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Research Paper

Experimental meso scale study on the distribution and evolution of methane adsorption in coal



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HIGHLIGHTS

• The SEM-EDS is used to test and classify the meso structures of coal.

- Temperature changes of coal absorbed methane are tested by infrared thermal imager.
- The methane adsorption characteristics of meso structures in coal are studied.
- The heterogeneity of methane distribution and evolution in coal are revealed.

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ABSTRACT

To reveal the nature of methane storage in coal under different adsorption pressures, a method combining scanning electron microscopy and energy dispersive spectrometry (SEM-EDS) with infrared thermal imaging is used to observe meso structures, methane distribution, and evolution characteristics in coal. The results indicate that the different meso structures of coal have different methane adsorption characteristics, leading to a non-uniformity of the methane distribution and evolution. In other words, compared with the cavity pores and meso fractures in telocollinite, which are compactly filled with clay minerals, the cell cavity pores and meso fractures in telinite, which are non-compactly filled with clay minerals, have more inter-gravel pores and broken coal structures at different scales, and can store great amounts of methane owing to a larger surface area and greater number of adsorption sites for methane molecules. Therefore, the methane content in coal increases sharply in these meso structures with increasing adsorption pressure, resulting in a centralization of the adsorption locations and increasing inhomogeneity of methane storage rate of the adsorption sites in these meso structures increases more slowly during an increase in pressure, leading to a decreased aggregation of methane storage in coal.

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1. Introduction

The depletion of fossil fuel reservoirs and the escalating threat of global warming owing to the harmful emissions of greenhouse gases have made clean energy research [1] a priority. As a potential alternative to fossil fuels, the exploitation and storage of methane (CBM) is a large issue in the field of energy production [2]. The US Department of Energy (DOE) has fixed CH₄ storage targets for adsorbents at 350 cm³ CH₄ (STP) per square centimetre of adsorbent, and 0.5 g CH₄ per gram of adsorbent under ambient condi-

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http://dx.doi.org/10.1016/j.applthermaleng.2016.10.164 1359-4311/© 2016 Elsevier Ltd. All rights reserved. tions. As a natural adsorbent, coal has a great methane adsorption capacity. However, compared with other adsorbents, such as Maxsorb III, ACF, and MOFs [3], the diversity of the macerals, variations in mineral species, and an uneven distribution of pores and fractures in coal create inhomogeneous methane adsorption characteristics [4–6], rendering an evaluation of the storage characteristics difficult, and hindering the industrial exploitation of CBM reserves. Past studies have shown that the micro pores (<10 nm) in coal are the main sites of methane storage owing to their large surface area, and that the intercrystalline pores and intragranular corrosion pores of clay minerals also have a fair methane adsorption capacity [1,2,7]. Based on methane adsorption capacity tests of different microlithotypes, Chalmers [8] hypothe-



