Invited Review

Sorption characteristics in coal and shale: A review for enhanced methane recovery

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Abstract:
The exploration and exploitation of hydrocarbon resources within coal and shale reservoirs is an engineering challenge. Well-developed internal micro-pore structures, complex sorption mechanism as well as numerous influencing factors affecting the gas flow are generally not well-accounted in the commercial life-cycle of shale gas and coalbed methane wells. Although large number of studies have been conducted to propose improved sorption models and study the influencing factors on adsorption and desorption characteristics of methane and CO_2 in coal and shale reservoirs, a systematic review of such studies for efficient understanding of the accumulated literature is missing, especially with a focus towards coal and shale reservoirs. In that context, this study presents a review of sorption characteristics of methane in coal and shale. Firstly, theoretical mechanisms for methane sorption are introduced, followed by description of sorption models. Further, three factors influencing the sorption of gas in coal and shale are described: total organic carbon and clays, pore structures, and reservoir conditions. Finally, the preferential sorption characteristics of hydrocarbons and carbon dioxide are described, and the methods to promote methane desorption for enhanced recovery are discussed, which include technologies such as gas injection, microwave heating, and hydraulic fracturing.

1. Introduction

The development and utilization of natural gas over other relatively more polluting fossil fuels (e.g., coal, heavy oil) can be effective towards reducing greenhouse gas emissions. Methane is the dominant component in natural gas, which can exist in coal and shale matrix in an adsorbed state (Li et al., 2017; Rani et al., 2019), besides existing in other states (e.g., as free gas in pore space). Although the initial production rates of methane from coal and shale reservoirs are dominated by the flow of free gas existing between the fractures and cracks, desorption of methane and its overall contribution to the gas flow rate over the life cycle of shale gas and coalbed methane (CBM) wells is an area that remains under-investigated. Unlike large number of studies investigating the sorption behavior in coal and shale in laboratory, contribution of desorption to shale gas production is lacking supportive field studies to investigate flow mechanisms contributing to the gas production; however, conducting such studies is possible as exhibited by the large number of similar studies investigating fracturing fluid flowback to understand the origin and mechanisms of produced water (Singh, 2016). In absence of such field studies, the laboratory studies are the sole basis to understand the importance of sorption in gas production from coal and shale reservoris, but it is possible that the role of sorption in the field is relatively more important than what the laboratory-scale studies are able to capture.

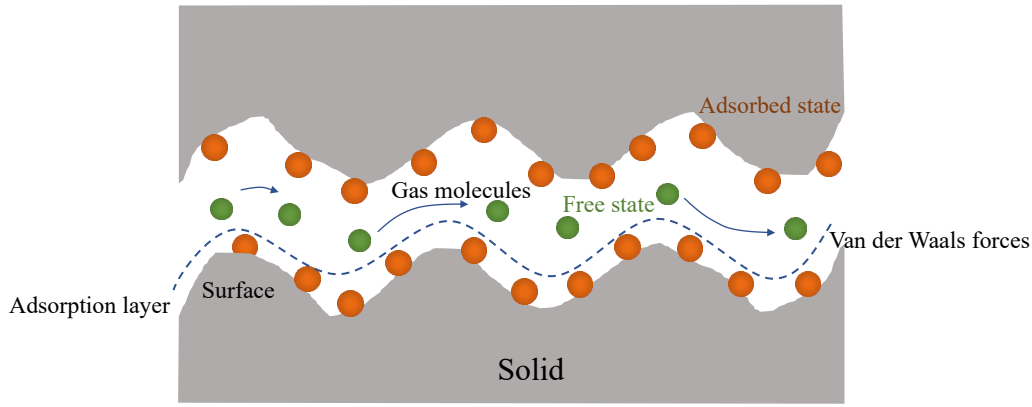In the field of hydrocarbon reservoir geology, adsorption

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Fig. 1. Monolayer adsorption in reservoir.

mainly refers to the interaction between solid surfaces and gas molecules due to van der Waals forces. Desorption is the process during which the adsorbed gas in pore surface changes from adsorbed state to free state. During gas extraction, adsorbed methane is first desorbed from the surface of micropores due to pressure drop (below a certain threshold), and then diffused into fractures to be extracted (Thararoop et al., 2012; Karimpouli et al., 2020). The sorption characteristics of methane are influenced by internal factors (pore-fracture structures, composition) as well as by reservoir conditions (temperature, pressure, moisture content), which will directly affect the gas yield (Liu et al., 2018; Zheng et al., 2019). Many scholars have conducted isothermal adsorption experiments on specimens under different conditions and clarified the factors influencing the sorption of methane and the mechanism of competitive adsorption between different molecules (Guo et al., 2013; Wang et al., 2020). On this basis, a series of studies related to promoting methane desorption have been carried out to improve the gas recovery (Foroozesh et al., 2019). Great progress has been made in both theoretical research and technological innovation.

