Prediction of methane adsorption capacity in different rank coal at low temperature by the Polanyi-based isotherm model

Pengtao Zhao1 | Haiqiao Wang1 | Long Wang2 | Dongfang Xu3 | Heyi Ma1 | Huaiguang Guo4

1School of Resource, Environment and Safety Engineering, Hunan University of Science and Technology, Xiangtan, Hunan, China
2College of Environment and Resources, Xiangtan University, Xiangtan, Hunan, China
3Hunan Coal Science Research Institute Co., Ltd., Changsha, China
4State Key Laboratory of Coal Mine Safety Technology, Shenyang Research Institute, China Coal Technology & Engineering Group, Shenyang, China

Abstract
To investigate the adsorption properties of methane in coal under low temperatures, the isothermal adsorption tests of the three coal samples with different metamorphic degrees were conducted at the ambient temperatures of 253.15–293.15 K, and the low-temperature nitrogen adsorption (LNA) tests of coal were also performed. Then a relational expression of equilibrium pressure, temperature, and methane adsorption capacity (T–P model) was deduced to predict the adsorption isotherm at any other temperature based on the Polanyi adsorption theory. The results show that the gas adsorption capacity of coal can be significantly increased at low temperatures (below 273.15 K), and the adsorbed methane in anthracite is obviously more than that in lean coal and coking coal by the virtue of possessing a larger micropore/transition pore volume and specific surface area. The relations between adsorption potential (ε) and adsorption volume (ω) at different temperatures can be drawn on one single logarithmic curve, and a suitable pseudo-saturation pressure can be obtained by the improved Amankwah’s method. The predicted adsorbed capacities via the T–P model are in line with the measured results at other equilibrium conditions, indicating that the model can contribute to the deep coalbed methane resources estimation and the gas disaster prevention and control in coal mines.

1 INTRODUCTION

As a substitute for conventional fossil fuels in electricity generation, coalbed methane (CBM) seems a promising solution for the energy crisis.1 The estimated world CBM resources buried above 2000 m are around 240 Tm3, showing that the global CBM resource is abundant and has a huge potential for production.2 China has 36.8 Tm3, ranking the third-largest in the world after Russia and Canada.3 CBM reservoirs are different from the conventional natural gas...
reservoirs due to coalbed as hydrocarbon source rocks, which results in that there are mainly two types of gas states in coal formation: free gas and adsorbed gas.4–6 The adsorbed gas on the internal surface of coal micropores makes up a sizeable share rather than the free gas in the fracture space. Thus, it is significant to understand the adsorption characteristics of methane on coal not only for CBM resource evaluation and productivity prediction but also for evaluating the potential severity of gas disasters in new mines or in unmined areas of existing mines.7

The isothermal adsorption experiments targeted at the organic-rich coal from different formations are commonly used to investigate the methane adsorption behavior on coal, which reveals the influences of various factors on the methane adsorption capacity, including gas pressure,8,9 temperature,10 moisture,11,12 organic matter,13 clay minerals,8 pore structure,14,15 and fracturing fluid,16,17 and so forth. The pressure and temperature of CBM reservoirs are both increased with the increased depth. The methane adsorption on coal reservoirs is all above the critical temperature of methane (190.6 K). When the reservoir pressure is higher than 4.59 MPa, it belongs to a type of supercritical adsorption. Therefore, a series of isothermal adsorption tests at different temperatures are needed to estimate the adsorption capacity of methane on the relevant reservoir occurrence conditions. For the methane adsorption modeling, many scholars have made valuable contributions, in which the Langmuir equation (single site) is the most widely used by scholars have made valuable contributions, in which the monolayer assumption of the Langmuir model and the saturation vapor pressure of pore filling model20–22 are not valid for describing the supercritical methane adsorption in coal, as these models are proposed for describing the subcritical gas adsorption behavior, and there are distinguishable differences between the measured and the actual adsorption values of the reservoir at high pressures.23 Besides this, the Langmuir model can not predict the adsorption isotherms beyond test conditions, impeding its application in the deep CBM resources estimation.24