Nomeno	clature		
-q n	isosteric adsorption heat of methane in coal (kJ/mol) the amount of methane adsorption in coal (mol)	$N_{\Delta T_{i,0-1}}$	number of coal units with temperature increase from $\Delta T_{i,0-1}$ to $\Delta T_{i,0-1} + 0.1$ °C
Q	the heat released through methane adsorption in coal (k])	$P_{\Delta T_{i,0-1}}$	the proportion of temperature increase on coal surface (%)
ΔT	the temperature increase in coal during methane adsorption (°C).	N_1	the proportion of average methane content in remark- able methane adsorption regions
C S ²	the specific heat of coal containing methane (J/kg °C). variance	<i>N</i> ₂	the proportion of average methane content in non- remarkable methane adsorption regions
$T_{i,0}, T_{i,1}$	the temperature of the i-th coal unit before and after methane adsorption, respectively (°C)	<i>S</i> ₁	the average proportion of remarkable methane adsorp- tion regions
$\Delta T_{i,0-1}$	the temperature increase of the i-th coal unit during methane adsorption (°C)	<i>S</i> ₂	the average proportion of non-remarkable methane adsorption regions
$\Delta \overline{T}_{i,0-1}$	the average value of all coal units during methane adsorption ($^{\circ}$ C)	n_1	the average methane content per unit area of remark- able methane adsorption regions
$egin{array}{c} N \ heta \end{array}$	number of coal units in total coverage rate of adsorption sites	<i>n</i> ₂	the average methane content per unit area of non- remarkable methane adsorption regions
а	the maximum methane adsorption amount of coal, i.e., the number of methane adsorption sites	<i>a</i> ₁	the maximum methane adsorption capacity of remark- able methane adsorption regions
b p	parameter associated with the adsorption rate. adsorption pressure (MPa)	<i>a</i> ₂	the maximum methane adsorption capacity of non- remarkable methane adsorption regions
b _m T	proportionality constant temperature of adsorption system (°C)	b_1	the methane adsorption rate in remarkable methane adsorption regions
k E	Boltzmann constant, 1.3806488(13) \times 10 ⁻²³ J/K potential well depth (kl/mol)	<i>b</i> ₂	the methane adsorption rate in non-remarkable methane adsorption regions
a _T	the maximum temperature increase in coal (°C)	η	the ratio of n_1 to n_2

sized that methane is held as a solution gas in liptinite-rich coals, and in micropores in liptinite-poor coals through physical sorption. Similar to porous coal, Anutosh Chakraborty's [9] research revealed the heterogeneity of activated carbons for (1) microporous and (2)mesoporous activated carbons; the interactions of non-polar gases on activated carbon were also found to be more sensitive to the adsorbent pore geometry and the adsorbate size. Karacan et al. [10,11] observed and evaluated the differences in the gas transport and adsorption rate in different types of coal microstructures using X-ray CT imaging technology, and showed that clay minerals in coal have high porosity and density, whereas the pore structures in a coal matrix have a higher gas storage capacity. The practices utilized by many projects have indicated that during the drilling of soft coal seams with high crustal stress, coal and gas spews often occur from boreholes with different spray quantities, with durations ranging from several to tens of minutes [12,13]. As indicated by Yu et al. [14], one of the main reasons for these phenomena is that coal pits with considerably higher gas pressure and gas content than their adjacent areas exist in coal seams, which can be called gas bags. However, owing to the restrictions of the observation methods applied, an uneven distribution and evolution of methane adsorption in coal have been rarely reported, and the theory of gas bags in coal remains only a hypothesis.

Many studies have indicated that heat is released during methane adsorption on coal [15], leading to an increase in temperature, which can be used not only to evaluate the methane adsorption and/or desorption capacity, but also to predict dynamic geological disasters, such as coal gas outbursts [16–18]. Infrared imaging spectrometry can be used to obtain multipoint, noncontact temperature measurements of an object's surface with a high sensitivity, fast response, and high spatial resolution over a wide temperature range [19]. This approach was used by Liu et al. [20] to test the temperature variation in coal during gas adsorption and desorption. An analysis of the surface morphology of coal using scanning electron microscopy and energy dispersive spectrometry (SEM-EDS) can be used to differentiate between regions of different compositions, detect the contents of elements at different locations, and reveal the microstructure of a material surface [21–23]. Such analysis was employed by Pan [24] and Zeng [25] to examine the meso structures of coal, including the pore characteristics, fissure distribution, and mineral composition.

Methane adsorption mainly occurs in pores with a width of less than 2 nm. Because the meso structures of coal contain different quantities of these micro pores, methane adsorption in coal is heterogeneous. For the present study, the methane distribution and evolution characteristics in different meso structures in coal, with a scale ranging from 1 to 100 μ m (mainly telocollinite and clay minerals filling in the pores and fractures), under different adsorption pressures were observed using a method combining SEM-EDS and infrared thermal imaging, which is aimed at revealing the mechanism of methane storage in coal to better exploit coalbed methane reservoirs.