In this study, sorption characteristics of methane in coal and shale are reviewed through three aspects, which are: 1) methane adsorption models and the influencing factors, 2) means to promote methane desorption for enhanced recovery, 3) research progress and prospects.

2. Sorption mechanism

Micro-pore structures are developed in coal and shale, and large quantities of methane exist in adsorbed and free states. At equilibrium, the adsorption rate is equal to the desorption rate. When reservoir conditions change, the van der Waals forces between the solid surface and methane molecules change, resulting in a change in adsorbed amount and the desorption process of methane begins (Ayawei et al., 2017). The monolayer adsorption in reservoir is shown in Fig. 1.

The common mode of methane desorption in reservoirs is pressure drop desorption, during drainage depressurization, gas in the pores of matrix will desorb due to concentration differences and diffuse into fractures. There is also displacement desorption due to competition between different molecules for

Table 1. Langmuir model and empirical equations for monolayer sorption.

Type	Model
Langmuir model (Langmuir, 1918)	$V = \dfrac{V_m b p}{1 + b p}$
Freundlich model (Freundlich, 1909)	$V = b p^n$
Toth model (Toth, 1971)	$V = \dfrac{V_m b p}{(1 + b p^n)^{1/n}}$
Langmuir-Freundlich model (Turiel et al., 2003)	$V = V_m \dfrac{b p^n}{1 + b p^n}$
Expand-Langmuir model (Song et al., 2017)	$V = \dfrac{V_m b p^n}{1 + b p^n + n\sqrt{b p}}$

Notes: b is the adsorption constant, n is the equilibrium constant which reflects the heterogeneity of adsorbent.

adsorption sites, and warming-up desorption which not only increases the thermal motion of molecules but also decreases the number of adsorption sites and gas-solid interaction potential energy.

2.1 Classical adsorption models

The adsorption of methane in coal and shale is commonly described by monolayer adsorption models, multilayer models, multi-phase gas adsorption models, and adsorption potential theory models. The adsorption of methane on the surface of coal and shale mainly occurs in a single layer, which is described by monolayer models. The monolayer models assume that the solid surface is homogeneous and the heat of adsorption is constant. The commonly used monolayer models are Langmuir model, Langmuir's extended model, and empirical equations, as shown in Table 1.

The multilayer adsorption model is an extension of the monolayer adsorption model,which assume that the adsorption heat of first layer is constant, and sorption occur on the surface of gas phase. Commonly used multilayer model is Brunauer-Emmett-Teller (BET) adsorption model (Eq. (1)) (Bruanuer et al., 1938), which considers that the adsorption layer is discontinuous, and each layer may have adsorption sites. BET

adsorption model is often used in low temperature nitrogen adsorption experiments to measure the specific surface area of solids,

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{p}{p_0} \tag{1}$$

where V is the adsorption amount, cm^3/g; V_m is the maximum adsorption amount, cm^3/g; p is the gas pressure, MPa; p_0 is the saturation vapor pressure, MPa; C is a constant.

The adsorption potential theory model assumes that there is an adsorption potential field on the solid surface, and the filling of pore volume by methane molecules is achieved based on the magnitude of adsorption potential (Dubinin, 1960). It is also called the pore filling model, which does not assume the surface adsorption of a single layer, and can be applied to the adsorption of gas on nanoporous materials. Therefore, the adsorption potential theory is a more complete and mature theory to describe the gas adsorption in carbon micropores, and it mianly includes Dubinin-Astakhow (D-A) and Dubinin-Radushkevich (D-R) equations, which are commonly used to explain isothermal adsorption behavior quantitatively (Ayawei et al., 2017), as shown in Eqs. (2)and (3a). Based on this, Sakurovs et al. (2007) revised the D-R model and proposed using the adsorption phase density instead of p_0 and the gas density instead of p. The revised model (Eq. (3b)) can be applied to supercritical conditions. Besides, Singh and Cai (2018) used adsorption potential theory to calculate the density of adsorption phase, and used the modified D-R model to illustrate adsorption effect on molecular and pore scale,

$$\text{D-A: } W_{ads} = W_0 \left(1 - \frac{\rho_g}{\rho_a}\right) \exp\left(-D \ln^N \frac{p_0}{p}\right) \tag{2}$$

$$\text{D-R: } W_{ads} = W_0 \left(1 - \frac{\rho_g}{\rho_a}\right) \exp\left(-D \ln^2 \frac{p_0}{p}\right) \tag{3a}$$

$$\text{Modified D-R: } W_{ads} = W_0 \left(1 - \frac{\rho_g}{\rho_a}\right) \exp\left(-D \ln^2 \frac{\rho_a}{\rho_g}\right) \tag{3b}$$

where W_{ads} is the excess sorption, kg/t; W_0 is the surface adsorption capacity, kg/t; ρ_a is the adsorption phase density, kg/m^3; ρ_g is the gas density, kg/m^3; N is the empirical parameter; D is the affinity constant.

