Effect of Different Placement Sequences of Water on the Methane Adsorption Properties of Coal

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ABSTRACT: After the coal seam is injected with water, the moisture content in the coal body increases, which affects the output capacity of coalbed methane (CBM). In order to improve the effect of CBM mining, the classical anthracite molecular model has been selected. To analyze the influence of different placement orders of water and methane on the characteristics of coal-adsorbing methane from the micro point of view, a molecular simulation method is used for comprehensive consideration in the study. The results show that H_2O does not change the mechanism of CH_4 adsorption by anthracite, but it inhibits the adsorption of methane by anthracite. When water enters the system afterward, there arises an equilibrium pressure point where water plays the most significant role in inhibiting methane adsorption by anthracite coals, which increases with increasing moisture content. When water enters the system first, no equilibrium pressure point occurs. The excess adsorption of methane by anthracite when water enters second is higher. The reason is that H_2O can replace CH_4 at the higher energy adsorption sites of the anthracite structure, while CH_4 can only be adsorbed at the lower energy sites, and some of CH_4 is not adsorbed. For the coal samples with a low-moisture content system, the equivalent heat of adsorption of CH_4 increases first rapidly and then slowly with the increase of pressure. However, it decreases with pressure in the high-moisture content system. The variation of the equivalent heat of adsorption further explains the variation of the magnitude of methane adsorption under different conditions.
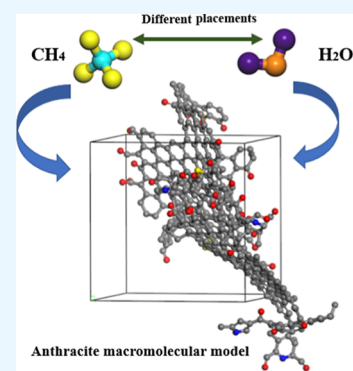
1. INTRODUCTION

Coalbed methane (CBM) is mainly composed of methane. In comparison, methane is cleaner and more environmentally friendly than other energy sources.[1,2] In addition, methane can contribute to the greenhouse effect and is up to 21 times more harmful to global warming compared to CO_2.[3,4] Given that CBM resources are abundant in China. In order to increase the permeability of coal seams and improve the efficiency of gas extraction, hydrodynamic measures are widely used. During the implementation of hydrodynamic measures, the injected water affects the adsorbed-state methane in coal, so it is important to study the effect of different placement sequences of water and methane on the adsorbed methane properties of coal.[5,6]

In recent years, hydrodynamic measures have played an increasingly important role in the field of CBM promotion, and numerous scholars have studied hydraulic fracturing,[7] hydraulic slotting,[8] hydraulic punching,[9] coal seam water injection,[10] hydraulic reaming,[11] and so on. Among them, coal seam water injection is widely used in coal mines and is playing an increasingly important role in improving the efficiency of gas extraction. Coal seam water injection can change the internal structure of the coal body through artificial high pressure, expand the seepage channel, and play a role in macroscopic reservoir reconstruction. At the same time, the external liquid can also penetrate into the pores to produce a

microscopic reaction with gas, play a role in displacement desorption, and thus improve the gas drainage effect.[12] In addition, coal seam water injection is also a mine disaster prevention and control technology that integrates the functions of dust reduction, dust removal, erosion prevention and pressure relief, and coal rock softening.[13,14] So, coal seam water injection has become a hot spot in current research. First, some scholars studied the presence of water in coal and the characteristics of methane transport law and discussed to derive the gas transport law and stress changes in coal caused by the water movement. It was shown that the water−methane repulsion effect objectively exists; free methane can be produced by competitive adsorption and replacement desorption of methane and water.[15−17] According to the mechanism of the influence of water on the methane adsorption properties of coal, coal seam water injection for mining has become an important tool in engineering practice. Pu conducted a series of experiments to study the differences
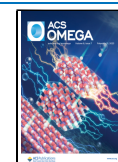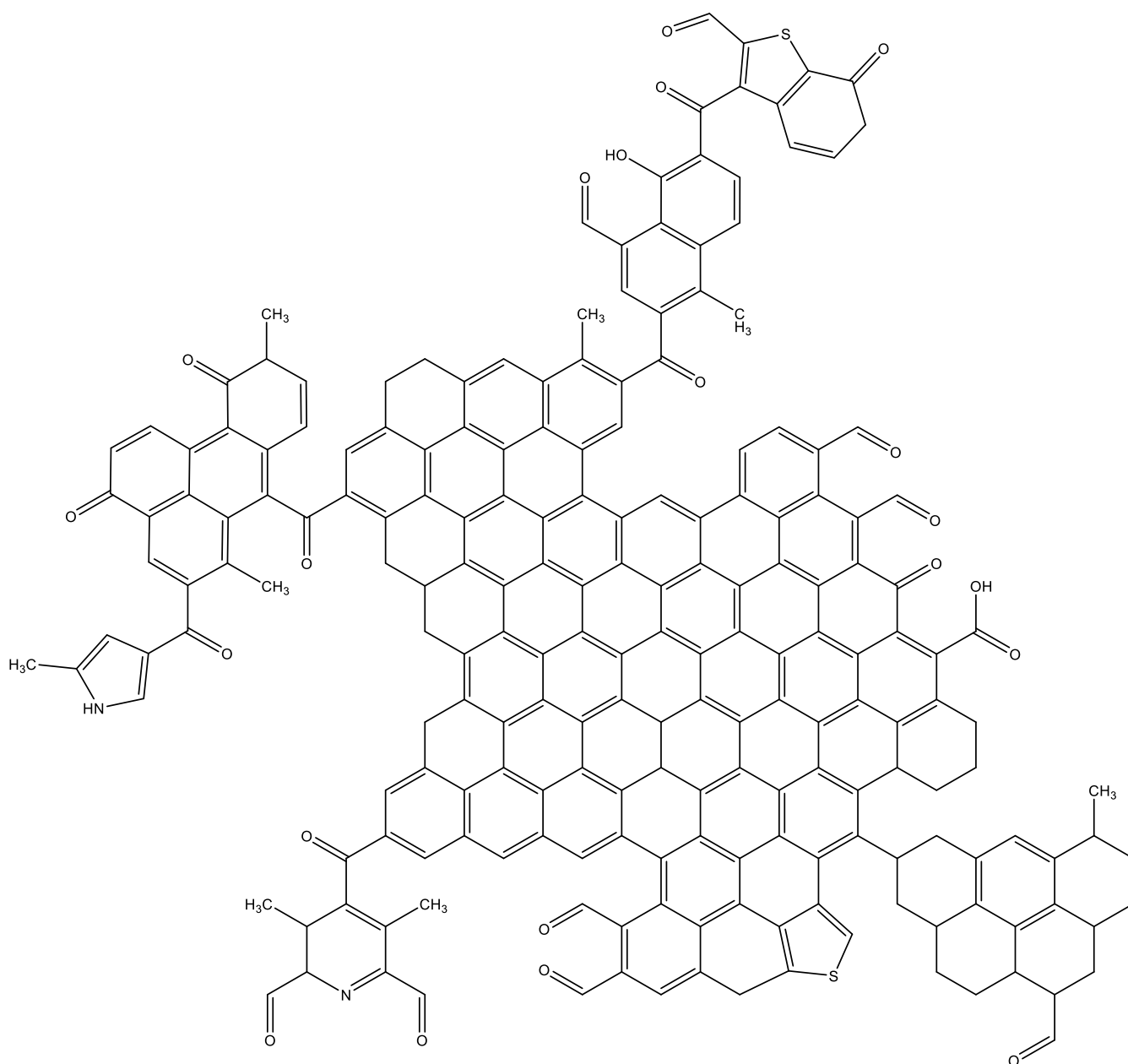
Figure 1. Anthracite macromolecular model.