2. Experimental

2.1. Coal sample preparation

As shown in Fig. 1, two anthracite coal samples used for the experiments, called coal sample A and coal sample B, were obtained from the Sijiazhuang mine (Yangquan Coal Industry Group, Shanxi, China), and were machined to a size of $\Phi 8.5 \times 12$ mm. Two lines were cut across the radial surface of coal sample A to provide a position coordinate axis so that specific locations on the surface could be accurately identified during SEM-EDS scans and infrared thermal imaging. Before testing, the two coal samples were cleaned and dried. Basic information regarding the coal samples is provided in Table 1.

2.2. SEM-EDS scanning and infrared imaging of methane adsorption in coal

SEM was conducted using a JSM-7001F thermal field emission scanning electron microscope with a 5 kV scanning voltage and

Table 1



Fig. 1. Selection of coal sample for tests.

Table	. 1		
Basic	information	of coal	samples.

Coal reservoir	Rank	Weight /g	Maximum reflectance of vitrinite (%)	Proximate analysis			
				Moisture (%)	Aah (%)	Volatile matter (%)	Fixed carbon (%)
15#	Anthracite	0.966	2.45	1.39	13.13	7.12	78.36

10 mm width, and adopting an INCA X-Act energy dispersive spectrometer to qualitatively analyse the elements of the micro area on the sample surface. A Uti380D infrared thermal imager was used for infrared scanning of methane adsorption in coal at a wavelength of 8–14 μ m with a thermal sensitivity of 0.05 °C.

As shown in Fig. 2, this system consists of the following parts: (1) A pressure cylinder made of a titanium alloy in which the coal and gas adsorption experiment was conducted; the alloy was tested and confirmed to have good air tightness. A piece of glass with a high infrared transmittance (>90%) was positioned at the top of the cylinder. (2) A base was used to fix the cylinder clamping device to the infrared thermal imager, thereby ensuring stability of the scanned infrared images. (3) A precise digital pressure gauge was used for measuring the pressure of methane in the cylinder. (4) A gas injection device incorporating a pressure reduction valve to keep the injection pressure constant, along with a methane cylinder and a corresponding pipeline, was applied. Testing was accomplished by first placing the coal samples horizontally in the cylinder such that their radial surface was close to the infrared glass with high-transmittance, and therefore visible to the infrared thermal imager. The experiments were then carried out at a constant room temperature of 20 °C using the following procedure:

(1) **Coal sample placement and vacuum treatment:** To reduce heat loss from the coal during methane adsorption and eliminate the influence of environmental temperature factors, the side surface of the coal sample was wrapped with insu-



Fig. 2. Infrared scanning device for measuring coal methane adsorption.

lating cotton to keep it as adiabatic as possible. The coal sample was placed into the pressure cylinder horizontally, keeping its radial surface with the cross lines closely attached to the infrared transmitting glass (the placement angle of coal sample A was adjusted to make sure that the largest area of the coal surface divided by the cross lines was located at the upper-right). The clamping device was then adjusted and fixed to ensure that the coal sample was parallel to the detector shot of the infrared thermal imager in the cylinder. Using a 2XZ-0.5 double rotary vane vacuum pump, a pressure of 0.6 Pa was produced in the cylinder for more than 1 h to remove all gases from the coal sample and cylinder.

- (2) **Methane adsorption of coal sample A under different pressures:** The focal length of the infrared thermal imager was manually adjusted so that the surface of the coal sample could be clearly observed, and a reference shot was then taken of the coal surface before the methane adsorption. The pressure reduction valve was then opened, and methane gas (99.99%) was injected at five different times to maintain constant pressures of 0.3, 0.6, 0.9, 1.2, and 1.5 MPa, respectively, in the cylinder while simultaneously recording the adsorption time. Infrared thermal images were captured and saved every 1 s for more than 20 min during each group of experiments.
- (3) **Methane adsorption-desorption of coal samples A and B under 1.2 MPa:** After placement and vacuum treatment of coal sample A, setting 60 s for the period of methane adsorption, the methane adsorption process of coal sample A was continuously photographed using the infrared thermal imager. The valve was then opened, thereby causing the pressure cylinder to connect with the atmosphere. Meanwhile, photographs of the methane desorption process of coal sample A were taken continuously for 60 s. Finally, coal sample A was replaced with coal sample B, and the same experiment was repeated.