For physical adsorption, the interaction between adsorbate and adsorbent mainly depends on the dispersion force, as well as called van der Waals force, which is independent of temperature.25 Thus, the Polanyi adsorption potential theory26 provides a framework for such predictions, relying on the characteristic curve of an adsorbate–adsorbent system. In the theory, any adsorbate molecule near the adsorbent surface has some adsorption potential, which is a function of its proximity to the surface and the nature of the adsorbate. Based on the relationship between the adsorption potential and the adsorbate volume, the adsorption isotherms at different temperatures can be transformed into a single characteristic curve. Dubinin et al.27 successfully applied the theory to vapor adsorption equilibrium on activated carbon and zeolite for nonpolar and weakly polar substances. Manes et al.28 extended the theory to the adsorption in an aqueous solution. Subsequently, the Dubinin–Astakhov (D–A) equation29 was used to describe the characteristic curves of CH4 and CO2 adsorption on activated carbons. Du et al.30 investigated adsorption isotherms of hydrogen on four kinds of zeolites above the critical temperature at different pressures. Giraldo et al.31 applied the D–A equation to describe the characteristic curves for asphaltene on a rock surface. Liu et al.32 deduced a calculation model of partition coefficient of volatile organic compounds to study the relations between air emission and building materials. Askalany and Saha33 proposed a new thermodynamic equation on adsorbed phase volume to calculate the isosteric heat of adsorption. Then, an exponential equation34 was proposed in the prediction of CO2 and CH4 adsorption on carbon molecular sieves.

The reduction of gas desorption capacity and kinetics by cooling coal samples below 273.15 K is probably a feasible way to improve the accuracy of CBM content estimation.35 Although the D–A equation36 and the polynomials37 were also applied to discuss the adsorption and thermodynamic characteristics of methane on coals, very few studies on the methane adsorption on coal at low temperature were conducted via the adsorption potential theory by far. In the current work, we tried to establish the relations between gas pressure, temperature, and methane adsorption capacity on coal. By choosing the different rank coal, the isothermal adsorption tests and the LNA tests were conducted to explore the coal affinity on methane at 253.15–293.15 K. Based on the Polanyi adsorption theory, a relational expression (T–P model) of adsorption capacity, pressure, and temperature was then deduced and verified to predict methane adsorption isotherms at other equilibrium conditions, which can contribute to the CBM storage historical course, resource estimation, and gas disaster prevention.

2 | EXPERIMENTAL METHODS AND THEORY

2.1 | Adsorbent preparation

The three fresh coal samples with different ranks as adsorbents were respectively collected from Xingwu coal mine (Liulin, Shanxi province of China), Liulong coalmine (Liuzhi, Guizhou province of China), and Jiulishan coal mine (Jiaozuo, Henan province of China), as shown in
In the reservoir conditions, the obtained samples are more similar to the molded coal than coal powder by the compaction action. Therefore, the three kinds of coal samples were firstly ground and sieved using 0.17−0.25 mm metal sifters, and evenly mixed with an appropriate amount of distilled water. Then they were placed into a mold and loaded with 60 kN pressure for 30 min. After molding and dehydration for 3 h at 378.15 K, the prepared samples were stored in a dehydrator for later use. The physical parameters of coal samples were determined by Chinese national standards (GB/T 212−2008, 217−2008, 6949−1998) as shown in Table 1: ash content (Aad); volatile matter (Vad); moisture (Mad); true relative density (TRD20); apparent relative density (ARD20); firmness (f) and porosity. The mass sofd dry ash-free basis in coal (mr) is evaluated as follows:

$$m_r = m_t (100 - M_{ad} - A_{ad}) \frac{100}{100},$$

where m_t is the total mass of coal sample, kg.

### 2.2 Isothermal adsorption experiments

The isothermal adsorption tests of methane (at 253.15, 263.15, 273.15, 283.15, and 293.15 K) on the coal samples with different ranks were separately conducted with the self-developed low-temperature isothermal apparatus (Figure 2). It consists of an airtight sample canister, a low-temperature incubator, vacuum degassing devices, quantitative gas charging system, a data acquisition system, and pipelines. The operating temperature range of the incubator is 223.15−373.15 K.

Based on the volumetric method, the general procedures of isothermal adsorption are shown as follows:

1. Place the molded coal samples into the coal canister and double-check the tightness of the whole test system with soap water.

2. Vacuum the coal canister below 10 Pa, and then charge a certain amount of methane into the canister via the reference cell. The adsorbed gas content is calculated by the following equation:

$$m_a = m_g - m_f = \frac{\Delta P V_{cell}^{ref} M}{ZRT} - \frac{P_1 V_f M}{ZRT},$$

where m_g is the total mass of charged gas, kg; m_a is the mass of adsorbed gas; m_f is the mass of free gas; ΔP is the pressure difference of the reference cell when the sorption system reaches equilibrium state at the setting pressure, MPa; V_{cell}^{ref} is the volume of reference cell (here the gas reduction in reference cell is actually the total amount of charged gas into coal canister), cm³; P_1 is the gas pressure in coal canister; V_f is the volume of free gas in coal canister; T is the ambient temperature, K; Z is the compressibility coefficient of methane, derived by the Redlich−Kwong equation; M is the molar mass of methane, 16 g/mol; and R is the universal gas constant, 8.314 J/(mol K).