The adsorption models shown above are for single component gases. In addition to methane, the reservoir also contains a small proportion of other gases, most notable of which are nitrogen and carbon dioxide. There are differences in the adsorption capacity of different gas components, and each component competes for adsorption sites, and the molecules with strong adsorption capacity will occupy a large number of adsorption sites with large adsorption volume. The adsorption theories of multi-phase gases, mainly contain ideal adsorbed solution theory, BET multi-component gas adsorption model, extended Langmuir isothermal adsorption equation, and extended adsorption potential theory.

2.2 Extended adsorption models

The fluid-solid interface is heterogeneous in the real adsorption process. Langmuir (1918) established dual-site Langmuir equation for heterogeneous interfaces using temperature and pressure parameters (Eq. (4)), and this model was used by Tang et al. (2016) to accurately estimate the gas content of deep shale formations,

$$V = V_m \left[(1-\alpha)\frac{K_1(T)P}{1+K_1(T)P} + \alpha\frac{K_2(T)P}{1+K_2(T)P}\right] \tag{4}$$

where $K(T)$ is the temperature-dependent equilibrium constant, $K_1(T) = A_1\exp(-E_1/RT)$, $K_2(T) = A_2\exp(E_2/RT)$; α is the fraction of the second type of adsorption site.

The classical sorption models are limited by isothermal conditions, so their applicability can be limited and sometimes poor (Meng et al., 2020). Li et al. (2014) found that the adsorption capacity and desorption pressure measured in the laboratory based on classical models differed significantly from those in the field, and they concluded that the adsorption of CBM and shale gas belong to solid-liquid interface adsorption. The amount of adsorption in solid-liquid interface adsorption is related to the concentration of the solution and obeys the Langmuir adsorption law at the solid-liquid interface as follows,

$$W = \frac{hW_s c}{1 + hc} \tag{5}$$

where h is the adsorption equilibrium constant, c is the concentration, mol/kg; W is the adsorption volume,mol; W_s is the saturation adsorption capacity, mol.

In subsequent studies, Li et al. (2016) found that methane adsorption in shale is related to the interaction of three phases (i.e., gas-liquid-solid), and analyzed the behavior of methane, water film, and clay in the adsorption, as shown in Fig. 2.

Meanwhile, due to the strong heterogeneity in coal and shale, there is an obvious error between the calculated methane content and isothermal adsorption curve. Yao et al. (2019) introduced low-field nuclear magnetic resonance into isothermal adsorption experiments to reflect the methane content using
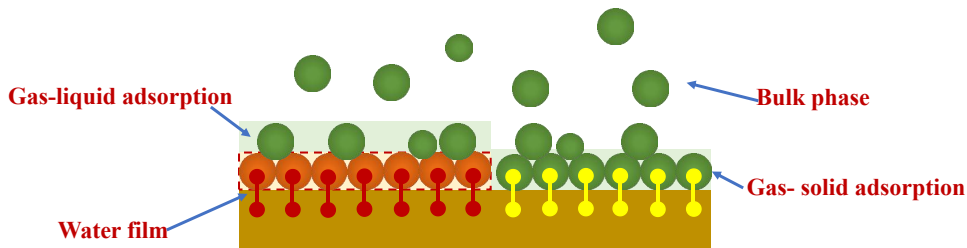

Fig. 2. Monolayer adsorption in the reservoir.Schematic diagram of gas-liquid-solid interaction (Li et al., 2016).

Table 2. Deficiencies of the traditional adsorption models and the improved models.

Model	Deficiency	Improvement principle/method	Extended adsorption models and equations
Langmuir (1918)	Single-site Langmuir model cannot describe the real adsorption system	Consider the difference in adsorption energy of different sites on the heterogeneous surface	Dual-site Langmuir equation
Sakurovs et al. (2007)	D-R model is not suitable for adsorption under supercritical conditions	Use gas density instead of pressure to apply to a wider range of temperature and pressure conditions	Modified D-R Model
Li et al. (2014)	Langmuir model of solid-gas interface cannot reflect the particularity and complexity of actual reservoirs	Consider the relationship between methane adsorption, desorption and diffusion process and formation water	Langmuir adsorption model of solid-liquid interface
Yao et al. (2019)	Conventional methods are cumbersome, error-prone, and difficult to apply to shale reservoirs due to their non-homogeneous characteristics	Detect the multiphase methane in reservoir using nuclear magnetic resonance	The formula for calculating multiphase methane: $V_f = 0.286T_{2f}$, $V_{ad} = 0.4207\ T_{2ad}$
Meng et al. (2020)	Traditional models are limited by isothermal conditions and shale formation type	Consider the factors that affect adsorption to reveal hidden patterns and unknown correlations between variables	Extreme gradient boosting algorithm in machine learning

V_f is the volume of free methane, cm^3; V_{ad} is the volume of adsorbed methane, cm^3; T_{2f} is the signal amplitude of free methane; T_{2ad} is the signal amplitude of adsorbed methane.

