Competitive adsorption of methane and carbon dioxide at nanometer level

Pengliang Yu[1, a], Cao-Yun[2] and Xiangfang Li[1]

[1]MOE Key Laboratory of Petroleum Engineering, China University of Petroleum (Beijing), Beijing 102249, PR China

[2]Baikouquan oil production plant， Xinjiang Oilfield Company, PetroChina, Karamay, Xinjiang 834000, China

[a]3162748935@qq.com

Keywords: Competitive adsorption; Methane;CO_2; Nanometer level

Abstract. From macro perspective, main factors affecting adsorption of CH_4 by coals include coal particle size, pore structure, coal rank, moisture, temperature and pressure, etc.. The adsorption capacity of CH_4 by coals is affected by multiple factors. The adsorption experiment of single component gas showed that the absorption of CO_2 was higher than that of CH_4 by coals, finding that the adsorption capacity of CO_2 by coal surface was higher than that of CH_4, and the absorption capacity ratio of CO_2/CH_4 changed with pressure and coal rank, but the pressure was not directly proportional to absorption capacity ratio of CO_2/CH_4. With the increase of pressure, adsorption ratio of CO_2/CH_4 decreases gradually. When the pressure is high, the adsorption capacity of CH_4 is higher than that of CO_2, so it is appropriate to use CO_2 to displace coal seam CH_4 under low pressure. In addition, adsorption- desorption characteristic curve obtained from pure gas and carbon dioxide adsorption isotherm experiment could not demonstrate true adsorption situation of CH_4 and CO_2 mixed gas in coal seam.

Introduction

In fact, coals adsorb gas by surface action between solid surface of coal and gas molecules, as the atomic force field of solid surface is not saturated and there remains residual valence force. Valence force can only reach the range equivalent to the diameter of a molecule, gas molecules are absorbed only when they collide with surface which has not adsorbed gas, and when the solid surface has been covered with a layer of adsorbed molecules, both surface force field and absorption are saturated s, so the adsorption belongs to monolayer adsorption type.

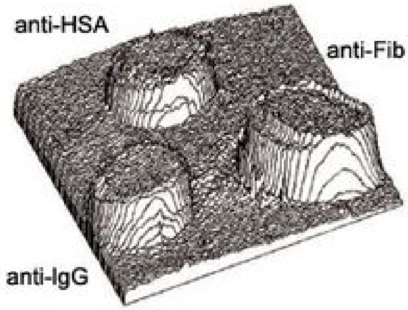

Figure 1 Monolayer adsorption

Monolayer adsorption theory was proposed by French chemist Langmuir (Langmuir) from the perspective of kinetics. He studied the adsorption characteristics of solid surface to put forward a monolayer adsorption equation, that is, Langmuir Equation. Theoretical analysis and experimental results have showed that Langmuir Equation is applicable to studying adsorption characteristics of CH_4 by coal surface, so equation is appropriate to be used to calculate the adsorption capacity of CH_4. The relationship between CH_4 adsorption and CH_4 pressure can be expressed in the Langmuir isotherm equation as below:

$$V = a\frac{bp}{1+bp} \quad (1)$$

V denotes adsorption capacity, unit cm3/g; a stands for Langmuir adsorption constant, unit cm3/g; b refers to Langmuir pressure constant, 1/MPa; P represents gas pressure, unit Mpa.

Adsorption isotherm is as shown in Figure 1, as the pressure is very low, formula (1) is derived to Henry's formula:

$$V = a \bullet b \bullet p \quad (2)$$

Langmuir Equation can describe the adsorption of gas by micro-pores and cracks of coals. All micro cracks are filled with gas under very high pressure, and the maximum adsorption capacity value is expressed by adsorption constant a. When the pressure is very low, Henry's law is applied to calculate the slope of isotherm, that is, the curvature of isotherm. The greater the pressure constant a is, the greater the slope is and the closer the isotherm to pressure axis is. Theoretically, adsorption constant a is not affected by temperature, so limit adsorption capacity is the same at any temperature. While the pressure constant is related to temperature, the relationship equation is as below:

$$b = b_0 \exp\left(-\Delta H / RT\right) \quad (3)$$

In the above equation, b0 refers to constant, unit 1/Mpa; ΔH stands for absorption energy; unit cal/g • mol; R denotes universal gas constant, unit 1.987cal/g • mol • K; T means absolute temperature, unit K.

In equation (1), a is only related to the specific surface area of coals and adsorbed gas, and mainly reflects the differences in the adsorption capacities of various coal samples. b is a parameter related to temperature and absorbed gas, and demonstrates the change in absorption capacity at different temperatures. In summary, the changes in the adsorption capacity of CH_4 and CO_2 can be reflected by value a and b.