in mechanical property changes under wetting conditions with different coal samples. The experimental results show that the elastic modulus and compressive strength decrease as an exponential function with increasing water pressure and developed a coupled gas−liquid−solid model containing effective stress changes and gas desorption based on the experimental results. The established gas drainage model is validated by field data and can reflect the pattern of borehole damage and gas drainage under water injection. It can be considered that the coal seam wetting effect is an important parameter in the coal seam water injection mining process.[18] Some experts determined the effects of the amount of injected water, the injection rate, the seam moisture content, and the coal dust level on gas extraction through experiments as well as field measurements, made qualitative and quantitative analyses of effective water injection duration and water injection rate, and derived a range of values.[19−21] In order to clarify the effect

of coal seam water injection, Yue utilized a device integrating the isobaric water addition and isobaric desorption, and spontaneous imbibition height was measured. Based on the dimensionless analysis method, this study realizes the recognition of coal seam water injection technology. It provides a certain theoretical basis for the efficient implementation of coal seam water injection in subsequent engineering practice.[22] During the implementation of coal seam water injection, experts found that the wetting of the coal seam was not effective when pure water injection was used to promote mining, and some scholars configured additives to solve the problem. Liu added different ionic liquids and surfactant compound solutions in water to optimize the different compound solutions and found that a new type of composite wetting agent was prepared, and the wetting mechanism between coal and the wetting agent was clarified from the perspective of functional groups. It was clarified that

the wettability of the complex solution was indeed better than that of pure water, and the efficient value of the additive was affirmed.[23] Subsequently, Sun proposed the preparation of three kinds of high-efficiency wetting enhancers and compared the wettability of different solutions by experiment and contact angle analysis to arrive at the best enhancer. The molecular dynamics simulation was used to verify the relationship between them, and finally, the mechanism of action was deduced. A new direction was provided to improve the water injection effect in coal seams.[24] Many scholars through a series of theoretical reasoning, physical experiments, and engineering practice have affirmed the status of coal seam water injection in the field of coal mining and the practical value of the presence of water for the extraction and management of gas in coal.

Investigating the "effect of different placement sequences of water on the methane adsorption properties of coal" can comprehensively explain the influence of coal seam water injection on gas adsorption and desorption characteristics from a microscopic perspective and then reveal the microscopic effect of solid–liquid–gas three-phase coupling after coal seam water injection. The effect of water and methane on the methane adsorption by anthracite coal is explored from the molecular point of view, and the mechanism of water adsorption on methane in anthracite coal is analyzed to lay the theoretical foundation for CBM mining, which improves the theoretical system of coal seam water injection to control gas and realizes safe and efficient exploitation of coal seam gas.

2. RESEARCH METHODS

Based on the previous research, this study chose anthracite coal as the research object and conducted the study at the temperature of 30 °C and the adsorption equilibrium pressure of 0–10 MPa. When water is placed first, water molecules are first adsorbed on the anthracite molecular model to form a water injection coal with different moisture contents, and then methane is adsorbed in the simulation; when water is placed second, the anthracite molecular model is first saturated with methane and then water molecules are added to form different applied water injection conditions. The changes of the excess adsorption and the equivalent heat of adsorption of methane by anthracite coal were compared under different orders of water and methane placement.

2.1. Model Construction of the Anthracite Macromolecular Structure. Cui studied the structure of anthracite coal and constructed a molecular structure model of anthracite coal with the molecular chemical formula $C_{202}H_{104}O_{21}N_2S_2$.[25] This structural model can reasonably characterize the structural properties of anthracite coal molecules, so this study cites this molecular structure model of anthracite coal. The two-dimensional structure of the anthracite molecule is drawn using the software ChemDraw, as shown in Figure 1. It is imported into Materials Studio software, and through the Forcite section, the structure is energy-optimized, geometrically optimized, and annealed, and periodic boundary conditions are added to finally obtain the optimal anthracite molecular configuration, as shown in Figure 2.

The anthracite molecular structure cell parameters $a = 19.58$ Å, $b = 19.58$ Å, $c = 19.58$ Å and a cell density of 1.565 g/cm³ are listed in Table 1.