T_2 profiles. The P_1 peak ($T_2 < 1$ ms) represents the adsorbed methane and the P_2 peak ($T_2 \sim 1\text{-}50$ ms) represents the free methane.

For the adsorption of methane in coal and shale is influenced by a variety of factors. Meng et al. (2020) used machine learning approach to consider four variables of pressure, temperature, moisture, and Total Organic Carbon (TOC) and selected 352 sets of data to predict methane adsorption in shale, and the extreme gradient boosting algorithm gave better prediction results.

The defects of the traditional models and the extended models are summarized in Table 2. In addition, the process of methane sorption will lead to swelling/shrinkage deformation of reservoir matrix and pore-fracture structures, resulting in changes in electrical conductivity and permeability (Zhou et al., 2017; Zhang et al., 2020a).

3. Factors influencing gas sorption

Both coal and shale are sedimentary rocks, oil and gas resources mainly occur in clay minerals and organic matter. The content and distribution of these substances can affect the adsorption characteristics of methane (Chen et al., 2017; Abunowara et al., 2020). Pores are the main place where oil and gas resources are enriched, and the adsorption characteristics of methane in different structures and types of pores are different. In addition, methane adsorption is influenced by reservoir properties (temperature, pressure and water content), and when these conditions change, the original adsorption equilibrium is broken (Saleman et al., 2015; Ye et al., 2016). Therefore, the effect of methane adsorption is reviewed here

in three aspects: 1) TOC and clays, 2) Pore structures, 3) Pressure, temperature, and moisture content.

3.1 Effect of TOC and clays on sorption

TOC content represents the amount of organic carbon in the geological formation. In shale, large amounts of methane are lodged in nanoscale pores within the organic matter, and many studies have shown that the adsorption capacity of shale reservoirs is related to TOC content. Kim et al. (2017) measured TOC content, specific surface area, and methane adsorption isotherm of 14 shale samples. As TOC content and specific surface area increase, the adsorption capacity increases. TOC content and specific surface area together control the adsorption characteristics. Shi et al. (2019) found that the methane desorption rate of samples with high TOC content is fast through the adsorption experiment on 7 samples and desorption experiment on 30 samples. Li et al. (2021) also derived a positive linear correlation between saturated adsorption capacity and TOC content (Fig. 3), and a multi-factor shale gas adsorption prediction model based on the Langmuir model was developed using multiple regression methods (Eq. (6)). In addition, Ekundayo et al. (2021) derived a strong correlation between TOC content and Langmuir volume and hysteresis in their experiments.

$$N_{ab} = \frac{(-0.0196T + 0.8296\gamma - 0.2203W_t + 2.4838) \times P}{P + (0.046T - 1.1214\gamma + 0.4834W_t + 7.3366)} \quad (6)$$

where N_{ab} is the adsorption amount at pressure p, cm^3/g; W_t is the moisture content, %; γ is the TOC content, %.

In addition to organic matter, shale also contains clay minerals. Methane can occur in the pores of clay minerals
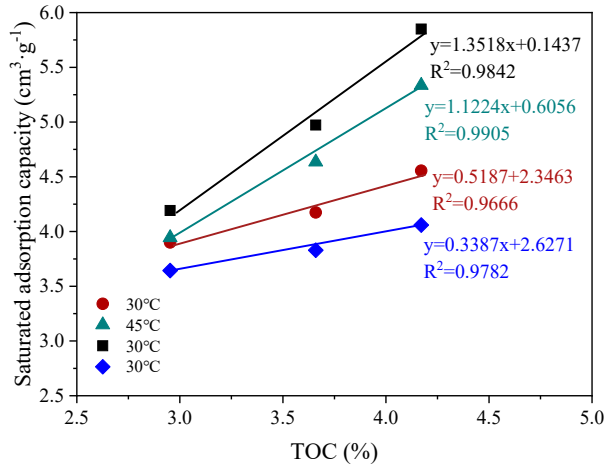
Fig. 3. Effect of TOC content on adsorption (Li et al., 2021).

in both adsorbed and free states. The surface of clay particles is negatively charged, Jin and Firoozabadi (2013) explored the adsorption of methane and carbon dioxide molecules on clay surfaces using the method of Monte Carlo simulations, where the adsorption of methane is related to clay interactions and the cation exchange of charges in clay is the main contribution to carbon dioxide adsorption. In a follow-up study, Jin and Firoozabadi (2014) studied the effect of water content on methane adsorption in clay minerals, indicating that clay minerals are hydrophilic, and water can significantly reduce methane adsorption in minerals. Li et al. (2019a) demonstrated that the adsorption of methane in clay minerals is physical adsorption, and the adsorption performance is affected by mineral type, pressure, and water saturation. The adsorption capacity of different minerals is ranked as follows: montmorillonite, chlorite, illite. Grekov et al. (2020) experimentally demonstrated that the cation exchange of montmorillonite leads to clay expansion and increases the interlayer spacing of clay, thus enhancing its ability to adsorb methane.

