Competitive adsorption characteristics of N$_2$ and CH$_4$ gas mixtures on coal and its geological significance

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Abstract. Coalbed methane (CBM) is an important unconventional natural gas resource and has achieved great advances in recent years. In this study, single and binary component adsorption experiments of N$_2$ and CH$_4$ on dry coal from eastern Yunnan and western Guizhou area were conducted on a high-pressure isothermal adsorption equipment to investigate the competitive adsorption characteristics of N$_2$ and CH$_4$. The results show that absolute adsorption capacity of methane is higher than that of nitrogen for coal samples in this area. Moreover, maximum mixture gas adsorption isotherms lie between the pure N$_2$ isotherms and pure CH$_4$ isotherms. There is an obvious increasing trend for P$_L$ as the content of nitrogen increases, it can be ruled out that critical desorption pressure increases along with the increasing nitrogen content in coal seam. This investigation is significative to understand CBM recovery processes considering N$_2$ injection.

1. Introduction
As an important unconventional natural gas resource, coalbed methane (CBM) is characterized by high-calorific value and low-pollution, which is considered as a clean energy source. In recent years, the development of CBM industry has achieved great significance, which is of great benefit of optimizing energy structure and ensuring energy security.

In general, it has been widely acknowledged that China has abundant CBM resource and its CBM industry is expected to prosper in the next years [1]. It is widely accepted that CBM is a mixture of organic and inorganic gas components, mainly including CH$_4$, N$_2$, C$_2$H$_6$ and CO$_2$. The major component in CBM is methane, which is mainly existed as adsorbed state on coal. Generally, the high-pressure isothermal adsorption experiment is considered as an essential part for estimating CBM reserves and the recoverable amount of the resources. Studies on multi-component gas competitive adsorption on coal sample started from 1990s [2], mainly focusing on CH$_4$/N$_2$/CO$_2$ ternary gas adsorption [3-5], CH$_4$/CO$_2$ binary gas adsorption [6-8], and CO$_2$/CH$_4$ displacement effect [9-11]. The results reveal that the adsorption ability between different gas molecules can lead to competitive adsorption and displacement behavior. CH$_4$ production of CBM can be significantly enhanced by the design of CO$_2$ injection due to the different adsorption energy [12-13] and the results are widely applied in CBM development. N$_2$ is an important component during kerogen cracking. The generated N$_2$ and CH$_4$ may exist competitive adsorption relationship. However, most of current work are still focused on CH$_4$/CO$_2$ competitive adsorption, the characterization and capacity of CH$_4$/N$_2$ competitive adsorption are still poorly studied and documented [14-15].

In this study, single and binary component adsorption experiments of N$_2$ and CH$_4$ on dry coal were conducted on a high-pressure isothermal adsorption equipment to investigate the competitive adsorption behaviors.
adsorption characteristics of N₂ and CH₄. The results could indicate and evaluate the feasibility of CBM recovery by injection of N₂. This investigation is significance to understand CBM recovery processes considering N₂ injection.

2. Samples and experiments

2.1. The Samples
Two coal samples were collected from 2 coal mines in eastern Yunnan and western Guizhou area, China. The sampling area for above two samples are tectonically located in the eastern part and the middle part of the east Yunnan-north Guangxi-Guizhou-west Hunan fault-fold tectonic belt. The CBM resource is abundant in the study area, accounting for 13% of CBM resources of China, and with high gas content and complex gas system of coal seam. The coal bearing strata mainly includes the Xuanwei formation of Late Permian in eastern Yunnan and Qianxi Longtan and Changxing formations of Late Permian. In general, the theoretical gas content of primary mineable seam coal is up to 22 m³/t [16]. Meanwhile, the Rₒ of the two samples (S7-1 and S12-1) are 3.33% and 2.21%, respectively.

2.2. Experiments
The procedures of the adsorption experiments can be described as following: (1) Sample pretreatment: the samples were crushed and sieved into grains of about 60-80 mesh size, then dried at 105°C for 4 hours under vacuum; (2) Buoyancy test: the dried samples and magnetic suspension balance system were pressurized with helium ranging from 0 to 6MPa (7 pressure points), the balance readings were recorded at 7 points respectively; (3) Sorption measurement: pure and mixture gases adsorption were carried out at the set temperature up to 16MPa (10 pressure points), when mass changes less than 50μg in 20 minutes, the adsorption equilibrium was assumed to be achieved. Then high pressure absolute adsorption capacity, Langmuir pressure and volume of the samples were obtained and calculated by appliance of adapted 3-parameter excess sorption Langmuir equation as following:

\[ m_{\text{excess}} = m_{\text{balance}} + \rho g(P,T) \cdot V_{\text{container}} + \text{sample} - m_{\text{container}} + \text{sample} \]