2.2. Adsorption Masses' Construction—CH₄ Molecules and H₂O Molecules. The sorbent is an anthracite molecule. The adsorbed masses are CH_4 and H_2O, which need to be drawn under the Visualizer module of Materials Studio
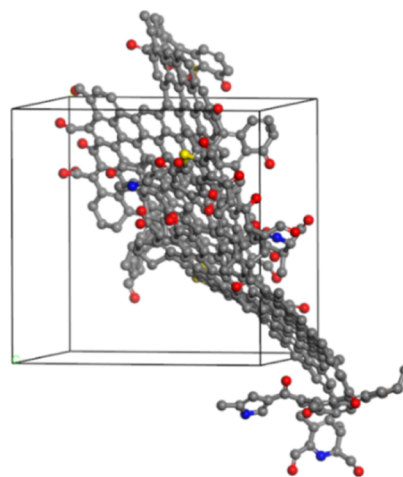

Figure 2. Optimal molecular configuration of anthracite.

software. After geometry optimization, energy optimization, and annealing, CH_4 and H_2O molecules with neutral surface charge and minimum energy were obtained for subsequent grand canonical Monte Carlo's method. The optimized parameters of CH_4 and H_2O molecules are listed in Table 2, and the corresponding molecular structure models of CH_4 and H_2O are shown in Figure 3.

2.3. Simulation Scheme and Parameter Setting. In order to study the effect of water-injected anthracite on the methane adsorption effect, this study learns from the calculation of the molecular weight that when anthracite coal molecules absorb 0, 5, 10, and 15 water molecules, it can make the moisture content of coal reach 0, 1.49, 2.95, and 4.37%. Considering that the simulation object involves water in the study, the influence of hydrogen bonds cannot be ignored. The Dreiding force is selected in this study because it can fully consider the role of hydrogen bonds. Locate task is chosen. The specific parameter settings are listed in Table 3.

Then, we chose the adsorption conformation with the minimum energy, and again by molecular mechanics optimization, as shown in Figures 4–7.

The amount of methane adsorbed and the heat of adsorption was simulated using the fix pressure and adsorption isotherm task items of the Sorption module in the Materials Studio software. The specific parameter settings are listed in Table 4.

In order to explore the effect of water injection on methane adsorption in coal, this study uses the locate task item of the Sorption module to load 5, 10, 15, and 20 water molecules, respectively, to form different external water injection conditions. Then, we use fix pressure and adsorption isotherm task items to calculate the adsorption capacity and adsorption heat of the CH_4 molecule. The temperature is 303 K. The pressure range is 0–10 MPa (0 to 2.5 MPa with an interval of 0.5 MPa and 2.5 to 10 MPa with an interval of 1.5 MPa). The parameter settings are consistent with the above.

The amount of adsorbed gas molecules obtained from molecular simulation calculations is usually the amount of molecular adsorption present inside the pores of porous materials and is called the absolute adsorption.[26] It contains not only those adsorbed on the surface of the pore wall but also the free gas molecules inside the pore that are not adsorbed. However, physical experimental data often refer to the amount of gas molecules adsorbed in the pore, which is

Table 1. Pore Size Distribution Parameters of the Molecular configuration of Anthracite

number of anthracite molecules in the cell	occupied volume (Å³)	volume of voids (Å³)	specific surface area (Å²)	accessible solvent specific surface area (Å²)	percentage of specific surface area accessible to solvents (%)
2	5509.28	1991.53	2300.25	1691.48	76.86

Table 2. Optimization Parameters of CH₄ and H₂O Molecular Conformations

molecular structure	energy (kcal/mol)	charge (e)	length (nm)	angle (deg)
CH_4	0.223120			
C		−0.587061		
H		0.146765		
C−H			1.09859	109.471
H_2O	0.0000720			
O		−0.672302		
H		0.336151		
H−O			0.956999	104.520
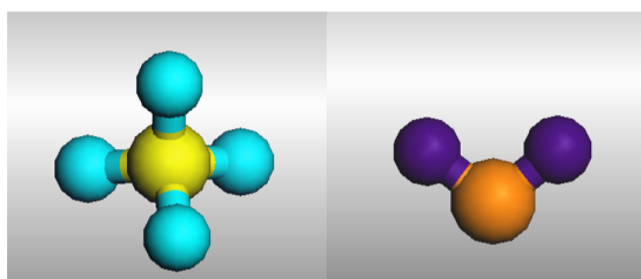
Figure 3. Optimal CH_4 molecular structure model (left) and H_2O molecular structure model (right).

Table 3. Locate Task Parameter Settings

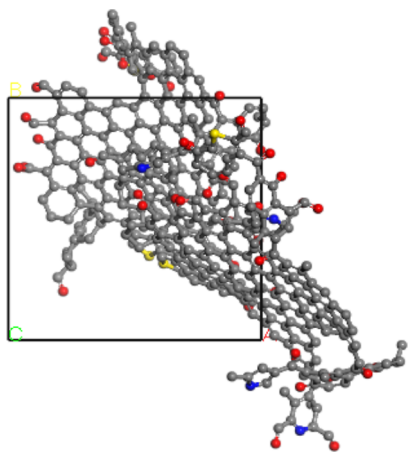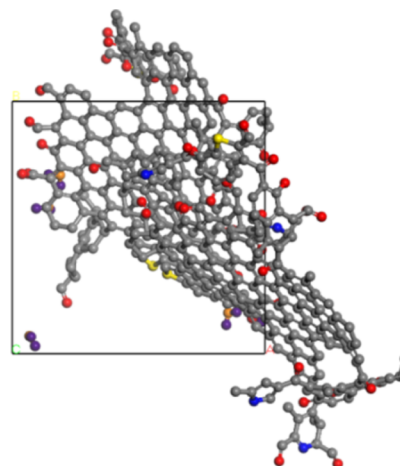| option	adsorptive term
task items	locate
sampling method	metropolis
optimize quality items	medium
adsorbate	CH_4, H_2O
force field	Dreiding
charge	use current
number of temperature cycles	10
maximum temperature	500.15 K
final temperature	303.15 K