3.2 Effect of pore structures on sorption

The extraction of methane from reservoirs consists of three stages: desorption-diffusion-fluid flow (Cai et al., 2018). During the development process, the adsorbed methane is first desorbed from the micropores and then diffused into the cracks. Therefore, the structural characteristics of micropores and cracks have an important influence on sorption. Blanco et al. (2016) constructed microporous materials with different pore structures and specific surface areas to investigate the adsorption capacity of methane. They concluded that the volume and specific surface area of micropores are directly related to the storage capacity of methane. The larger the pore volume and specific surface area are, the greater the adsorption capacity occurs. Chen et al. (2018) studied the effects of different bedding plane angles on methane adsorption, desorption and flow characteristics. The methane adsorption rate increases with increasing bedding plane angle, and the more effective paths for methane flow within the specimen, the faster the initial flow rate. Li et al. (2019b) concluded from methane desorption and diffusion experiments that larger coal particle

size in coal will result in a slower gas diffusion rate and longer desorption time. Zhou et al. (2019) analyzed the potential energy change characteristics of methane near the pore throat based on Leonard-Jones potential function (Eq. (7)). As the radius of pore throat increases, the barrier effect of pore throat on methane gradually decreases. The nanopore structures in kerogen has important implications for methane storage, and Gonciaruk et al. (2021) used focused ion beam in combination with scanning electron microscopy and transmission electron microscopy to reveal that the structure of nanosorbent pores in kerogen is in an indefinite phase and also includes flakes and fibrils.

$$E_{p,total} = 2\varepsilon_a \left[\left(\frac{R}{r_0} \right)^2 + \left(\frac{x}{r_0} \right)^2 \right]^{-6} - 4\varepsilon_a \left[\left(\frac{R}{r_0} \right)^2 + \left(\frac{x}{r_0} \right)^2 \right]^{-3}$$

(7)

where ε_a is the adsorption energy between coal and methane molecules, kJ/mol; r_0 is the diameter of methane molecule, nm; R is the pore-throat radius, nm; x is the coordinate of methane molecule relative to pore-throat.

3.3 Effects of pressure, temperature, and moisture content on sorption

The sorption characteristics of methane are also influenced by reservoir conditions. When the temperature change, the original adsorption equilibrium state will be broken. Cai et al. (2014) measured the adsorption characteristics of coal at temperatures of 20 °C, 35 °C, and 50 °C. The increase in temperature has a significant effect on the reduction of low-rank coal adsorption. For the methane sorption characteristics under high temperature conditions (higher than 80 °C), Zhu et al. (2019) concluded that maximum methane adsorption shows a linear negative correlation with temperature, and the trend is more pronounced with higher carbon content. In addition, the sorption of methane is influenced by reservoir pressure, and the Langmuir model can describe the characteristics of methane adsorption under low pressure conditions. As the pressure increases, the adsorption amount increases. However, a large amount of shale has a higher burial depth and a higher pressure and there is a large gap between the absolute adsorption amount and excess adsorption amount, Xiong et al. (2016) carried out methane adsorption experiments under the pressure of 0-50 MPa, and found that excess methane adsorption amount increased first and then decreased with the increase of pressure. During the extraction of CBM, the negative extraction pressure has an important influence on the desorption of methane, Du et al. (2018) demonstrated that at each adsorption equilibrium pressure, the higher the negative extraction pressure, the greater the gas desorption, and the negative pressure environment increases the amount and rate of methane facilitates methane desorption and diffusion. The supercritical temperature and pressure of methane are -82.6 °C and 4.6 MPa, respectively, and methane usually exists in a supercritical state in coal and shale reservoirs. Meng et al. (2019) investigated the adsorption characteristics of supercritical methane, which increases with pressure and decreases with temperature. Li et al. (2020) comprehensively analyzed the effects of temperature, pressure, and moisture

content on methane sorption. Under different pressure conditions, temperature and moisture have obvious effects on sorption. When pressure is lower than 8 MPa, moisture is the dominant factor, and when the pressure is higher than 8 MPa, temperature is the dominant factor.