3. Infrared imaging characteristics of coal methane adsorption

By subtracting the coal surface temperature arrays obtained before adsorption from the infrared scans at different adsorption times under each adsorption pressure and displaying them using the same colour bar, the temperature variations on the coal surface during methane adsorption and/or desorption under different adsorption pressures could be obtained. As shown in Figs. 3 and 4, each pixel of these images corresponds to the absolute size of the coal sample surface of $35.4 \times 35.4 \,\mu\text{m}^2$. As shown in Fig. 3, for the methane adsorption-desorption of coal samples A and B at 1.2 MPa, it is clear that the temperature of the surrounding environment remained essentially constant during methane adsorption, whereas the temperatures of the two coal sample surfaces increased non-uniformly. The temperature increase of coal sample A mainly occurred in the right-centre region of the coal surface, whereas that of coal sample B mainly occurred in the upper part. During the methane desorption processes, the temperatures of the two coal surfaces gradually decreased. The temperature decreases of both sample surfaces mainly occurred at the same positions at which the temperature mainly increased during methane adsorption. As shown in Fig. 4, for methane adsorption of coal sample A under different pressures, the temperature increase was from 0 to 4.5 °C under pressures of 0.3 to 1.5 MPa. respectively, and at higher pressures, the temperature increase was more notable.

The temperature increase of each coal sample during methane adsorption was caused by the adsorption heat of the coal surface and the methane molecules, which is closely related to the amount of methane adsorption in coal, namely [1,2],

$$\mathbf{Q} = -q\mathbf{n}.\tag{1}$$

Assuming that methane adsorption in coal is carried out under adiabatic conditions, the heat released has no physical effects other than an increase in the temperature of the coal, and thus from Eq. (1),

$$\Delta T = \frac{qn}{C}.$$
 (2)

Therefore, from Eq. (2), assuming that the different locations of coal containing methane [9] have their own specific heat capacity, and that the isosteric heat of adsorption is a constant value, the

Coal sample A (Adsorption time is in white, desorption time is in red)

temperature increase of each coal unit (pixel) is proportional to the amount of methane adsorption. Larger temperature increases and decreases are the result of a larger amount of methane adsorption and desorption, respectively.

Taking coal sample A as an example, as shown in Fig. 4, during methane adsorption, the right-centre region of the coal surface exhibited a larger temperature increase than that of the adjacent areas, which is supported by the heterogeneity of the methane adsorption capacities of the coal structures, whereas the rightcentre region of the coal surface had a larger amount of methane adsorption. The deviation between the temperature of an arbitrary unit on the coal surface and its mathematical expectation can be represented through the variance in mathematical statistics:

$$S^{2} = \frac{1}{N} \sum_{1}^{N} \left(\Delta T_{i,0-1} - \Delta \overline{T}_{i,0-1} \right)^{2}$$
(3)

where

$$\Delta \overline{T}_{i,0-1} = \frac{1}{N} \sum_{1}^{N} \Delta T_{i,0-1}.$$

 $\Delta T_{i,0-1} = T_{i,1} - T_{i,0}$

Such variance can characterize the uneven evolution process of the coal surface temperature increase during methane adsorption. Greater inhomogeneity corresponds to a larger variance. As shown in Fig. 5, during the process of methane adsorption under different pressure levels, the inhomogeneity of the temperature rise on the coal surface increased rapidly, and then ultimately decreased slowly to zero. In the experiment using coal sample A, the temperature variation reached zero within 20 min. This suggests that the adsorption time of 0-10 s pertains to the methane adsorption equilibrium process of the coal radial surface, and the temperature variation was mainly caused by adsorption of heat. Owing to the



Fig. 3. Temperature (°C) variation of coal samples during methane adsorption and desorption of 1.2 MPa.