3. Monitor the pressure variation in the coal canister to determine the point of the adsorption equilibrium state or suspend the adsorption time. Only when the gas pressure remains unchanged at the set temperature for 12 h, can the equilibrium point be reached and the adsorption capacity be obtained.

4. Repeat Steps 2−3 until all the scheduled adsorption pressures are reached, and eventually, the gas adsorption isotherms can be drawn at different temperatures.

### 2.3 Low-temperature nitrogen adsorption (LNA) tests

Affected by various coalification processes, the pore structure in coal has different shapes and sizes, not only rich in micropores and transition pores but also macro-pores, visible pores, and fractures, which provide a place
and channel for gas adsorption, storage, and migration.\textsuperscript{39} LNA method is conducive to understanding the nanopore (<100 nm) structure of coal. Therefore, the LNA experiments were conducted with an ASAP2020 specific surface area analyzer (Micromeritics). Firstly, the three coal samples were ground and sieved to 0.5 mm, and then dehydrated at 353.15 K for 6 h. After the coal samples were cooled, they were respectively tested by pressurized nitrogen injection under the low-temperature condition of 77 K, and then the adsorption isotherms can be drawn according to the corresponding N\textsubscript{2} adsorption capacities in different relative pressures. The specific surface area and pore volume of coal were calculated by the BET multilayer adsorption model and BJH model, respectively.

2.4 Polanyi adsorption potential theory

The adsorption potential (\(\epsilon\)) is a function of its proximity to the surface and the nature of the adsorbate, which can be quantitatively described as follows:\textsuperscript{40}

\[
\epsilon = \int_{P_1}^{P_s} \frac{RT}{P} dP = RT \ln\left(\frac{P_s}{P_1}\right),
\]

where \(P_s\) is the saturated vapor pressure of methane, MPa; and \(P_1\) is the adsorption equilibrium pressure, MPa.

When the temperature is below the critical temperature, the saturation vapor pressure of methane can be obtained via the National Institute of Standards and Technology (NIST). However, the methane adsorption on coal surface at high pressure is a type of supercritical adsorption, and the vapor pressure would lose physical meaning above the critical temperature (190.6 K). Thus, the concept of pseudo-saturation vapor pressure was proposed, and the saturated vapor pressure \(P_s\) can be derived from the Amankwah’s improved equation as follows:\textsuperscript{41}

\[
P_s = P_c \left(\frac{T}{T_c}\right)^m,
\]

where \(P_c\) is the critical pressure of methane, 4.62 MPa; \(T_c\) is the critical temperature of methane, 190.6 K; \(m\) is a specific parameter related to the adsorption system.

The adsorbed phase volume of the absolute adsorption capacity is defined as the volume at the boundary where the density is practically equal to the bulk density. Hence, the volume of adsorbed phase (\(\omega\)) can be evaluated as follows:\textsuperscript{42}
where $n_{\text{ad}}$ is the absolute adsorbed amount of methane at the equilibrium pressure, mol; $\rho_{\text{ad}}$ is the density of the adsorbed phase, g/cm$^3$.

Here, we adopt the empirical equation proposed by Ozawa et al.\textsuperscript{42} to determinate the density of the adsorbed phase as follows:

$$\rho_{\text{ad}} = \rho_0 \exp[-0.0025(T - T_b)],$$

where $\rho_0$ is the methane density at the normal boiling point, 0.424 g/cm$^3$; and $T_b$ is the boiling point of methane, 111.5 K.

3 | RESULTS

3.1 | Adsorption isotherms

On the assumptions of monolayer adsorption and uniformity on the adsorbent surface, the Langmuir model (Equation 3) is widely used to describe the adsorption characteristics of methane owing to simplicity and functionality. The adsorption isotherms of different coal samples are shown in Figure 3 at the ambient temperatures of 253.15–293.15 K.

$$Q = \frac{abP}{1 + bP},$$

where $Q$ is the adsorbed methane quantity by the dry ash-free basis in coal under specific pressure and temperature, cm$^3$/g; $P$ is the equilibrium pressure, MPa; $a$ and $b$ are the adsorption constants.

