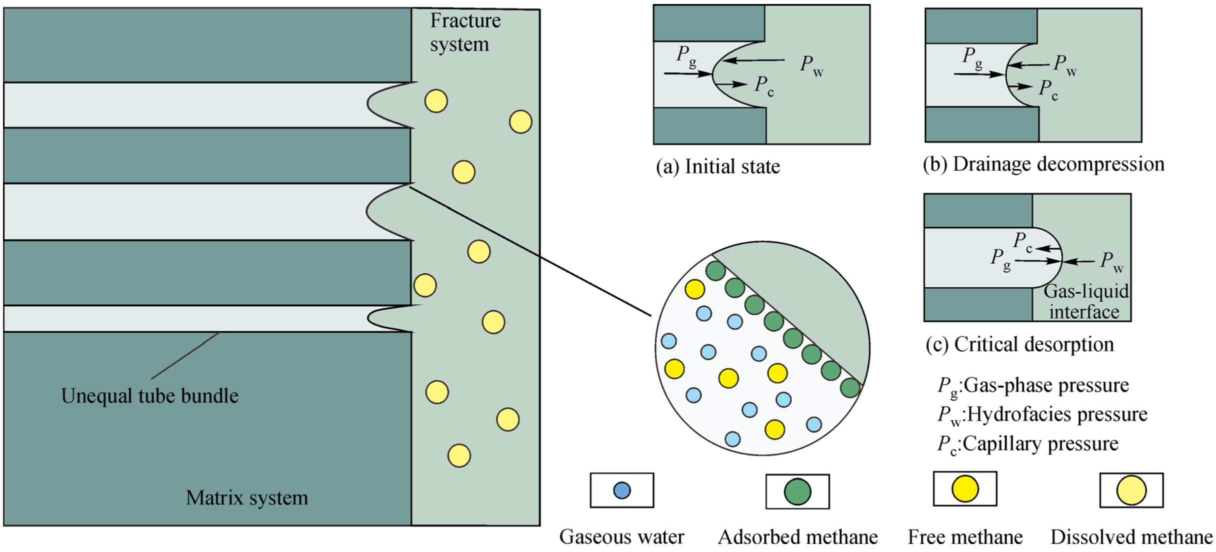


Fig. 6 Schematic of the hydrodynamic sealing mechanism (Li and Horne, 2007).

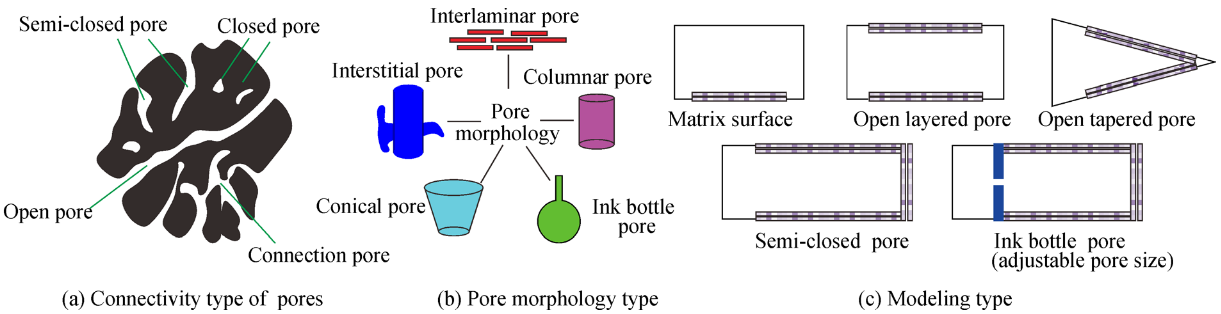


Fig. 7 Schematic diagram of modeling types for molecular simulation.

coal sample adsorption and desorption capacity with different moisture content and different coal ranks; these adsorption and desorption changes are reflected by changes in the intermolecular interaction force. In the gas-water-coal three-phase system, hydrogen bonding between water molecules leads to formation of a water film covering the surface of the coal matrix so that methane can be desorbed. In addition, methane molecules have no polarity and are adsorbed on the surface of coal due to the control of dispersion forces, so this enhances desorption. By combining the adsorption–desorption quantitative equation and the diffusion equation, the changes in the desorption amount and rate were explained for one-dimensional and two-dimensional cases.

6.4 Kinetic process for desorption hysteresis

At present, the adsorption characteristics of the solid–liquid–gas three-phase coupling system are understood preliminarily; however, the desorption kinetic mechanism operating with the three-phase coupling condition and the desorption rate change caused by diffusion are still unclear. This content can be divided into two levels. The first level comprises the selection of adsorption and desorption curve fitting equations, optimization, derivation of the equation with the highest fitting accuracy, and quantitative evaluation of the degree of desorption hysteresis. The second level involves the establishment of a physical and chemical model of the solid–liquid–gas phase for calculating a) the force between coal macromolecules and methane molecules and b) the desorption diffusion coefficient resulting from the interactions between liquid water molecules and gas molecules.

This will deepen the theoretical understanding of the methane desorption mechanism. Molecular simulation of CBM hysteresis is mainly based on current analytical simulation technology for porous materials (Fig. 7). For example, Materials Studio (material calculation software) was used to simulate the desorption hysteresis phenomenon seen with different temperatures, pore structures and surface strengths; the molecular structure of different coal grades was simplified to a graphite structure with different carbon:oxygen ratios for modeling and analysis. These results not only complemented the analysis of causes for desorption hysteresis but also helped determine the influence of different pore structures on desorption hysteresis.

7 Conclusions

1) The study of desorption hysteresis mainly describes the desorption process through molecular simulation and numerical solution, establishes a mathematical model of desorption hysteresis, and reveals the changes in desorption performance of CBM and shale gas.

2) Maceral composition and pore structure of coal and rock are the main causes of desorption hysteresis, which is also affected by other factors such as reservoir temperature, pressure, coal and rock particle size, and water saturation.

3) Chemical changes caused by the interactions among coal, water and methane are the internal causes of desorption hysteresis. The molecular dynamics and thermodynamics of methane desorption largely determine the effect of desorption.

4) Desorption and diffusion influence each other, and a dynamic equilibrium exists between them. Moreover, the influence and interaction between desorption and diffusion are inconsistent and they differ for different stages of gas production.

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