Fig. 4. Temperature (°C) variation of coal sample A during methane adsorption.

different adsorption characteristics between different locations, the right-centre region of the coal surface had a much greater amount of methane, resulting in an inhomogeneous increase in temperature. The adsorption time period after 10 s pertains to the temperature equilibration process of the coal surface, and with the methane adsorption equilibrium of the coal surface, the inhomogeneity of its temperature rise decreased as the heat was transferred between different locations in the coal.

4. Methane adsorption characteristics of different meso structures in coal

4.1. Characteristics of meso structures in coal

According to meso mechanics, the meso structures of a material refer to the subtle structures visible through optical or conventional electron microscopy with scales ranging from 10 nm to the



Fig. 5. Variance of temperature rising of coal sample A at different adsorption time.

millimetre range [26,27], which has an important significance on the quantitative research of the macroscopic physical properties. During the SEM scans, a rectangular region (4.5 mm \times 2.2 mm) at the upper-right corner of the surface of coal sample A along the cross line was set to the full-width scanning area, as shown in Fig. 6, and non-uniform structures within the meso scale of the area ranging from 1 to 100 µm could be clearly observed: this area was mainly composed of vitrinite in the coal matrix and clay minerals. Among them, telocollinite has a compact and less porous structure at the meso scale, whereas telinite contains numerous meso fractures and cell cavity pore groups with clay minerals filled in at different compaction degrees, which are distributed in a stripshape with a certain orientation. Energy spectrum test results on the coal matrix and clay minerals in coal are shown in Table 2. The main element of the coal matrix is carbon, with a weight proportion of up to 86.36%. An energy spectrum peak for the elements silicon and aluminium appeared in the clay mineral, which proves that the main component in the clay mineral is aluminium silicate. For a better observation of the full-width scanning area, further amplification of the SEM scanning was targeted to a strip region with a width of 4.5 mm and a height of 0.075 mm. By setting the magnification to 1000×, SEM images with an absolute size of $0.1 \text{ mm} \times 0.075 \text{ mm}$ were obtained, and the four meso structure types of the coal sample can be classified as follows:

a, cell cavity pores non-compactly filled with clay minerals.

As shown in regions A, B, C, and D in Fig. 6, meso structures with a large number of $1-20-\mu$ m plant cell cavity pores were noncompactly filled with clay minerals, and were formed during the coalification process. Owing to the mechanical factors related to a geological structure such as extrusion and friction, larger numbers of inter-gravel pores (C, D) and broken coal structures (A, B) at different scales were formed in these meso structures. In addition, owing to the long-term dissolution effect, the filled-in clay minerals have large numbers of intercrystalline pores and intragranular corrosion pores.

b, **cell cavity pores compactly filled with clay minerals.** As shown in the E region in Fig. 6, compared with the cavity pores and meso fractures non-compactly filled with clay minerals, the meso structures of the cell cavity pores compactly filled with clay minerals have still-intact cell cavity structures. These clay minerals have an internal bedded or granular crystallization, and owing to fewer pores in the crystals, the connectivity between the cell structures is poor.

c, **telocollinite**. As regions F and G show in Fig. 6, the meso structures of telocollinite are compact and uniform.

d, **meso fractures.** As regions H, I, and J show in Fig. 6, the meso fractures with a width of $0-20 \,\mu\text{m}$ are partly or fully filled with clay minerals, forming different scales of clay mineral strips.