Figure 3 shows that the adsorbed methane capacities of different coal samples all increase with the ambient temperature drop, and the adsorbed quantities below 273.15 K are significantly larger than these above 273.15 K. At the same temperature, the adsorbed methane quantity in coal increases with the equilibrium pressure rising. When the pressure reaches a threshold value, the adsorbed methane tends to be stable and saturated. Furthermore, the adsorbed quantity in Jiulishan anthracite is obviously larger than that in Xingwu coking coal and Liulong lean coal.

The effect of temperature on the methane adsorption capacity can be reflected by the Langmuir adsorption constants $a$ and $b$. Adsorption constants $a$ represents the saturated adsorption capacity on the total coal surface, and $b$ is affected by the physical properties of adsorbent, the adsorbate–adsorbent interaction, and the state of the adsorption system. The variations of adsorption constants $a$ and $b$ with temperature are listed in Table 2.

As shown in Figure 4, the adsorption constants $a$ and $b$ of the three coal samples all decrease with the temperature rising. The saturated adsorption capacity $a$ at the low temperature (below 273.15 K) is obviously higher than that at 293.15 K, which is mainly related to the changes in the kinetic energy and the free path of methane molecules. Cooling weakens the kinetic energy of gas molecules, and more gas molecules would be adsorbed on the surface of coal when the kinetic energy is lower than the adsorption potential well. Additionally, the average free path of a gas molecule is decreased by cooling,\textsuperscript{43} and therefore, the...
FIGURE 3 Adsorption isotherms of coal samples at different temperatures: (A) Xingwu coking coal; (B) Liulong lean coal; (C) Jiulishan anthracite [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 The adsorption constants of $a$ and $b$ of coal samples at different temperatures

| Temperature (K) | Coking coal | Lean coal | Anthracite |
|-----------------|-------------|-----------|------------|
|                 | $a$ (cm$^3$/g) | $b$ (MPa$^{-1}$) | $a$ (cm$^3$/g) | $b$ (MPa$^{-1}$) | $a$ (cm$^3$/g) | $b$ (MPa$^{-1}$) |
| 293.15          | 23.4712     | 0.8683    | 31.3942    | 0.6293    | 38.7857    | 1.3745 |
| 283.15          | 25.3065     | 0.9177    | 31.9628    | 0.7686    | 39.5929    | 1.8492 |
| 273.15          | 26.3909     | 0.9490    | 32.5208    | 0.9447    | 41.5636    | 2.3363 |
| 263.15          | 30.3270     | 0.9658    | 33.4697    | 1.1471    | 41.8902    | 2.8783 |
| 253.15          | 32.4519     | 1.0051    | 35.0395    | 1.3069    | 43.6124    | 3.3382 |

The LNA curves of the three samples slightly differ in shape (Figure 5), and they all accord with the characteristics of II-type adsorption isotherm based on the IUPAC classification criteria. In the low-pressure range ($0 < P/P_0 < 0.2$), the N$\textsubscript{2}$ adsorption quantity increases slowly with the relative pressure rising; the adsorption curve is almost flat with no increment of adsorption.

3.2 Pore structure characteristics

The probability of collision with coal matrix largely increased.

$$\lambda = \frac{KT}{\sqrt{2\pi d_0^3}} P.$$  (8)

where $\lambda$ is the average free path of methane molecule; $d_0$ is the effective diameter of the methane molecule, nm; $K$ is the Boltzmann constant, $1.38 \times 10^{-23}$ J/K.
quantity in the middle-pressure section (0.2 < \( P/P_0 < 0.8 \)), which indicates that N\(_2\) adsorption on the coal pore surface has reached saturated state; and the adsorption curve increases sharply with the relative pressure further rising (0.8 < \( P/P_0 < 1 \)), which is related to the multilayer adsorption and capillary condensation existing in pores. The desorption curve of each coal sample is associated with the pore morphology. There is an obvious adsorption hysteresis loop in the high-pressure section of each coal. It can be roughly estimated that a certain amount of open-type pores exist in each sample. When the relative pressure approaches 0.5, there is a sharp downward inflection point in the desorption curves of coking coal and lean coal, indicating that the semiopen flask pores account for a certain proportion. When the relative pressure is below 0.5 (pore size < 4 nm), the desorption curves of coking coal and lean coal almost coincide with the adsorption curves, indicating that these micropores are sealed at one end and have poor connectivity. However, there is no sudden drop point near the relative pressure of 0.5 in the anthracite desorption curve, indicating that open-type pores account for the main part of micropores in anthracite.