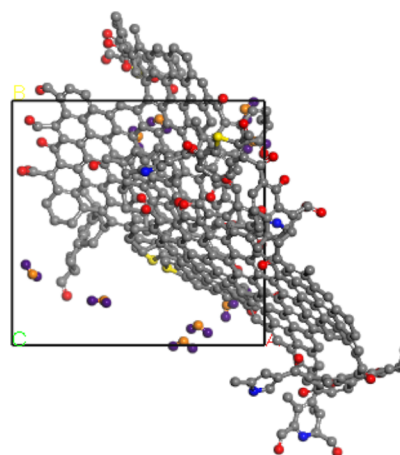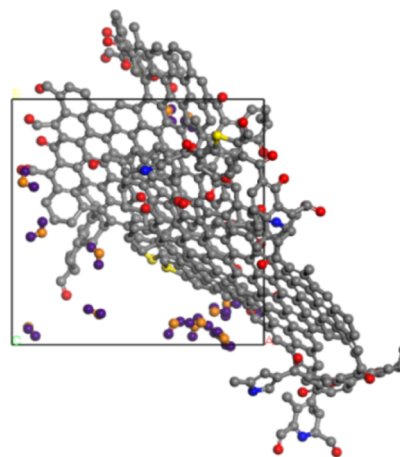**Figure 4.** Molecular structure model of water-injected anthracite coal with 0 moisture content.

Figure 5. Molecular structure model of water-injected anthracite coal with 1.49% moisture content.

Figure 6. Molecular structure model of water-injected anthracite coal with 2.95% moisture content.

Figure 7. Molecular structure model of water-injected anthracite coal with 4.37% moisture content.

Table 4. Fixed Pressure and Adsorption Isotherm Task Parameter Settings

option	adsorptive term	
task items	fix pressure	adsorption isotherm
sampling method	metropolis	metropolis
optimize quality items	customized	medium
pressure range	0−10 MPa	0−10 MPa
force field	Dreiding	Dreiding
charge	use current	use current
ensemble	NVT	NVT
temperature	303.15 K	303.15 K
temperature control method	Andersen	Andersen
electrostatic energy	Ewald	Ewald
van der Waals energy	atom based	atom based

Figure 8. Variation curve of the excess adsorption of CH_4 in different water injection coals.

called the excess adsorption. Moreover, there is a corresponding relationship between the excess adsorption amount and the absolute adsorption amount: excess adsorption = absolute adsorption − density of the gas × free volume of the cell, which is calculated by the following equation[27−29]

$$M_{e(g/g)} = \frac{1}{M_{c(g/u.c.)}} \left(\frac{16.0428 \times M_{a(N/u.c.)}}{6.02 \times 10^{23}} - 1.0 \times 10^{-24} V_{f(Å^3/u.c.)} \times \rho_{(g/cm^3)} \right) \quad (1)$$

where M_e is the excess adsorption of the gas, g/g; M_a is the absolute adsorption of the gas, indicating the number of molecules adsorbed in a cell, N/u.c.; M_c is the mass of a single cell, g/u.c.; V_f is the pore volume of the adsorbent, which is generally approximately equal to the free volume of the constructed model, Å³/u.c.; and ρ is the density of the gas, g/cm³.

3. RESULTS

In order to investigate the effect of different placement sequences of water and methane on the methane adsorption properties of coal, the research plan developed in this study is as follows: ① when water is placed into the system first, the anthracite molecules are preferentially adsorbed with 0, 5, 10, and 15 water molecules to form water-injected anthracite with different moisture contents, and when methane is placed into the system later, the effect of water-injected anthracite on the adsorption amount and heat of adsorption of methane is analyzed; ② when methane is placed into the system first, the anthracite coal is saturated with adsorbed methane, and then 0, 5, 10, and 15 water molecules are added to it later to form different additional water injection conditions, and the effect of water injection on the adsorption amount and heat of adsorption of methane adsorbed by anthracite coal is analyzed.

3.1. Effect of Water Injection Coal on the Methane Adsorption Amount.
The variation curves of the excess adsorption of CH_4 by water-injected anthracite with different moisture contents at different pressures at a temperature of 30 °C are shown in Figure 8.

According to Figure 8, the excess adsorption of methane by the four different injection coals first increases rapidly, then increases slowly, and then tends to a constant value when the temperature is 30 °C and the pressure range is 0−10 MPa. When the adsorption rate of methane molecules on the anthracite surface and the desorption rate of methane
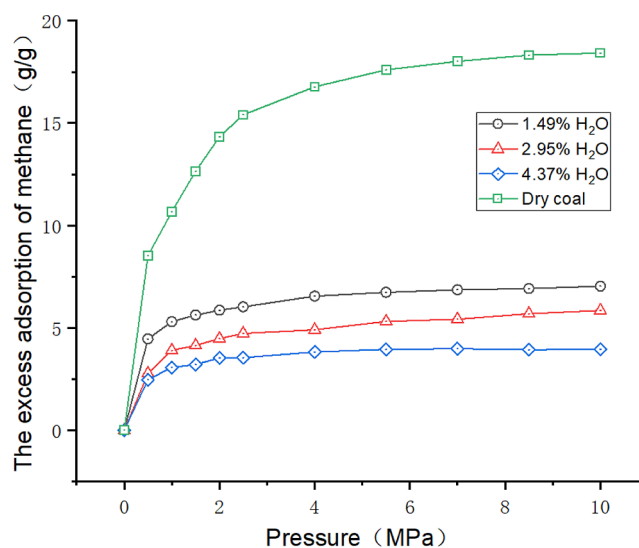
molecules on the coal surface reach equilibrium, the adsorption of methane molecules on the coal surface reaches equilibrium. With the increase of pressure, methane adsorption capacity also increases. When the pore surface that can pass through the gas molecules is gradually covered by methane molecules, the adsorption capacity will not increase and the adsorption will reach equilibrium.[30,31] It shows that increasing the adsorption equilibrium pressure is beneficial to the methane adsorption. Compared with dry anthracite, the excess adsorption of methane by water-injected anthracite is significantly lower, and the excess adsorption of methane decreases as the moisture content increases. The difference of the excess adsorption between water-injected anthracite and dry anthracite coal samples was larger with increasing pressure at the same moisture content.

