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Physical chemistry mechanism of influence of liquid water on coalbed methane adsorption

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Abstract

Free emission of mine gas brings out serious environmental pollution. Abundance of coalbed methane resource should be exploited, so cognition of coal adsorption characteristic has significance on the exploration and development of coalbed methane. Preparation of water injection coal sample and its isothermal adsorption experiment were carried out under simulated reservoir condition using coal samples from Feicheng mine in Shandong province of China. The experimental results indicated liquid water in coal has remarkable influence on coalbed methane adsorption. Then on the view of physics and chemistry, the essence of coal matrix adsorbing methane and the influence mechanism of gaseous and liquid water were analyzed, and the differences on adsorbing methane abilities of dry coal samples, equilibrium moisture samples and water injection samples were explained quantitatively. The conclusion is that the change of wetted coal matrix adsorbability is the fundamental reason for liquid water influencing coal adsorbability, comparing with dry or equilibrium moisture coal, which also effects on coalbed methane adsorption volume. The surface potential of wetted coal matrix, the long range force between coal and methane and methane density all can prove the change.

Keywords: intermolecular forces; adsorption; methane; water injection sample

1. Introduction

In stratum, liquid water exits in the in-situ coal reservoirs more or less, and fills in pores and fractures, and then wets coal surface. The result that liquid water had no effect on coal adsorption [1,2] was got under such an experimental condition: water content was got usually by means of dry coal samples adsorbing vaporous water or being immersed in liquid water at normal temperature and pressure. As a matter of fact, for action of pores interfacial tension, liquid water can only wet coal and inside surface of some macropores (seeping pores) which have few effects on coal adsorption capacity [3]. That is, liquid water can’t overcome interfacial tension to get into pores with small aperture and micropores, so liquid water have no apparent influence on coal adsorbability in the former experiments. However, does not liquid water influence coal adsorption under stratum temperature and pressure? Then under the simulated stratum condition, the adsorption isothermal experiments of water injection coal

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samples were carried out to investigate the physical chemistry mechanism of liquid water influence coal methane adsorption.

2. Experiment and results

Experiment samples are from Feicheng mine in Shandong province of China. Moisture, ash, volatile and fixed-carbon percent of those air dried coal sample respectively are 1.14%, 5.18%, 43.18% and 53.26%. The apparatus, for water injection coal sample preparation, is Electrohydraulic Servo Rock System Model MTS815, and the experimental temperature is 298 K and the range of injection pressure is from 8MPa to 20 MPa. The apparatus of adsorption isotherm experiment is Isothermal Adsorption/Desorption System Model IS-100, and the experimental temperature is 298 K.

The process of water injection experiment can be separated four steps[3-4]: the first is put the chosen coal samples with the granularity of 2-5 mm in an oven for 2-4 hours at the temperature of 105°C, and weigh them. The second is put the samples in self-made sample tins respectively, seal the tins and attach the tins to a vacuum pump, vacuumize continuously for 8 hours at room temperature. The third is dip the vacuumized tin into distilled water in a vessel; immerse the sample for 15 hours, and then remove the sample to a self-made sample cell; weigh the cell when there is no water dripping from the hole at its bottom (the cell’s dry weight and wet weight are given). Finally, put them into airtight pressure capsule of the Electrohydraulic Servo Rock System; inject water at high pressure from both sides of the sample cell. The experimental conditions follow: room temperature is 25±3°C, pressures are 8 MPa, 12 MPa, 16 MPa and 20 MPa, injection time is 3 hours under a stable pressure, the injected water is distilled water. After withdrawing pressure and stopping water injection, take the sample cell out and weigh the cell when there is no water drops from the bottom hole; then send coal sample for the isothermal adsorption experiment within 10 minutes.

The experimental results of dry coal samples, equilibrium moisture samples and injection water samples are shows in Table 1, where $V_L$ represents Langmuir volume ($m^3/t$), $P_L$ Langmuir pressure (MPa), $T_E$ adsorption time (h), $W_E$ the amount of equilibrium moisture (%), $P_I$ water injection pressure (MPa), $W_I$ the amount of injection water (%).