To directly compare the distribution of the BET-specific surface area of different rank coal, the results of LNA tests were drawn into a histogram, as shown in Figure 6. It can be seen that the cumulative specific surface area of the three samples gradually increases with the increase of coal metamorphic degree; and the total pore area of anthracite is 2.77 m\(^2\)/g, which is significantly larger than that of coking coal and lean coal. The micropores of the samples account for the largest proportion of the total surface area, in which the micropore proportion of anthracite reaches 70.36%, so the adsorption capacity of anthracite is the strongest among them. Additionally, the transition holes of coal samples also account for a high proportion, ranging from 26.07% to 54.35%. The mesopore proportion of samples can be

**FIGURE 4** Variations of adsorption constants \( a \) and \( b \) with temperature: (A) Xingwu coking coal; (B) Liulong lean coal; (C) Jiulishan anthracite [Color figure can be viewed at wileyonlinelibrary.com]
almost ignored, which is mainly related to the measurement range of pore size of 1.9–300 nm by the LNA tests. The distribution of BJH pore volume of coal samples is shown in Figure 7. The total pore volume of the three samples also gradually increases with the increase of coal metamorphic degree. But unlike the distribution of BET special surface area, well-developed mesopores make a major contribution to BJH pore volume for coking coal and lean coal, accounting for 71.43% and 66.23%, respectively. The total pore volume of the anthracite sample is 0.011 ml/g; the mesopore proportion is 36.36%, and the proportions of transition pores and micropores cannot be ignored, which reach 45.46% and 18.18%, respectively. Therefore, anthracite coal should be of stronger gas adsorption and reservoir capacities.
DISCUSSION

4.1 Polanyi-based isotherm model

To explore the methane adsorption characteristics on coal via the Langmuir model, it is inevitable to carry out isothermal adsorption experiments at multiple temperature points, which brings difficulties to the prediction of CBM content under extreme conditions. The advantage of the adsorption potential theory is that the adsorption isotherm at any temperature can be evaluated based on the relationship between the adsorption potential ($\varepsilon$) and the adsorption volume ($\omega$) at one temperature. It is before establishing the characteristic curve of adsorption potential. Here the specific parameter $m$ is temporarily taken as 3, and then the adsorption characteristic curves of $\varepsilon-\omega$ are fitted based on the adsorption results of the

FIGURE 7 Pore volume distribution of different rank coal [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 8 Adsorption characteristic curves of $\varepsilon-\omega$ of coal samples: (A) coking coal; (B) lean coal; (C) anthracite [Color figure can be viewed at wileyonlinelibrary.com]
three samples at 293.15, 273.15, and 253.15 K, as shown in Figure 8.

It can be seen from Figure 8 that the $\varepsilon-\omega$ characteristic curves of coal samples at different temperatures are almost on the same curve, which means the $\varepsilon-\omega$ curve is temperature-independent. Consequently, the interaction between coal and methane molecules is mainly on dispersion forces, and the process belongs to physical adsorption. The relation between $\varepsilon$ and $\omega$ conforms to the logarithmic equation ($\varepsilon = -A \ln \omega + B$), where $A$ and $B$ are the fitting constants.

### 4.2 Derivation of the $T-P$ model

Since the relation between the adsorption potential ($\varepsilon$) and the volume of adsorbed phase ($\omega$) conforms to the logarithmic equation ($\varepsilon = -A \ln \omega + B$), and there is a linear relation between $\omega$ and the adsorbed quantity ($Q$), Equation 9 can be obtained as follows:

$$\varepsilon = -f \ln Q + g,$$

where $f$ and $g$ are also the fitting constants. By taking exponents on both elements of the above equation, we can get:

$$Q = e^{g/f} e^{\varepsilon/f}.$$

By inputting $C = e^{g/f}$ into Equation 10, the Polanyi-based isotherm prediction model of temperature–pressure ($T-P$ model) can be written according to Equations (3) and (4):

$$Q = C/e^{RT \ln[1/(T/T_c)^{m}P]/f}.$$  

![Figure 9](wileyonlinelibrary.com)
The above equation can be also expressed as a logarithmic form:

\[
\ln Q = \ln C + \frac{RT}{f} \ln P - \frac{RT}{f} \ln \left[ P_c \left( \frac{T}{T_c} \right)^{m} \right]. \tag{12}
\]

Then, the following equation can be written by taking \( M = \frac{RT}{f} \) and \( N = \ln C - \left( \frac{RT}{f} \right) \ln \left[ P_c \left( \frac{T}{T_c} \right)^{m} \right] \) into Equation 12:

\[
\ln Q = M \ln P + N, \tag{13}
\]

where \( M \) and \( N \) are defined as the characteristic constants of adsorption isotherm.

