Experimental study on methane adsorption behaviour of different rank coals under variable temperature and pressure

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Abstract. To comprehensively study the methane adsorption behaviour of coals under variable temperature and pressure, a series of methane adsorption measurements were conducted at different temperatures and pressures for different rank coals from Ordos Basin and Qinshui Basin. The results show that the methane adsorption capacity and temperature exhibit a negative linear correlation under the same pressure series. The combined effects of the temperature and pressure reveal that the high-rank coal has the maximum methane adsorption capacity and the low-rank coal owns the least. During the low pressure region, the increase of adsorption capacity of high-rank coal is the largest, whereas the low-rank coal has the least change with the temperature and pressure increasing. However, in the high pressure region, the decrease of adsorption capacity of high-rank coal is the least, and the low-rank coal owns the largest of that.

1. Introduction
Coalbed methane (CBM), as a high-quality and alternative hydrocarbon resource, has attracted considerable attention around the world in recent years [1-5]. Generally, the majority of total CBM (~95%) may be stored in the pore space with the adsorbed state due to the reservoir pressure [6]. Therefore, the adsorption capacity of coal is an important physical parameters of coal reservoir, which has an important role in the gas content, gas saturation and CBM recovery [7-9].

Knowledge of the Langmuir constants (VL and PL) are usually used to analyze the adsorption behaviour of coals. Bustin and Clarkson [10] found that the adsorption capacity was decreased at a certain rate with the temperature increasing, and the adsorption isotherms could reflect the adsorption capacity of coals with the pressure increasing at a stationary temperature. However, as a matter of fact, the temperature and pressure change at the same time when the coal reservoir uplift or subside during the geological history. Zhong et al. [11] considered that the pressure plays an important role in the adsorption capacity in lower temperature and pressure region. In contrast, the temperature plays an important role. Ma et al. [12] indicated that temperature plays an important role in the adsorption capacity of coals at a certain stage during the tectonic uplift. However, the coupling effects of temperature and pressure on the adsorption capacity of different rank coals still need more works.

In this study, three representative coal samples of different coal ranks were selected to conduct the experiments, and then quantitatively described variation of the adsorption capacity of different coal
ranks during the comprehensive change of temperature and pressure. Finally, the coupling effects of temperature and pressure on methane adsorption behavior of coals were discussed in detail.

2. Coal samples and experiments

2.1. Samples collection and coal analyses
Fresh bulk coal samples (~15×15×15 cm³) were collected from the working faces of the Baode and Panlong coalmines of eastern Ordos basin, and the Duanshi coalmine of the Qinshui Basin. The samples were carefully packed and sent to the laboratory for analysis as soon as possible, including maximum vitrinite reflectance ($R_{o,m}$), maceral composition analysis and proximate analysis. The procedures of these tests were the same as those in our previous work [4].

2.2. Experimental procedure
The isothermal adsorption experiment refers to GB/T 19560-2004. Firstly, coal samples were crushed to the particle size of 0.25-0.20mm. Secondly, the coal particles were preceded with equilibrium moisture content before the isothermal adsorption experiment, which would make the moisture of the coal samples close to the in-situ moisture of coal reservoir. Finally, the samples were recorded the weight and quickly put into the sample chamber. After that, the isothermal adsorption experiment was conducted at the temperature of 25℃, 35℃, 45℃ and 55℃, respectively.

3. Results and discussions

3.1. Coal rank, maceral and adsorption capacity
Table 1 shows the result of coal petrology and chemistry analysis. The coal samples from Wangtian, Panlong and Duanshi coalmines belong to low-rank coal ($0.57\% R_{o,m}$), medium-rank coal ($1.65\% R_{o,m}$) and high-rank coal ($2.61\% R_{o,m}$), respectively. Of all the samples, the moisture content ranges from 0.52 to 2.48%, ash yield content ranges from 15.51 to 39.15%, volatile matter is between 15.67 and 39.68%, and fixed carbon content ranges from 60.32 to 84.33%. Meanwhile, the vitrinite ranges from 47.0 to 77.5%, while inertinite is between 22.5 and 53.0%. The liptinite only presents in low-rank coal (10.8%).