4.2. Methane adsorption characteristics of meso structures in coal

To research the methane adsorption characteristics of the meso structures in coal, the average values of the temperature increase under different pressures were set to the thresholds, and the fullwidth scanning area was distinguished under each adsorption equilibrium state (10 s). Namely, regions with a temperature increase of greater than the average are defined as remarkable methane adsorption regions, and the other areas are defined as non-remarkable methane adsorption regions. As shown in Fig. 6, as the adsorption pressure increased, the average temperature increase of the full-width scanning area increased. Under low adsorption pressures (0.3 and 0.6 MPa), the remarkable methane adsorption regions contained various types of meso structures. As the adsorption pressure increased, the cell cavity pores (regions A, B, C, and D) and meso fractures (region I and J) non-compactly

filled with clay minerals were the main meso structures comprising the remarkable methane adsorption regions. For example, with methane adsorption at 0.3, 0.9, and 1.5 MPa, the temperature increases were up to 0.95 °C, 2.881 °C, and 4.028 °C, respectively. The telocollinite (regions F and G), cell cavity pores (region E), and meso fractures (H region) compactly filled with clay minerals were the main meso structures of the non-remarkable methane adsorption regions, whose temperature increases under 0.3, 0.9 and 1.5 MPa were only 0.664 °C, 1.584 °C, and 2.349 °C, respectively. As the adsorption pressure increased from 0.3 to 1.5 MPa, the difference in temperature increase between the remarkable methane adsorption regions and non-remarkable methane adsorption regions increased from 0.286 °C to 1.679 °C, i.e., the difference in methane adsorption between the two is more obvious. This suggests that the methane adsorption capacities at different locations of coal are closely related to the meso structures of the pores and clay minerals filling states. Compared with the cavity pores and meso fractures compactly filled with clay minerals in telocollinite, the meso structures of the cell cavity pores and meso fractures non-compactly filled with clay minerals in telinite have a larger number of inter-gravel pores and broken coal structures at different scales, and thus the methane storage capacity is larger.

Methane adsorption in coal is a physical surface adsorption process. At adsorption equilibrium, the relationship between the adsorption pressures and the methane adsorption capacity in coal can be described through the Langmuir equation of the adsorption kinetics [28–30].

$$n = a\theta = \frac{abp}{1 + bp},\tag{4}$$

where

$$b = b_m Exp\left(-\frac{\varepsilon}{kT}\right). \tag{5}$$

Using Eq. (5), neglecting the influence of the temperature variation of the adsorption system on the methane adsorption capacity of coal, the deeper the potential well depth is, the stronger the methane adsorption capacity of the coal, as shown through Eqs. (4) and (5). From Eqs. (2) and (4),

$$\Delta T = -\frac{q}{C} \times \frac{abp}{1+bp} = \frac{a_T bp}{1+bp}.$$
(6)

In Eq. (6), ΔT is the temperature increase of coal during methane adsorption in °C. When *p* tends toward infinity, $\triangle T = a_T$. Thus, a_T is the maximum temperature increase of coal, the value of which is determined based on the number of adsorption sites a. Based on Eq. (6), the curve fittings of the temperature increase for various types of meso structures in Fig. 6 under different adsorption pressures are shown in Table 3. In the remarkable methane adsorption regions (regions A, B, C, D, I, and J) a_T is 14.54 °C and b is 0.33 on average, which are 2.95- and 0.62-times of the values of a_T (4.93 °C) and b (0.61) in the non-remarkable methane adsorption regions (regions E, F, G, and H), respectively. Based on Eqs. (5) and (6), this finding suggests that compared with the cavity pores and meso fractures compactly filled with clay minerals in telocollinite, i.e., the meso structures in the right-centre region of the surface of coal sample A, the cell cavity pores and meso fractures non-compactly filled with clay minerals in telinite have a considerably larger surface area and more adsorption sites for methane molecules; therefore, their methane storage capacities are larger under the same adsorption pressure, which leads to a larger amount of methane adsorption and higher temperature increase of the right-centre region of the coal sample surface, whereas the potential well depth of these meso structures is relatively shallower owing to the complex structures of the coal molecules and clay mineral crystals [1,2,7,8].



Fig. 6. Temperature increase of different meso structures in coal.