Here, the experimental adsorption results of coal samples at 283.15 K are adopted to calculate the characteristic constants \( M \) and \( N \) (Figure 9). Hence, \( M_{\text{XW}} = 0.361, N_{\text{XW}} = 2.478; M_{\text{LL}} = 0.367, N_{\text{LL}} = 2.663; \) and \( M_{\text{JLS}} = 0.237, N_{\text{JLS}} = 3.30. \) By substituting these constants into Equation 11, the adsorption prediction relations of the coal samples are given as follows:

\[
\begin{align*}
Q_{\text{XW}} &= 34.557/e^{\frac{RT \ln \left[ P_c \left( \frac{T}{T_c} \right)^{m} \right]}{(\ln 6.526)}} \\
Q_{\text{LL}} &= 38.921/e^{\frac{RT \ln \left[ P_c \left( \frac{T}{T_c} \right)^{m} \right]}{(\ln 6.411)}} \\
Q_{\text{JLS}} &= 51.072/e^{\frac{RT \ln \left[ P_c \left( \frac{T}{T_c} \right)^{m} \right]}{(\ln 9.916)}}.
\end{align*}
\tag{14}
\]

### 4.3 Prediction of adsorption isotherms

To validate the prediction performance of the \( T-P \) model in adsorption isotherms, the predicted adsorption capacities of coal samples at 263.15 and 253.15 K are calculated to compare with the measured values, as shown in Figure 10.
The results show the predicted adsorption capacity of methane by the $T$–$P$ model is very close to that by the isothermal tests under the corresponding pressures. Overall, the predicted adsorption capacity is slightly smaller than the measured at the equilibrium pressures of 0–7 MPa, and if taking the difference ratio between predicted and measured value as the relative error, its ranges are within 6%. Despite the same value of specific parameter $m$ being adopted at each temperature point, the relative error is not large enough to affect the predicted results of the $T$–$P$ model. The predicted adsorption capacity also increases with the equilibrium pressure rising, and the adsorption capacity of anthracite is larger than these of coking coal and lean coal at the same equilibrium conditions.

**FIGURE 11** Predicted adsorption isotherms of coal samples at different temperatures by $T$–$P$ model: (A) coking coal; (B) lean coal; (C) anthracite [Color figure can be viewed at wileyonlinelibrary.com]

The isothermal adsorption tests of different rank coal were conducted at the temperatures of 253.15–293.15 K, and the LNA tests of coal were performed to analyze the pore structure characteristics of samples. Based on the Polanyi adsorption theory, a relational expression of equilibrium pressure, temperature, and adsorption capacity ($T$–$P$ model) was deduced and verified to predict should meet as close to the practical conditions of the reservoir as possible. Consequently, it can be concluded that the $T$–$P$ model proposed here is applicable in the estimation of methane adsorption capacity of coking coal at any temperature and pressure, which can provide a reliable reference for the estimation of deep CBM resources and the design of coal mine gas prevention and control.

### 5 CONCLUSIONS

The isothermal adsorption tests of different rank coal were conducted at the temperatures of 253.15–293.15 K, and the LNA tests of coal were performed to analyze the pore structure characteristics of samples. Based on the Polanyi adsorption theory, a relational expression of equilibrium pressure, temperature, and adsorption capacity ($T$–$P$ model) was deduced and verified to predict...
the methane adsorption isotherm at any other temperature. The following conclusions can be drawn:

(1) The methane adsorption capacity of coal samples can be increased at low temperatures (below 273.15 K); furthermore, the adsorbed quantity of anthracite is significantly larger than that of coking coal and lean coal by the virtue of possessing a larger micropore/transition pore volume and specific surface area.

(2) In the Polanyi isotherm model, the relations between adsorption potential (ε) and adsorption volume (ω) at different temperatures are drawn on a single logarithmic curve, and then a suitable pseudo-saturation pressure is obtained by the improved Amankwah’s method; consequently, a relational expression of adsorption capacity, pressure, and temperature (T–P model) is proposed.