3.2. Effect of Water Injection on the Amount of Methane Adsorbed in Coal.
To obtain the corresponding molecular structure of anthracite coal that has been saturated with adsorbed methane, this study simulated the adsorption process of methane by the anthracite molecular structure under the conditions to be set. Moreover, in order to facilitate the study of the effect of different water injections on the methane adsorption characteristics of anthracite coal, the locate task term was used to constitute different applied water injection conditions with 0, 5, 10, and 15 water molecules. The adsorption amount of gas molecules obtained by the software Materials Studio simulation is the absolute adsorption, which is not consistent with the data measured in the laboratory. Therefore, it is necessary to use the equation between the absolute adsorption and the excess adsorption for conversion. The variation of the excess adsorption of CH_4 in the anthracite structure at a temperature of 30 °C with different applied water injection conditions is shown in Figure 9.

As shown in Figure 9, under different water injection coals, the excess adsorption of CH_4 increases rapidly and then slowly with the increase of pressure. It shows that water does not affect the adsorption law of anthracite to methane, and it still satisfies the Langmuir equation.[32] The larger the water injection content is, the more water molecules are likely to occupy the adsorption site of anthracite. At the same time, water is easy to enter microporous pores, forming capillary
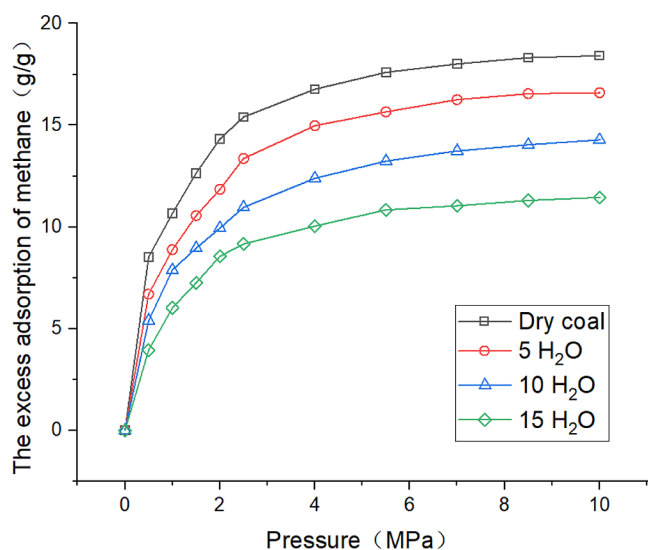
Figure 9. Variation of the excess adsorption of methane by coal under different water injection coals.

Figure 10. Equivalent heat of the adsorption variation curve of methane adsorption for different water injection coals.

Figure 11. Equivalent heat of adsorption curves of coal adsorption of methane under different water injection conditions.

resistance inside the pores, which hinders anthracite from absorbing methane molecules and affects the adsorption performance of anthracite on methane. This leads to a lower excess adsorption of CH_4.[33]

3.3. Effect of Water Injection Coal on the Equivalent Heat of Adsorption of Methane.

The equivalent heat of adsorption is an important basis for assessing the magnitude of the adsorption capacity of a gas in a coal structure model.[25] The larger the equivalent heat of adsorption, the stronger the force of this gas molecule with the coal structure model. It can be calculated from the isothermal adsorption line to obtain the temperature value as well as the pressure value under the corresponding adsorption volume conditions using the Clausius−Clapeyron equation with the following equation[29,34]

$$Q_{st} = -\Delta H = RT^2 \left(\frac{\partial \ln P}{\partial T} \right) \tag{2}$$

where P is the gas pressure, MPa; R is the universal gas constant, taken as 8.314; T is the absolute temperature, K; and Q_{st} is the equivalent heat of adsorption, kJ/mol.

In this study, the Adsorption isotherm module of Sorption is used to simulate the equivalent heat of adsorption of methane for different injection coal samples, and the trend is shown in Figure 10.

As can be seen from Figure 10, the equivalent heat of adsorption of CH_4 gradually decreases with the increasing moisture content of the injected coal at the same temperature and pressure. This indicates that with the increase of H_2O, the adsorption capacity of CH_4 gradually decreases.

3.4. Effect of Water Injection on the Equivalent Heat of Adsorption of Methane by Coal.

After the simulation processing by the Sorption module of Materials Studio, the equivalent heat of adsorption of CH_4 in anthracite coal under different applied water injection conditions was obtained, as shown in Figure 11.