Table 2

EDS energy spectrum detection of coal matrix and clay minerals.

Region	Vitrinite of coal matrix			Clay minerals	Clay minerals			
EL	C	0	S	C	0	Si	Al	
Norm. C (wt.%)	86.36	13.22	0.42	45.67	34.86	10.54	8.93	

Table 3

Curve fitting of temperature rising of different meso structures in coal.

Region type	Meso structure	Label	Curve fitting	Correlation coefficient
Remarkable methane adsorption regions	The cell cavity pores non compactly filled with clay minerals	А	$\Delta T = \frac{15.38 \times 0.25p}{1+0.25p}$	0.9834
		В	$\Delta T = \frac{22.99 \times 0.16p}{1+0.16p}$	0.9958
		С	$\Delta T = \frac{10.78 \times 0.44p}{1+0.44p}$	0.9996
		D	$\Delta T = \frac{11.76471 \times 0.33p}{1+0.33p}$	0.9904
	The meso fractures non compactly filled with clay minerals.	Ι	$\Delta T = \frac{17.76 \times 0.18p}{1+0.18p}$	0.999
		J	$\Delta T = \frac{8.55 \times 0.59p}{1+0.59p}$	0.9889
Non-remarkable methane adsorption regions	The telocollinite	F	$\Delta T = \frac{3.45 \times 0.8p}{1+0.8p}$	0.9902
		G	$\Delta T = \frac{5.156 \times 0.63p}{1+0.63p}$	0.9858
	The cell cavity pores compactly filled with clay minerals.	Е	$\Delta T = \frac{3.6 \times 0.98p}{1+0.98p}$	0.9777
	The meso fractures compactly filled with clay minerals.	Н	$\Delta T = \frac{7.53 \times 0.36p}{1+0.36p}$	0.9847

5. Distribution and evolution of methane adsorption in coal under different pressures

Owing to the various methane adsorption characteristics in different locations of the coal, the non-uniformity of the methane distribution and its evolution occurred under different adsorption pressures. Setting 0.1 °C as the statistical interval, the proportion of temperature increase, $\Delta T_{i,0-1}$, of the full-width scanning area can be determined following Eq. (7):

$$P_{\Delta T_{i,0-1}} = \frac{N_{\Delta T_{i,0-1}}}{N} \times 100\% (N_{\Delta T_{i,0-1}} > 0).$$
(7)

The statistical results of the adsorption equilibrium state (10 s) under each pressure amount are shown in Fig. 7. It is clear that all temperature increases of coal were between limited ranges under these different pressure rates. Under a low adsorption pressure, the methane adsorption capacities in different meso structures were relatively uniform, and were concentrated within a smaller range; therefore, the non-uniformity of the methane distribution is weak. As the adsorption pressure increased, the difference in adsorption content between various types of meso structures increased, resulting in an enhancement of the non-uniformity of the methane distribution.

Three-dimensional pseudo colour displays achieved by extracting the remarkable methane adsorption regions of the full-width scanning area under different pressures are shown in Fig. 8, and the methane (temperature rising) distribution characteristics are shown in Table 4. Based on the regional connectivity statistics of the remarkable methane adsorption regions under different pressures, the number of the connected domains ranges from 57 to 156, and the average connected domains area ranges from 0.032 to 0.0825 mm². With an increase in adsorption pressure, the number of connected domains decreased, and the average connected domain area increased. This suggests that under low adsorption pressures, all meso structures in coal have relative methane adsorption capacities; the advantages of methane adsorption in the remarkable methane adsorption regions are not obvious. With an increase in adsorption pressure, the methane adsorption content of the meso structures in the remarkable methane adsorption regions increased dramatically, resulting in a centralization of the adsorption locations.



Fig. 7. Area proportion in different temperature rising section of full-width scanning area.