(3) The predicted adsorbed capacities via the T–P model are in line with the measured results at 263.15 and 253.15 K, so the adsorption capacity of the CBM reservoir can be reliably predicted at the different equilibrium conditions.

ACKNOWLEDGMENTS
We gratefully acknowledge the funding received from the National Natural Science Foundation of China (Grant Nos. 52074107 and 52104224), and we also would like to thank editors and anonymous reviewers for their comments and suggestions.

CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT
The data of this study are available from the corresponding author upon request.

ORCID
Long Wang http://orcid.org/0000-0003-1184-9328

REFERENCES
1. Moore TA. Coalbed methane: a review. Int J Coal Geol. 2012;101:36-81.
2. Qin Y, Moore TA, Shen J, Yang Z, Shen Y, Wang G. Resources and geology of coalbed methane in China: a review. Int Geol Rev. 2018;60:5-6.
3. Zhang H, Cheng Y, Deng C, et al. A novel in-seam borehole discontinuous hydraulic flushing technology in the driving face of soft coal seams: enhanced gas extraction mechanism and field application. Rock Mech Rock Eng. 2021;1-23.
4. Ceglarsk G, Brzóska K. The effect of coal metamorphism on methane desorption. Fuel. 1998;77:645-648.
5. Ceglarsk G, Zarębska K. The competitive sorption of CO₂ and CH₄ with regard to the release of methane from coal. Fuel Process Technol. 2002;77:423-429.
6. Rice DD. Composition and origins of coalbed gas. AAPG Stud Geol. 1993;38:159-184.
7. Diamond WP, Schatzel SJ. Measuring the gas content of coal: A review. Int J Coal Geol. 1998;35(1-4):311-331.
8. Weishauplová Z, Pribyl O, Sykorová I, Machovic V. Effect of bituminous coal properties on carbon dioxide and methane high pressure sorption. Fuel. 2015;139:115-124.
9. Gensterblum Y, Merkel A, Busch A, Krooss BM. High-pressure CH₄ and CO₂ sorption isotherms as a function of coal maturity and the influence of moisture. Int J Coal Geol. 2013;118:45-57.
10. Wang Z, Tang X, Yue G, Kang B, Xie C, Li X. Physical simulation of temperature influence on methane sorption and kinetics in coal: benefits of temperature under 273.15 K. Fuel. 2015;158:207-216.
11. Wu J, Yu J, Wang Z, Fu X, Su W. Experimental investigation on spontaneous imbition of water in coal: implications for methane desorption and diffusion. Fuel. 2018;231:427-437.
12. Busch A, Gensterblum Y. CBM and CO₂-ECBM related sorption processes in coal: a review. Int J Coal Geol. 2011;87:49-71.
13. Hao S, Wen J, Yu X, Chu W. Effect of the surface oxygen groups on methane adsorption on coals. Appl Surf Sci. 2013;264:433-442.
14. Wei Q, Li X, Zhang J, et al. Full-size pore structure characterization of deep-buried coals and its impact on methane adsorption capacity: a case study of the Shihezi Formation coals from the Panji Deep Area in Huainan Coalfield, Southern North China. J Petrol Sci Eng. 2019;173:975-989.
15. Pan J, Lv M, Hou Q, Han Y, Wang K. Coal microcrystalline structural changes related to methane desorption/adsorption. Fuel. 2019;239:13-23.
16. Huang Q, Wu B, Liu Y, Guo Z, Wang G, Sun L. Experimental and simulation investigations of the impact of polyacrylamide on CBM adsorption/desorption. J Petrol Sci Eng. 2021;208:109300.
17. Huang Q, Li J, Liu S, Wang G. Experimental study on the adverse effect of gel fracturing fluid on gas sorption behavior for Illinois coal. Int J Coal Sci Technol. 2021;8:1250-1261.
18. Gasparik M, Bertier P, Gensterblum Y, Ghanizadeh A, Krooss BM, Littke R. Geological controls on the methane storage capacity in organic-rich shales. Int J Coal Geol. 2014;123:34-51.
19. Rexer TF, Benham MJ, Aplin AC, Thomas KM. Methane adsorption on shale under simulated geological temperature and pressure conditions. Energy Fuels. 2013;27(6):3099-3109.
20. Sakurovs R, Day S, Weir S, Duffy G. Application of a modified Dubinin–Radushkevich equation to adsorption of gases by coals under supercritical conditions. Energy Fuels. 2007;21(2):992-997.
21. Bae JS, Bhatia SK. High-pressure adsorption of methane and carbon dioxide on coal. Energy Fuels. 2006;20(6):2599-2607.
22. Clarkson CR, Bustin RM, Levy JH. Application of the mono/multilayer and adsorption potential theories to coal methane adsorption isotherms at elevated temperature and pressure. Carbon. 1997;35(12):1689-1705.
modeling for the adsorption of supercritical nitrogen on activated carbon. J Colloid Interface Sci. 2001;23(1):33-38.