Moisture and gas co-exist in reservoirs. The effect of moisture on methane adsorption can be investigated by conducting isotherm adsorption experiments under different moisture content conditions. Farzad et al. (2007) concluded that moisture trapped in the pores reduces methane adsorption. Wang and Yu (2016) through sorption experiments on dry and wet samples under high pressure conditions demonstrated that the adsorption capacity of wet samples is weak, and the effective adsorption sites of methane are mainly distributed in small pores (< 4 nm), and the pores in the range of 2-7 nm are competing adsorption sites for methane and water. Fan et al. (2018) carried out methane adsorption experiments under different temperature and moisture content conditions and concluded that methane adsorption shows a decreasing trend with increasing moisture content, and the changes can be divided into a linear decreasing stage, a flat stage, and a convex decreasing stage (Fig. 4). To clarify the adsorption mechanism between methane and water molecules, Zeng et al.
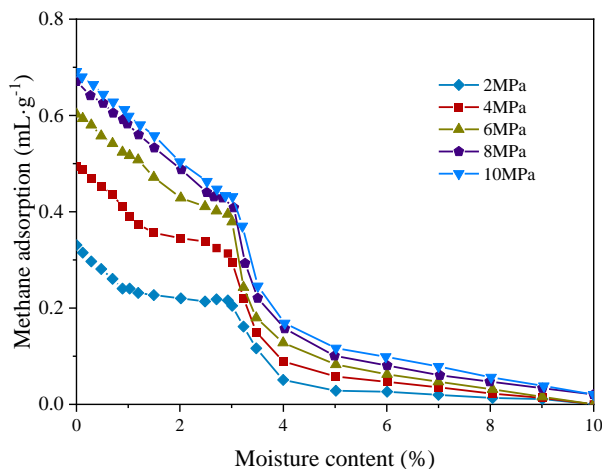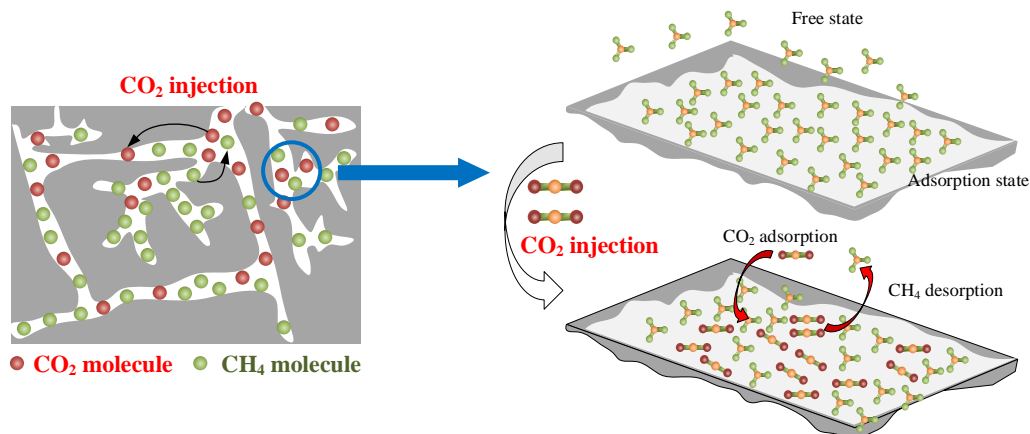
(2017) introduced a fluid mixing rule to describe the competitive adsorption process, where moisture competes with methane for adsorption sites, thus reducing the effective adsorption capacity of coal for methane. Gao et al. (2020) analyzed the effect of moisture content on methane sorption from an energetic perspective. The energy difference between adsorption and desorption leads to desorption hysteresis. Moisture molecules can reduce the free energy of coal surface. The molecular force between moisture and coal is stronger than that of methane, which can occupy the adsorption sites on the coal surface and promote the desorption of methane.

4. Controlling desorption for enhanced gas recovery

The factors influencing methane sorption have been described above. On this basis, numerous studies have taken corresponding means to promote the desorption of methane and enhance gas recovery.

On the other hand, with the global warming, the geological storage of carbon dioxide and the displacement of methane can obtain huge economic benefits and have good application prospects. Depending on the competing adsorption of different molecules, the desorption of methane can be promoted by injecting carbon dioxide. Since carbon dioxide is a polar molecule and methane is a non-polar molecule, there are a large number of charge imbalanced polar adsorption sites in reservoirs, which increases the adsorption capacity of carbon dioxide (Zhang et al., 2015). In addition, the dynamic diameter of carbon dioxide molecules is about 0.33 nm, while that of methane molecules is 0.38 nm, so carbon dioxide molecules can enter smaller nanopores and occupy more adsorption sites (Klewiah et al., 2020). Fig. 5 shows the schematic diagram of replacing methane with carbon dioxide.