Under different pressure levels, the methane content at different positions of the full-width scanning area can be obtained from Eq. (2). The proportion of methane content in the remarkable methane adsorption regions ranged from 60.06% to 70.37%, and the average proportion of methane content was 63.795%; the proportion of the remarkable methane adsorption region ranged from 47.5% to 50.47%, and the average proportion of this area was 48.99%. When the adsorption pressure increased, owing to the decrease in low methane adsorption area and the increase in average methane content, both the proportion of average methane content and the proportion of the average area showed a downward trend. The average per unit area of methane content in the remarkable methane adsorption regions and in the non-remarkable methane adsorption regions can also be obtained as follows:

$$n_1 = \frac{N_1}{S_1},\tag{8}$$

$$n_2 = \frac{N_2}{S_2}, \text{ and}$$
(9)



Fig. 8. 3D pseudo colour displays of the remarkable methane adsorption regions of the full-width scanning area.

Table 4

Statistics of methane adsorption (temperature rising) distribution characteristics.

$$\eta = \frac{n_1}{n_2}.\tag{10}$$

In Eq. (10), η characterizes the aggregation of methane adsorption in coal. The greater the value of η is, the higher the degree of aggregation. From the calculations, η ranged from 1.66 to 2.33, and clearly decreased as the adsorption increased, i.e., the aggregation of methane storage in coal decreased.

Based on the relationship between the adsorption pressures and the amounts of methane adsorption, the different meso structures obey the Langmuir equation. From Eqs. (4) and (8)-(10),

$$\eta = \frac{a_1 b_1 p}{1 + b_1 p} \left/ \frac{a_2 b_2 p}{1 + b_2 p} = \frac{a_1}{a_2} \times \frac{1 + 1/b_2 p}{1 + 1/b_1 p}.$$
(11)

From Eq. (11), it is clear that when b_1 is smaller than b_2 , η decreased with an increase in the adsorption pressure, i.e., from Eqs. (4) and (5), compared with the meso structures in the non-remarkable methane adsorption regions, the adsorption potential well depth ε of meso structures in the remarkable methane adsorption regions were shallower, leading to a slower increase in the rate of adsorption site coverage θ and a decrease in the aggregation of methane storage in coal.

6. Conclusions

The methane adsorption capacities at different locations of coal are closely related to the meso structures of their pores and the clay mineral filling states. Compared with the cavity pores and meso fractures compactly filled with clay minerals in telocollinite, the meso structures of the cell cavity pores and meso fractures non-compactly filled with clay minerals in telinite have a considerably larger surface area and more adsorption sites for methane molecules; therefore, the methane storage capacity is larger under the same adsorption pressure, whereas the potential well depths of these meso structures are relatively shallower owing to the complex structures of the coal molecules and clay mineral crystals.

Owing to the varying methane adsorption characteristics at different locations of coal, a non-uniformity in the methane distribution and evolution occurs under different adsorption pressures. The methane content in the remarkable methane adsorption regions increases sharply as the adsorption pressure increases, resulting in a centralization of the adsorption locations and an increased inhomogeneity of the methane storage at different locations in coal. The coverage rate of the adsorption sites in the remarkable methane adsorption regions increases more slowly, leading to a decrease in the aggregation of methane storage in coal.

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Adsorption pressure (MPa)	0.3	0.6	0.9	1.2	1.5
Average temperature rising of the full-width scanning area (°C)	0.7478	1.3201	1.9083	2.4354	2.9901
Average temperature issue of the remarkable methane adsorption regions (*C) Area proportion of remarkable methane adsorption regions $/\%$	50.47	2.4912 49.5	2.9557 48.99	2.4912 48.5	3.7856 47.5
Average methane content proportion of remarkable methane adsorption regions (%)	70.37	64.04	62.91	61.6	60.06
Aggregation of methane adsorption in the full-width scanning area η	2.331	1.817	1.766	1.703	1.662
Number of the connected domains of remarkable methane adsorption regions Average connected domains area of remarkable methane adsorption regions (mm ²)	156 0.032	134 0.0366	93 0.0522	82 0.0586	57 0.0825

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