24. Zou J, Rezaee R. A prediction model for methane adsorption capacity in shale gas reservoirs. Energies. 2019;12:280-293.

25. Dzyaloshinskii IE, Lifshitz EM, Pitaevskii LP. The general theory of van der Waals forces. Adv Phys. 1961;10(38):165-209.

26. Polanyi M. The potential theory of adsorption. Science. 1963;141:1010-1013.

27. Dubinin MM. Porous structure and adsorption properties of active carbons. Chem Phys Carbon. 1975;2:51-120.

28. Manes M, Wohleber DA. Application of the Polanyi adsorption potential theory to adsorption from solution on activated carbon. II. Adsorption of partially miscible organic liquids from water solution. J Phys Chem. 1971;75:61-64.

29. Himeno S, Komatsu T, Fujita S. High-pressure adsorption equilibria of methane and carbon dioxide on several activated carbons. J Chem Eng Data. 2005;50(2):369-376.

30. Du X, Wu E. Application of the adsorption potential theory to hydrogen adsorption on zeolites above critical temperature. Acta Phys Chim Sin. 2007;23(6):813-819.

31. Giraldo J, Nassar N, Benjumea P, Pereira AP, Cortés FB. Modeling and prediction of asphaltene adsorption isotherms using Polanyi’s modified theory. Energy Fuels. 2013;27(6):2908-2914.

32. Liu Y, Zhou X, Wang D, Song C, Liu J. A prediction model of VOC partition coefficient in porous building materials based on adsorption potential theory. Build Environ. 2015;93:221-233.

33. Askalany A, Saha B. Towards an accurate estimation of the isosteric heat of adsorption—a correlation with the potential theory. J Colloid Interface Sci. 2017;490:59-63.

34. Song X, Wang L, Li Y, Zeng Y, Zhan X, Gong J. Application of adsorption potential theory in prediction of CO₂ and CH₄ adsorption on carbon molecular sieves. Adsorpt Sci Technol. 2018;36:1669-1686.

35. Wang L, Wang Z, Qi C, Ma S, Yue J. Physical simulation of temperature and pressure evolution in coal by different refrigeration modes for freezing coring. ACS Omega. 2019;4(23):20178-20187.

36. Hao S, Chu W, Jiang Q, Yu X. Methane adsorption characteristics on coal surface above critical temperature through Dubinin—Astakhov model and Langmuir model. Colloids Surf A. 2014;444:104-113.

37. Yuan J, Zhang H, Guo Y, Cai N. Thermodynamic properties of high-rank tectonically deformed coals during isothermal adsorption. Arab J Geosci. 2017;10:278.

38. Mavor MJ, Owen LB, Pratt TJ. Measurement and evaluation of coal sorption isotherm data. SPE Annual Technical Conference and Exhibition. SPE; 1990.

39. Chu YP, Sun HT, Zhang DM, Yu G. Nuclear magnetic resonance study of the influence of the liquid nitrogen freeze-thaw process on the pore structure of anthracite coal. Energy Sci Eng. 2020;8(4):1681-1692.

40. Ramirez-Pastor AJ, Bulnes F. Differential heat of adsorption in the presence of an order—disorder phase transition. Phys A: Stat Mech Appl. 2000;283(1):198-203.

41. Amankwah KG, Schwarz JA. A modified approach for estimating pseudo-vapor pressures in the application of the Dubinin—Astakhov equation. Carbon. 1995;33(9):1313-1319.

42. Ozawa S, Kusumi S, Ogino Y. Physical adsorption of gases at high pressure. IV. An improvement of the Dubinin—Astakhov adsorption equation. J Colloid Interface Sci. 1976;56(1):83-91.

43. Vincenti WG, Kruger GH. Introduction to Physical Gas Dynamics. Wiley; 1965.

How to cite this article: Zhao P, Wang H, Wang L, Xu D, Ma H, Guo H. Prediction of methane adsorption capacity in different rank coal at low temperature by the Polanyi-based isotherm model. Energy Sci Eng. 2022;10:1384-1397. doi:10.1002/ese3.1108