As can be seen from Figure 11, the equivalent heat of adsorption of methane from anthracite coal was significantly lower than that of dry coal samples after the injection of moisture. Moreover, the equivalent heat of adsorption of CH_4 decreased with the increase of added moisture content.
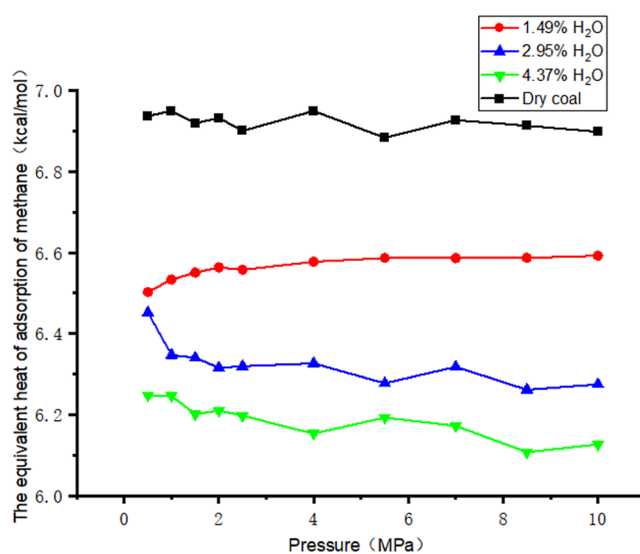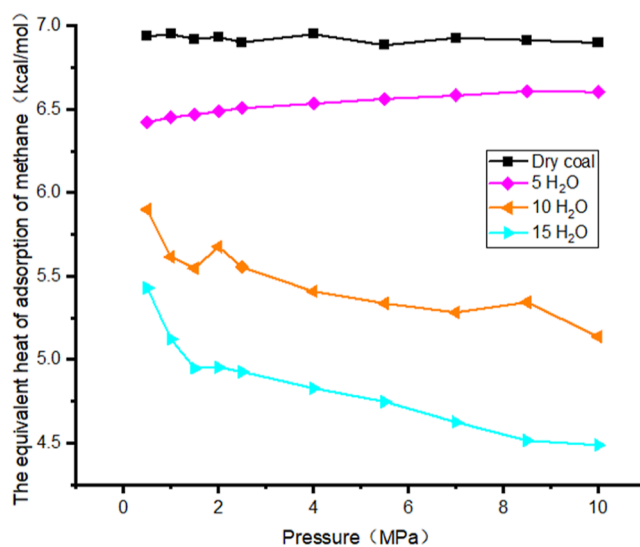
4. ANALYSIS AND DISCUSSION

Based on the simulation results of the effect of water injection anthracite on methane adsorption at fixed temperature and different pressure, the variation of the excess adsorption of CH_4 was plotted (Figure 8). Based on the simulation data of the effect of water injection on the change of methane adsorption by coal, the change of the excess adsorption of CH_4 was plotted (Figure 9). After extensive adsorption experiments, it was shown that the Langmuir single molecular-layer adsorption theory was used to describe the methane adsorption process with anthracite coal to obtain quite satisfactory results with the expression[35,36]

$$V = \frac{abP}{1 + bP} \tag{3}$$

where V is the gas adsorption volume at standard condition, cm^3/g; a is the gas limit adsorption volume, m^3/t; b is the Langmuir adsorption constant, MPa^{-1}; and P is the gas pressure at adsorption equilibrium, MPa.

In order to facilitate the analysis of the variation law of the effect of placement sequences of water and methane on the methane adsorption by anthracite coal, each set of data in Figures 8 and 9 is fitted with the Langmuir equation and integrated into the same coordinate system as shown in Figure 12 in this study.
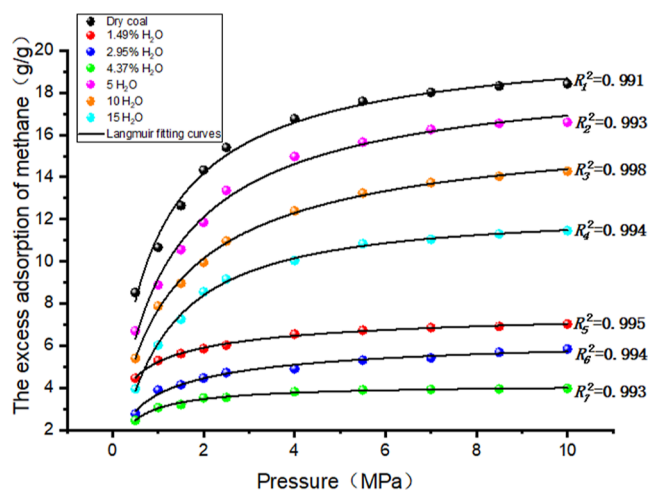

Figure 12. Variation of the excess adsorption of methane in anthracite coal for different placement sequences of water and methane.

According to Figure 12, it can be seen that the variation curve of the excess adsorption of CH_4 under different conditions is consistent with the Langmuir adsorption theory model, and the correlation coefficients R^2 are all greater than 0.99, which proves the reliability of the simulated data. The trend of CH_4 excess adsorption by anthracite under different conditions was consistent, which confirmed that the intervention of H_2O molecules did not change the adsorption mechanism of CH_4 molecules by anthracite. The change of CH_4 excess adsorption increased rapidly and then increased slowly. At the initial stage of contact between methane molecules and anthracite molecules, the adsorption vacancies on the surface of anthracite molecules are sufficient. This leads to a faster adsorption rate of methane and rapid increase of methane adsorption capacity. The reason for the slowing down of the adsorption rate with increasing pressure is that at higher pressure, more adsorption sites are required to be occupied in the coal body to reach the dynamic equilibrium between the free and adsorption phases than at lower pressure. The number of adsorption sites in the coal body is fixed, so the growth rate of adsorption volume slows down with the increase of pressure.[37] Compared with the dry coal samples, the excess adsorption of methane by water injection anthracite decreased, and the excess adsorption of methane decreased with increasing moisture content. The reason is that the relationship between the kinetic diameter of adsorbent masses is H_2O > CH_4, and the kinetic diameter is inversely proportional to the adsorbed amount. Therefore, the adsorption capacity of H_2O is better than that of CH_4. When water is present in the system, competition between methane molecules and water molecules will occur. The presence of water will have an inhibitory effect on the adsorption of methane by anthracite coal, resulting in a decrease in the amount of methane adsorbed.[38]