3. Results and discussions

3.1. Adsorption isotherms with different gas ratios
All test results that we obtained directly from the adsorption apparatus are excess adsorption capacity, then the data were calculated by adapted 3-parameter excess sorption Langmuir equation, finally, we got the absolute adsorption capacities and their isotherms. High pressure adsorption isotherm reveals maximum adsorption capacity and the characterization of sorption increase trend along with pressurization. Five isotherms with different gas ratios for sample S1-7 are presented in figure 1, and the isotherms for sample S2-12 in figure 2. The calculated \( V_L \) and \( P_L \) are shown in table 1.
Figure 1. Comparisons of adsorption isotherms with different gas ratios at 40℃ for sample S1-7

Figure 2. Comparisons of adsorption isotherms with different gas ratios at 40℃ for sample S2-12
Table 1. Adsorption parameters derived from experiments with different gas ratios for two samples

| Sample | Gas                | $P_L$ (MPa) | $V_L$ (m$^3$/t) |
|--------|--------------------|-------------|-----------------|
|        | pure CH$_4$        | 0.79        | 25.33           |
|        | 25%N$_2$+75%CH$_4$ | 1.12        | 22.04           |
| S1-7   | 50%N$_2$+50%CH$_4$ | 1.55        | 20.34           |
|        | 75%N$_2$+25%CH$_4$ | 2.56        | 20.55           |
|        | pure N$_2$         | 3.83        | 22.95           |
|        | pure CH$_4$        | 1.45        | 15.29           |
|        | 25%N$_2$+75%CH$_4$ | 1.41        | 12.12           |
| S2-12  | 50%N$_2$+50%CH$_4$ | 2.03        | 12.47           |
|        | 75%N$_2$+25%CH$_4$ | 2.48        | 11.35           |
|        | pure N$_2$         | 3.80        | 12.06           |

3.2. The competitive adsorption characteristics of N$_2$ and CH$_4$ gas mixture

It should be noted that the absolute adsorption capacities of the two samples in eastern Yunnan and western Guizhou area were above 10 m$^3$/t for all five different gas ratios. Our study reveals that this area has a good potential of natural gas. While comparisons between the two samples show that S1-7 has a higher adsorption capacity than S2-12, no matter what proportion of adsorbed gas mixture is.

In addition, as illustrated in Figure 1 and Figure 2, S1-7 can adsorb more pure CH$_4$ than N$_2$ under the same pressure at 40°C, the same trend were presented in pure gas sorption isotherms of S2-12. Therefore, the absolute adsorption capacity of methane is higher than that of nitrogen for coal samples in this area. Furthermore, the experimental results of mixture isotherms clearly confirm that methane is preferentially adsorbed on coal over nitrogen.

Generally, the mixture and pure gas adsorption experiments indicate that the maximum mixture gas adsorption isotherms lie above the pure N$_2$ isotherms, and below pure CH$_4$ isotherms. It shows that the maximum adsorption capacity of coal seam measured by the commonly used pure methane adsorption experiment is higher than the actual coalbed methane adsorption capacity. Therefore, we suggest to correct the common methane adsorption data to estimate CBM reserves more accurately when evaluating the gas content of coal seam.

Moreover, there is an obvious increasing trend for $P_L$ as the content of nitrogen increases, it can be ruled out that critical desorption pressure increases along with the increasing nitrogen content in coal seam, which leads to easier desorption in the process of CBM extraction, allowing for a faster recovery of methane.

4. Conclusions

In this study, a set of pure and mixed CH$_4$ and N$_2$ adsorption experiments were performed on coal samples from eastern Yunnan and western Guizhou area, China. Combined with the geological settings, and data and isotherms obtained, the conclusions can be described as following:

(1) S1-7 has a higher adsorption capacity than S2-12, and the coal samples in this area has a relatively strong adsorption capacity. Coal seam in this area has a good potential of natural gas.

(2) The absolute adsorption capacity of methane is higher than that of nitrogen for coal samples in this area.

(3) The mixture and pure gas adsorption comparisons indicate that the maximum mixture gas adsorption isotherms lie above the pure N$_2$ isotherms, and below pure CH$_4$ isotherms. We suggest to
correct the common methane adsorption data to estimate CBM reserves more accurately when evaluating the gas content of coal seam.

(4) Critical desorption pressure increases along with the increasing nitrogen content in coal seam, allowing for a faster recovery of methane. Considering that N₂ is relatively cheaper than CO₂, we can try to promote the exploitation of CBM by injecting N₂ instead of CO₂.

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