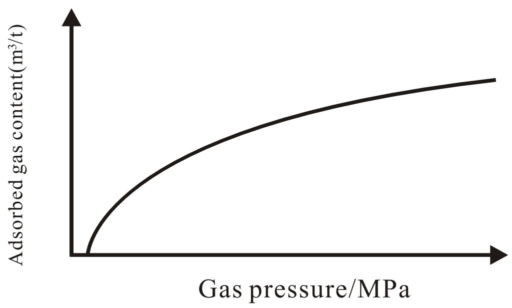

Figure. 2 Relationship between CH_4 pressure and CH_4 adsorption capacity

Based on previous research results, the adsorption capacity of methane by coals is in line with Henry's law under low pressure and reaches saturation limit under high pressure, therefore, Langmuir equation can demonstrate the adsorption of gas by coals. Isothermal adsorption constant is mainly determined by curve fitting isothermal adsorption data as shown in Figure 2, the Langmuir equation can be rewritten as below:

$$\frac{p}{V} = \frac{p}{a} + \frac{1}{\mathrm{ba}} \quad (4)$$

Adsorption constants a and constant pressure b can be calculated based on slope and intercept. Langmuir isothermal equation is usually written as follows:

$$V = a\frac{p}{p_L + p} \quad (5)$$

In the equation, PL=1/b refers to the pressure under which the adsorption capacity reaches 50% of limit, when P=PL, V=0.5a

2 Adsorption of CH_4 and CO_2 by coals

Generally, there are two kinds of CH_4 existing in coals such as free CH_4 and absorbed CH_4 (as shown in Figure 2). Adsorption capacity of CH_4 by coals is in line with Langmuir adsorption isotherm theory, coals absorb CH_4 mainly by VDW which is generated by surface interaction between solid surface of coal with gas or liquid. When gas or liquid contacts coal surface, residual force field is generated due to the difference in stress on surface molecules and internal molecules of coal cracks and pores, and thereby generating surface potential, to increase the concentration of gas molecules in pore walls of coals and thus giving rise to adsorption phenomenon and releasing adsorption heat [1].

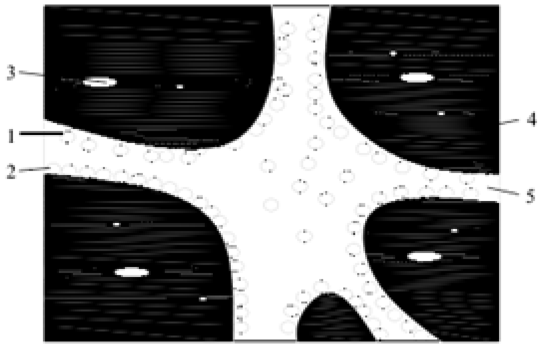

Figure 3 Gas occurrence state in coal

1.Free CH_4 2. Attached CH_4 3. Absorbed CH_4 4. Coal 5. Coal pores

2.1 Adsorption of single component CH_4 and CO_2 by coals

The adsorption experiment of single component gas showed that the absorption of CO_2 was higher than that of CH_4 by coals, finding that the adsorption capacity of CO_2 by coal surface was higher than that of CH_4, and the absorption capacity ratio of CO_2/CH_4 changed with pressure and coal rank, but the pressure was not directly proportional to absorption capacity ratio of CO_2/CH_4. With the increase of pressure, adsorption ratio of CO_2/CH_4 decreases gradually. When the pressure is high, the adsorption capacity of CH_4 is higher than that of CO_2, so it is appropriate to use CO_2 to displace coal seam CH_4 under low pressure.

2.2 Adsorption capacity of CH_4 and CO_2 mixed gas by coals

Adsorption- desorption characteristic curve obtained from pure gas and carbon dioxide adsorption isotherm experiment could not demonstrate true adsorption situation of CH_4 and CO_2 mixed gas in coal seam. So it is necessary to study the adsorption-desorption characteristics of mixed gas by coal seam when there are other gases existing in coal seam, which is important for the correct evaluation of the development potential of coal bed gas.

There are a lot of previous studies on the adsorption of CH_4 and CO_2 by coal surfaces. [2]. The results show that the adsorption capacity of mixed gas coal is between that of pure CH_4 with that of CO_2, and the adsorption of CH_4 and CO_2 mixed gas by coals show different characteristics; coal adsorbs CO_2 first, when pressure increases, the coal adsorbs more CO_2 and less CH_4 [3]. With the increased proportion of carbon dioxide in the gas, the curve is more similar to the adsorption curve of carbon dioxide [4].