In order to more accurately study the effect of different orders of water and methane placement on methane adsorption in the structural model of anthracite coal, the data on the decrease of the excess adsorption of methane by anthracite coal under each condition were plotted separately, as shown in Figure 13. In order to further compare the
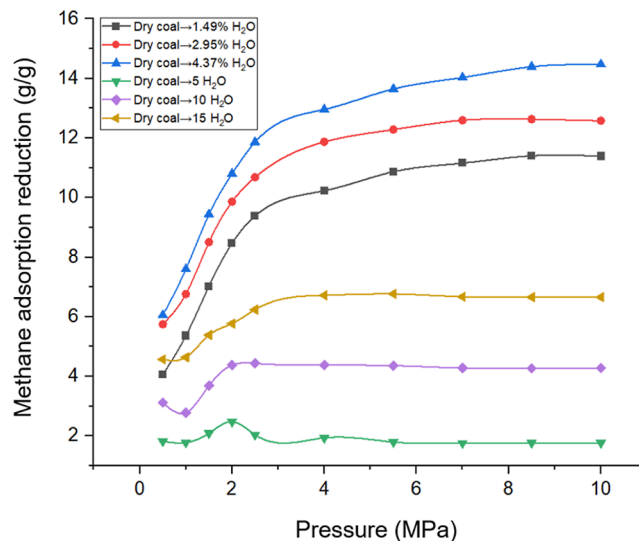

Figure 13. Decrease in the excess adsorption of methane in anthracite coal for different placement orders of water.

variation of methane excess adsorption by anthracite coal under the two cases of first and second placements of the same water molecules, the decrease of methane excess adsorption data was compared for the systems of 5, 10, and 15 water molecules, and the results are shown in Figure 14.

According to Figure 13, it can be seen that the drop-in methane adsorption by anthracite coal under different applied water injection conditions was first rapidly large and then slowly decreased. The maximum amount of decrease in methane adsorption was reached at 2.0, 2.5, and 5.5 MPa under three different water injection conditions. Therefore, there exists an equilibrium pressure point where water plays the most obvious inhibitory effect on methane adsorption in coal. In addition, the value of this equilibrium pressure point increases with the higher content of the applied water injection. The amount of decrease in methane adsorption by the water injection anthracite showed a similarity with anthracite-applied water injection, but there is no obvious equilibrium pressure point.

According to Figure 14, it can be seen that the drop of excess adsorption of methane by the molecular structure of anthracite coal is higher than that by the postmoisture entry when the water is placed into the system first when three different water molecule number systems containing 5 H_2O, 10 H_2O, and 15 H_2O are included. This indicates that the inhibition of methane adsorption is greater when water enters first than when water enters second. It was found that the boiling point of H_2O is 99.97 °C much higher than the boiling point of CH_4—161.5 °C. The higher the boiling point of the gas, the deeper the adsorption traps, resulting in a greater adsorption capacity of H_2O than CH_4.[39] Thus, compared with CH_4, the molecular structure of anthracite has a stronger capacity for H_2O adsorption and forms a more stable molecular system. When water enters the system first, it will occupy the higher energy adsorption sites of the anthracite molecular structure in advance and is closer to the anthracite molecules. When methane enters the system subsequently, the
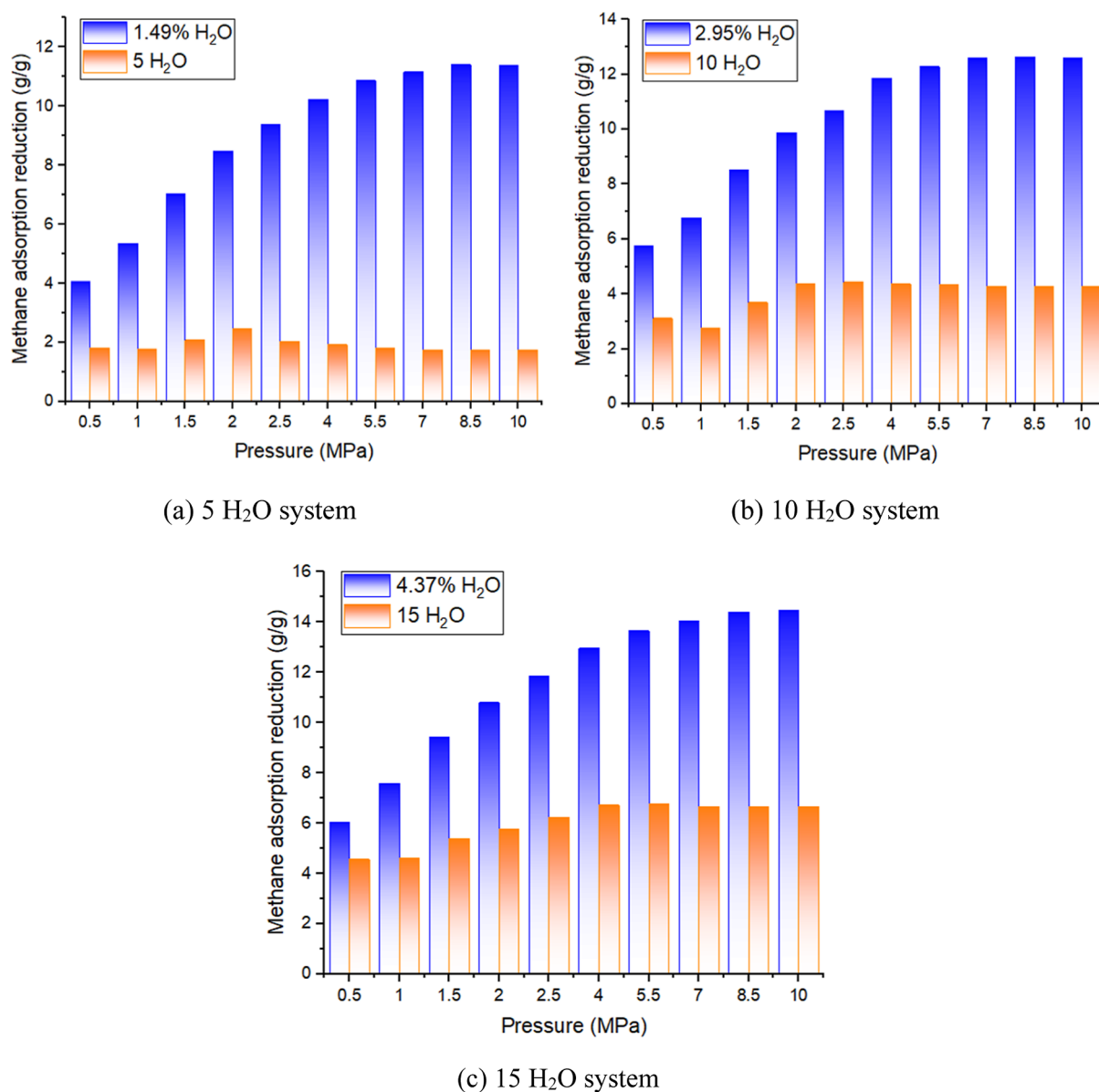
(a) 5 H₂O system