4.1 Alteration of reservoir pore structures or reservoir conditions

Hydraulic fracturing is the injection of high-pressure water into the borehole to fracture reservoir and improve permeability (Yuan et al., 2018; Shen et al., 2019). After fracturing, water penetrates into the microscopic pore structures through
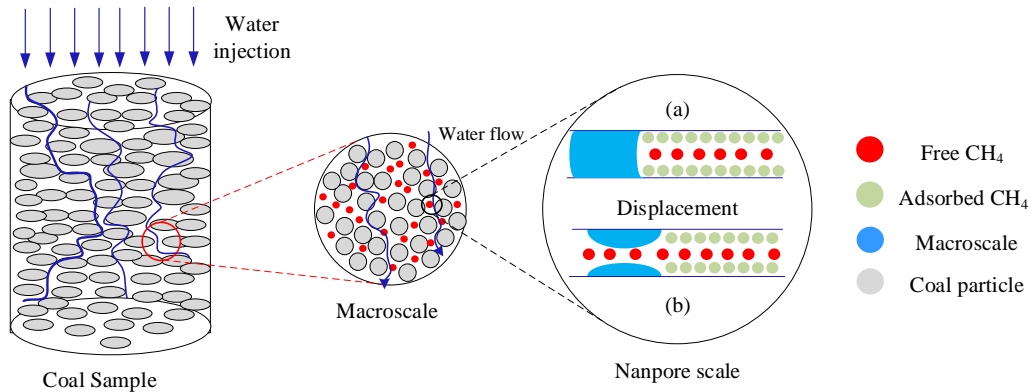

Fig. 4. Effect of moisture content on sorption (Fan et al., 2018).

Fig. 5. The schematic diagram of carbon dioxide injection to displace methane (Bai et al., 2020).

Fig. 6. The interaction of methane-water at the nanopore scale (Wang et al., 2018b).

spontaneous imbibition (Cai et al., 2021). In addition, due to the intervention of water molecules, it will compete with methane for adsorption sites, thus promoting the desorption of methane. Huang et al. (2016) performed hydraulic fracturing on methane-containing coal and concluded that pore pressure gradient caused by hydraulic fracturing can lead to methane displacement. Wang et al. (2018b) investigated the interrelationship between injected water and methane under high pressure conditions (Fig. 6). Water injection can displace the methane adsorbed in nanopores and increase the content of free methane. The higher water injection volume and the higher initial adsorption equilibrium pressure, the greater methane content of replacement. Besides, adding surfactants to fracturing fluid can promote the desorption of methane (You et al., 2015).

High temperature can promote the desorption of methane. Therefore, the reservoir temperature can be increased by microwave irradiation to promote the desorption of methane. Wang et al. (2018a) conducted methane desorption experiments with and without microwave radiation, and confirmed that microwave radiation increases diffusion coefficient and decreases decay coefficient of methane. The amount of methane desorption increased from 1.91 to 3.92 times, and it increased with the increase of microwave irradiation time. Xu et al. (2020) carried out desorption experiments in a heating system and concluded that 80 °C is the optimal oxidation temperature for CBM exploitation through functional group analysis.

4.2 Gas injection for enhanced methane recovery and CO_2 storage

In recent years, gas injection has made great achievements in increasing the production of CBM and shale gas. Several studies have shown that nitrogen injection can improve the recovery rate. Zhang et al. (2020b) analyzed the effect of nitrogen injection on methane desorption and coal deformation. They concluded that injecting nitrogen can reduce the partial pressure and promote methane desorption, while leading to coal deformation and shrinkage and increasing permeability.

With the escalating greenhouse effect, carbon dioxide geological storage has become a hot research topic (Kang et
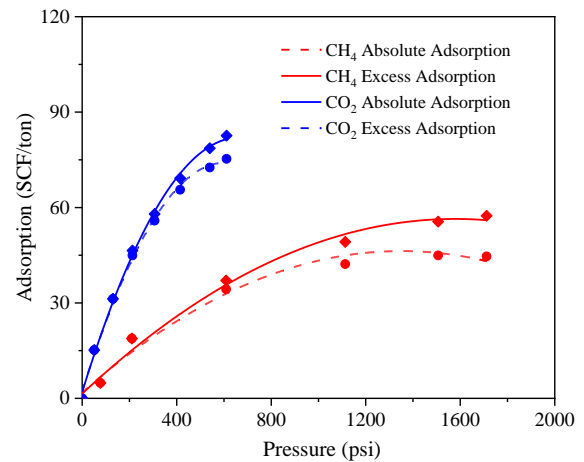

Fig. 7. Adsorption characteristics of methane and carbon dioxide (Heller and Zoback, 2014).

al., 2019; Zhou et al., 2020). The injection of carbon dioxide into reservoirs not only reduces the carbon content in the atmosphere, but also promotes methane desorption and improves recovery. Day et al. (2008) investigated the effect of coal rank on carbon dioxide adsorption in the supercritical state based on the D-R model, the carbon dioxide adsorption capacity increases with higher coal rank. Heller and Zoback (2014) carried out isothermal adsorption experiments of carbon dioxide and methane, and concluded that the adsorption capacity of carbon dioxide in pure mineral composition and actual shale is 2-3 times that of methane (Fig. 7).