According to the isothermal adsorption experiments, the Langmuir constants and the methane adsorption isotherms at the temperature of 25℃, 35℃, 45℃ and 55℃ can be obtained, as shown in Table 2 and Figure 1. The results show that the adsorption capacity ($V_L$) decreases with the temperature increasing, which is consistent with the previous studies [11, 12]. $P_L$ also decreases with the temperature increasing, but the decrease is different for varied rank coals. Therefore, it is important to study on the effects of temperature and pressure on the adsorption capacity of different rank coals.
3.2. Relationship between temperature and adsorption capacity

Previous studies found that the methane adsorption capacity of coals decreases with the temperature increasing [11, 12]. However, there are a few different viewpoints for the adsorption capacity variations with the temperatures for different rank coals. In this study, the methane adsorption capacity shows a negative linear correlation with temperature in the same pressure region. Moreover, the result show that the higher the pressure, the more obvious the negative linear correlation is (Figure 2). When the pressure is 2.0 MPa, the methane adsorption capacity of coal samples (a, b and c) decrease by 0.05 m$^3$/t/°C, 0.04 m$^3$/t/°C and 0.04 m$^3$/t/°C in the temperature range of 25℃~55℃. When the pressure is 8.0 MPa, the methane adsorption capacity of coal samples (a, b and c) decrease by 0.10 m$^3$/t/°C, 0.10 m$^3$/t/°C and 0.11 m$^3$/t/°C in the temperature range of 25℃~55℃. When the pressure is 50.0 MPa, the methane adsorption capacity of coal samples (a, b and c) decrease by 0.12 m$^3$/t/°C, 0.15 m$^3$/t/°C and 0.19 m$^3$/t/°C in the temperature range of 25℃~55℃. The above analysis shows that the effect of temperature on methane adsorption capacity of coals gradually increase with pressure increasing. The decrease of methane adsorption capacity of different rank coals almost unchanged with the temperature increasing in the low-pressure region. However, in terms of high-pressure region, the decrease of methane adsorption capacity of high-rank coal is the largest, whereas that of low-rank coal shows the least with the temperature increasing. According to the equation of temperature-adsorption capacity, the methane adsorption capacity at the entire temperatures under the same pressure can be calculated.
3.3. Relationship between pressure and adsorption capacity

During the tectonic uplift or stratum settlement, the temperature and pressure would be changed in a certain regular pattern. In this study, 15 ℃ as land surface temperature, 3 ℃/100m as geothermal gradient and 1.0 MPa/100m as pressure gradient of reservoir were selected to calculate the temperature and pressure of coal reservoirs at different depths. According to Langmuir constants and the temperature-adsorption capacity equation, the methane adsorption capacity of coal samples (a, b and c) at varied temperatures and pressures can be obtained (Figure 3).

Before the critical pressure, the methane adsorption capacity increases with temperature and pressure increasing, whereas the increase of methane adsorption capacity is different for the coal samples. After the critical pressure, the methane adsorption capacity of different rank coals decreases. The maximum methane adsorption capacity of coal samples (a, b and c) are 10.90 m³/t, 13.91 m³/t and 26.00 m³/t at the colligated influence of temperature and pressure, respectively. Meanwhile, the temperature reaches 34.65 ℃, 43.44 ℃ and 48.63 ℃ and the pressure reaches 6.55 MPa, 9.48 MPa and 11.21 MPa. When the temperature and pressure is below the critical value, the pressure plays an important role in the change of methane adsorption capacity of coals. On the contrary, temperature plays the leading role (Figure 3).

Based on the above analysis, the maximum methane adsorption capacity would increase with the coal rank increasing. The critical temperature and pressure of the maximum methane adsorption capacity increases with the coal rank increasing. In the low-pressure region, the increase of adsorption capacity of high-rank coal is the largest and the low-rank coal owns the least with the temperature and pressure increasing. However, in the high-pressure region, the decrease of adsorption capacity of high-rank coal is the least and the low-rank coal has the largest (Figure 4). The changes of the methane adsorption capacity of different rank coals are associated with multiple factors, such as the metamorphic degree of coal, coal macerals, moisture content, ash content, pore and specific surface area.
4. Conclusions
In this study, the methane adsorption capacity shows a negative linear correlation with temperature in the same pressure region. The decrease of methane adsorption capacity of different rank coals almost unchanged with the temperature increasing when the pressure is low. However, in the high-pressure region, the decrease of methane adsorption capacity of high-rank coal is the largest and the low-rank coal has the least with the temperature increasing.

The maximum methane adsorption capacity increases with the coal rank increasing. The critical temperature and pressure of the maximum methane adsorption capacity would increase with the coal rank increasing. The pressure plays an important role in the change of adsorption capacity when the temperature and pressure below the critical value. On the contrary, temperature occupies the leading role.

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