(b) 10 H₂O system

(c) 15 H₂O system

Figure 14. Variation of the decrease in the excess adsorption of methane in different H_2O molecular systems.

methane can only be adsorbed at the adsorption site with lower energy, resulting in some methane only existing in the system without being adsorbed. When methane enters the system first, the anthracite molecular structure saturates it first. When water enters the system afterward, it will strongly displace some of the methane molecules and occupy the adsorption sites with higher energy. A part of methane is also observed in the effective adsorption site, so the excess adsorption of methane is relatively high at this time.[40]

The simulation results of the impact of water injection anthracite on the equivalent heat of adsorption of methane under fixed temperature and different pressures (Figure 10) and the simulation data of the effect of water injection on the equivalent heat of adsorption of methane by coal (Figure 11) are integrated into a coordinate system, as shown in Figure 15.

According to Figure 15, it can be seen that for water injection coals with different concentrations, the equivalent heat of adsorption of CH_4 is dry coal > 1.49% H_2O > 2.95% H_2O > 4.37% H_2O. For coal with different added moisture concentrations, the equivalent heat of adsorption of CH_4 is dry
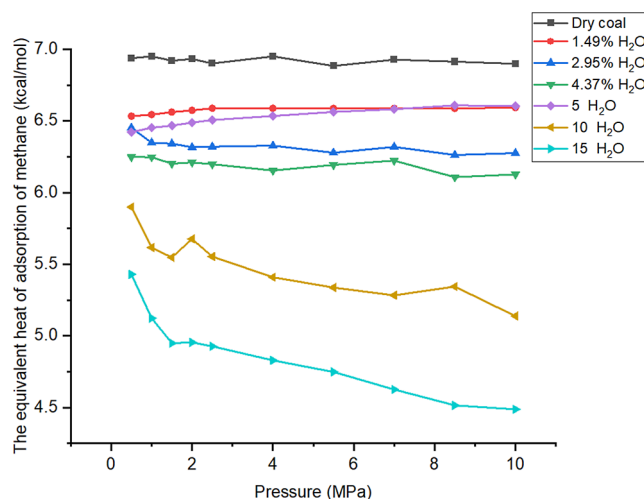

Figure 15. Variation of the equivalent heat of adsorption of methane by anthracite coal with different placement orders of water.

coal > 5 H_2O > 10 H_2O > 15 H_2O. The two different situations show the following rules: compared with the dry coal sample, the higher the moisture content, the lower the equivalent adsorption heat of CH_4. The interaction between CH_4 and anthracite structure is weakened, and the adsorption capacity of CH_4 is reduced. The reason is that the entry of H_2O will compete with methane for adsorption. With the increase of H_2O, the competition between water and methane will increase, resulting in the weak adsorption capacity of anthracite for methane.

Combining Figures 10, 11, and 15, it can be seen that for the low-moisture content system containing 5 H_2O molecules, the heat of adsorption of CH_4 equivalents increases first rapidly and then slowly with the increase of pressure in different orders of water placement, which has a similar trend with the change of the excess adsorption of CH_4. The reason is that there is almost no water in the medium and large holes of coal samples with low moisture content, and the adsorption effect is very small, so the equivalent heat of adsorption of CH_4 has a similar variation pattern to the excess adsorption of CH_4. However, for the high-water volume system containing 10 H_2O and 15 H_2O molecules, the equivalent heat of adsorption of CH_4 decreases gradually with increasing pressure in different orders of water placement, which is different from the trend of the equivalent heat of adsorption of CH_4 for the five H_2O molecule system. The reason is that as the H_2O content in anthracite coal increases, the competition between H_2O molecules and CH_4 molecules increases. This leads to a subsequent decrease in the equivalent heat of adsorption of CH_4 and a weakening of the adsorption capacity, which results in a decrease in the adsorption of CH_4 in the anthracite model.

5. CONCLUSIONS

(1) The presence of H_2O reduces the excess adsorption of CH_4 by anthracite in two different placement sequences of H_2O and CH_4. It shows that H_2O inhibits CH_4 adsorption.

(2) H_2O can replace CH_4 on the higher energy adsorption sites of the anthracite structure. In contrast, CH_4 cannot displace H_2O at the higher energy adsorption sites, and it can only be adsorbed at the lower energy adsorption sites. It further reveals the mechanism of action of liquid injection for mining.

(3) When CH_4 enters the system first, there arises an equilibrium pressure point where H_2O plays the most significant role in inhibiting CH_4 adsorption, which increases with the higher moisture content of additional injection. No equilibrium pressure point occurs when H_2O enters at the front. In engineering practice, coal seam water injection can improve the efficiency of mining promotion at this pressure value.

(4) The coal sample of the low-moisture content system has almost no moisture in the anthracite structure. The effect of CH_4 adsorption is very small, so the equivalent heat of adsorption of CH_4 increases first rapidly and then slowly with the increase of pressure. In the coal sample of the high-moisture content system, the competition between H_2O and CH_4 is enhanced with the increase of water content. As a result, the adsorption capacity of CH_4 is weakened and the equivalent heat of adsorption of CH_4 decreases with pressure. In engineer-

ing practice, the best effect can be achieved only when the water injection concentration reaches a certain value.

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Notes

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