Brown et al. (2017) studied the effect of carbon dioxide displacement of methane in reservoirs. Carbon dioxide displaces methane more effectively than water, producing more natural gas per tonne of carbon dioxide injected. Huang et al. (2018) concluded that the kerogen in the reservoir has a strong carbon dioxide storage capacity, and water can promote carbon dioxide to displace methane. Bai et al. (2020) showed in their study that injecting carbon dioxide into the reservoir can significantly improve methane recovery and shorten methane desorption time. Carbon dioxide injection increased the total desorption efficiency of methane by 19.89%, the desorption efficiency of methane per unit time by 14.108%, and the desorption of methane per unit mass of coal by 35.23%.
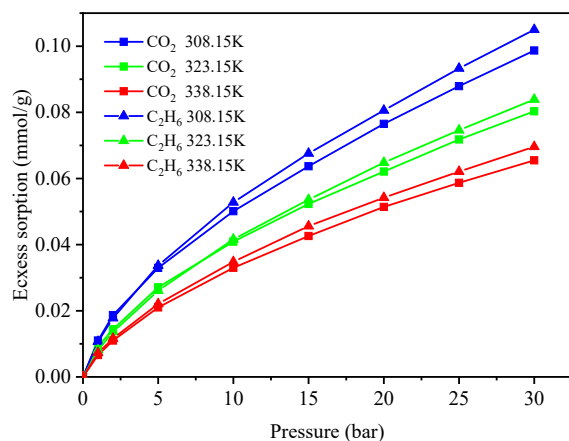
Fig. 8. Sorption characteristics of ethane and carbon dioxide (Zhao et al., 2017).

4.3 Adsorption of hydrocarbons and carbon-dioxide

Shale contains organic and inorganic matter, both present in nanopores. When carbon dioxide is injected, the adsorption in shale contains carbon dioxide as well as hydrocarbons (methane, ethane, propane, n-butane, iso-butane) adsorption. Elucidating the sorption mechanism of hydrocarbons and carbon dioxide in shale helps to understand the principle of carbon-dioxide injection to enhance recovery. Zhao et al. (2017) measured the adsorption characteristics of hydrocarbons and carbon dioxide in shale through experiments, and concluded that their adsorption characteristics are all functions of temperature and kerogen content, and the adsorption of ethane is close to that of carbon dioxide, as shown in Fig. 8. Zhao et al. (2018) investigated the sorption of hydrocarbons and carbon dioxide under high-pressure conditions. There is a hysteresis phenomenon in adsorption, and there is a significant difference between excessive adsorption and absolute adsorption of n-butane and iso-butane. Tang (2019) explored the thermodynamic potentials of hydrocarbon vapors and carbon dioxide in shale. The adsorption capacity is positively related to molecular mass, and the adsorption capacity of carbon dioxide is higher than methane and ethane.

Kerogen is the main organic component in shale, and the content of hydrocarbons is related to organic matter. Wu et al. (2019) explored absolute adsorption of light hydrocarbons and carbon dioxide in shale and kerogen. Adsorption is mainly controlled by kerogen. Desorption hysteresis is smallest for methane and most pronounced for ethane. For the multi-scale adsorption behavior of hydrocarbons and carbon dioxide in shale cannot be characterized by instantaneous equilibrium adsorption models, Singh and Cai (2019) considered micro-scale adsorption force and pore-scale heterogeneity, etc., established a multi-scale adsorption kinetic model in shale, and verified the accuracy of the model through experimental data. Huang et al. (2019) investigated the competing adsorption of carbon dioxide and methane in kerogen through molecular dynamics simulation. They demonstrated that carbon dioxide has a high affinity with kerogen and a low diffusion coefficient, and the injection of carbon dioxide can cause the kerogen to deform and increase production.

5. Outlooks

With the gradual decline of resources in conventional reservoirs around the world and the societal needs to transition to cleaner burning fuels, it is necessary to increase the development of methane resources in coal and shale by establishing a sound theoretical foundation and their application in technology development for optimum development of resources. In terms of theoretical basis, it is necessary to further improve methane adsorption model, consider a variety of key factors that play a role in desorption of methane, and benchmark the contribution of each factor towards gas flow rate. In terms of technology development, carbon dioxide geological storage should be combined with CBM/shale gas development that can not only help increase production capacity, it can also effectively reduce carbon emissions through permanent carbon sequenstration.

Desorption of methane from shale gas reservoirs is an active area of research mainly in the laboratory, but such studies are usually without a competing fluid flow mechanisms that exist in the field (e.g., free gas phase). Although these studies are helpful in advancing the understanding about sorption, they cannot capture a complete picture about the relative role of desorption in gas production in the field when compared to other competing mechanisms. Such efforts have been investigated through reservoir simulations, but the numerical predictions cannot be fully confirmed without supportive field studies. A number of similar studies have been conducted to investigate fracturing fluid flowback to understand the origin and mechanisms of produced water (Singh 2016), therefore, an equivalent effort is required to reveal the importance of desorption in gas production in the field.

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Conflict of interest

The authors declare no competing interest.

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