Studies have found the concentration of CH_4 in free phase is increasing in the process of adsorption and desorption of CH_4 and CO_2 mixed gas, while the CO_2 concentration decreases continuously, which fully proves that coals absorb more CO_2 than other gases, providing theoretical basis for coal seam storage of CO_2 and enhanced CH_4 output. The study of adsorption-desorption characteristics of multicomponent gases can predict the change trend of output gas composition and provide key basis for correct economic evaluation of coal bed methane development. Literatures [5] hold extended Langmuir equation is not very accurate in the prediction under high pressure.

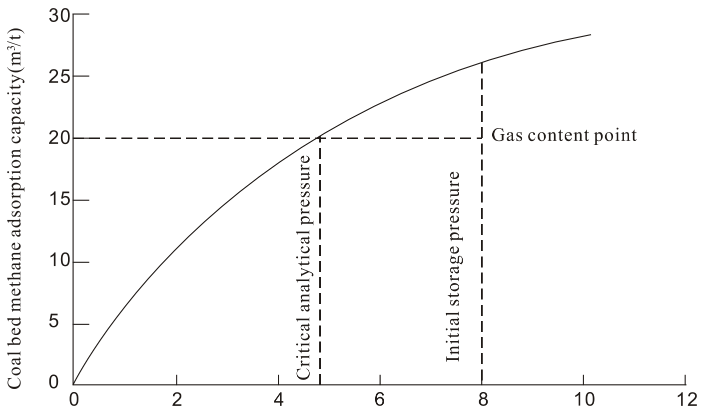

Figure 4 Schematic diagram of isothermal adsorption curve and critical desorption pressure of coals

2.3 Factors influencing adsorption capacity of CH_4 and CO_2 by coals

From macro perspective, main factors affecting adsorption of CH_4 by coals include coal particle size, pore structure, coal rank, moisture, temperature and pressure, etc.. The adsorption capacity of CH_4 by coals is affected by multiple factors.

2.4 Effect of temperature and pressure on coal adsorption

It is generally believed that coals adsorb CH_4 mainly by physical means, and its equilibrium adsorption capacity decreases with the increase of temperature. When the temperature increases, adsorption capacity of CH_4 by coal decreases. The adsorption capacity of CO_2 is higher than that of CH_4 at the same experimental temperature, but when the pressure increases, the adsorption capacity of CH_4 is higher than that of CO_2. This shows that when adsorption capacity of CO_2 by coal reaches a certain level, improving adsorption capacity of CO_2 only by increasing the pressure has little effect. However, studies have showed that adsorption capacity enhances with the increase of pressure as the density of gas molecules on the surfaces of pores increases.

Conclusion

Research shows that the absorption of CO_2 was higher than that of CH_4 by coals, finding that the adsorption capacity of CO_2 by coal surface was higher than that of CH_4, and the absorption capacity ratio of CO_2/CH_4 changed with pressure and coal rank, but the pressure was not directly proportional to absorption capacity ratio of CO_2/CH_4. With the increase of pressure, adsorption ratio of CO_2/CH_4 decreases gradually. When the pressure is high, the adsorption capacity of CH_4 is higher than that of CO_2, so it is appropriate to use CO_2 to displace coal seam CH_4 under low pressure, And that when adsorption capacity of CO_2 by coal reaches a certain level, improving adsorption capacity of CO_2 only by increasing the pressure has little effect. However, studies have showed that adsorption capacity enhances with the increase of pressure as the density of gas molecules on the surfaces of pores increases.

References

[1] Chathoth S M, Mamontov E, Melnichenko Y B, et al. Diffusion and adsorption of methane confined in nano-porous carbon aerogel: A combined quasi-elastic and small-angle neutron scattering study[J]. Microporous & Mesoporous Materials, 2010, 132(1-2):148-153.

[2] Billemont P, Coasne B, Weireld G D. Adsorption of carbon dioxide-methane mixtures in porous carbons: effect of surface chemistry[J]. Adsorption-journal of the International Adsorption Society, 2014, 20(20):453-463.

[3] Sudibandriyo M, Pan Z, Fitzgerald J E, et al. Adsorption of Methane, Nitrogen, Carbon Dioxide, and Their Binary Mixtures on Dry Activated Carbon at 318.2 K and Pressures up to 13.6 MPa[J]. Langmuir, 2003, 19(13):5323-5331.

[4] Ottiger S, Pini R, Storti G, et al. Adsorption of pure carbon dioxide and methane on dry coal from the sulcis coal province (SW Sardinia, Italy)[J]. Environmental Progress, 2006, 25(4):355 - 364.

[5] Heller R, Zoback M. Adsorption of methane and carbon dioxide on gas shale and pure mineral samples[J]. Journal of Unconventional Oil & Gas Resources, 2014, 8:14-24.