Table 1. Experiment results

<table>
<thead>
<tr>
<th>Coal sample</th>
<th>Dry sample</th>
<th>Equilibrium moisture sample</th>
<th>Water injection sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_L$</td>
<td>$P_L$</td>
<td>$W_E$</td>
</tr>
<tr>
<td>Parameters</td>
<td>11.1 0.54</td>
<td>5.91 3.75 0.19</td>
<td>8 14.86</td>
</tr>
</tbody>
</table>

The results show that, as water exits, Langmuir volumes of equilibrium moisture and water injection sample are lower than dry sample, but Langmuir volume of water injection sample is higher than equilibrium moisture sample. It is clear that the influences of liquid water in water injection sample and gaseous water in equilibrium moisture sample on coal adsorption are different.

Dry coal matrix adsorbs methane for the van der waals force. Gaseous water, in equilibrium moisture coal sample, is adsorbed by dry coal matrix more easily than methane for the hydrogen bond force, and the effective adsorption site decreases on the surface of coal matrix, so methane adsorption volume decreases. Liquid water, in water injection sample wets the surface of all pores and forms a monolayer water film, and then methane is absorbed on the surface of water film for the force from wetted coal matrix. This water film can provide more adsorption site than the surface of equilibrium moisture sample; therefore adsorption volume and capacity are higher than that of equilibrium moisture sample. However, adsorption capacity of wetted coal matrix is lower than that of dry coal matrix. And this paper will prove the above theoretical hypothesis by calculating surface potential, long range interaction between coal matrix and methane and intermolecular force of methane.
3. Analyses of long range interaction

Long range interaction is the interaction between objects by the transmission of dispersion force. It can be regarded as a long range force between an infinite thick plate, such as coal surface, and an \( r \) radius particle with \( d \) distance, which can be expressed as:

\[
E = \frac{H}{6} \left[ \frac{2r}{d} + \frac{2r}{d + 4r} + \ln \left( \frac{d}{d + 4r} \right) \right]
\]  

(1)

Where \( H \) is the Hamaker constant of object in vacuum.

Estimation of long range interaction must consider Hamaker constant. And Hamaker constants about the interaction between different particles can be gotten approximately by the Geometric Mean Law [6].

\[
H_{12} = \sqrt{H_{11} \times H_{22}}
\]  

(2)

Hamaker constant of water, methane and coal molecule is respectively \( 3.7 \times 10^{-20} \) J, \( 4.5 \times 10^{-20} \) J and \( 6.07 \times 10^{-20} \) J. Then the calculated Hamaker constant between dry coal matrix and methane is \( 5.23 \times 10^{-20} \) J on equation 2, and that between wetted coal matrix and methane is \( 4.62 \times 10^{-20} \) J. And the molecular radius of water is \( 1.35 \times 10^{-10} \) m, methane is \( 2 \times 10^{-10} \) m. The distance between coal surface and methane molecular is 3nm [6].

Based on equation 1, the calculated long range interaction between dry coal matrix and methane is \( -11.6 \times 10^{-3} \) kJ/mol, and that between wetted coal matrix and methane is \( -10.2 \times 10^{-3} \) kJ/mol. The result shows that long range interaction of wetted coal matrix is lower than that of dry coal matrix, which illustrates that liquid water decreases adsorption capacity of wetted coal matrix. In fact, as the low rank of Feicheng coal sample, lots of oxygen-containing function groups make matrix wetted easily on the surface of coal matrix, and water content of matrix is high, therefore the influence of liquid water and the decrease degree of adsorption capacity of wetted coal matrix are remarkable.

4. Analyses of adsorption potential

Relationship between adsorption potential and pressure is given as follow.

\[
\varepsilon = \frac{P}{P_e} \frac{RT}{P} dP = RT \ln \frac{P_0}{P}
\]  

(3)

Where \( \varepsilon \) is the adsorption potential, J/mol; \( P \) is the equilibrium pressure, MPa; \( P_0 \) is the virtual saturated vapor pressure when temperature is \( T \), K; \( R \) is the universal gas constant, 8.3144 J/mol·K and \( T \) is the absolute temperature, K.

The saturated vapor pressure loses its physical significance for the supercritical condition and is just regarded as a parameter because the experimental temperature is higher than critical temperature of methane. This paper calculates virtual saturated vapor pressure using following Dubinin calculation formula [7]

\[
P_e = P_c \left[ \frac{T}{T_c} \right]^{2}
\]  

(4)

Where \( P_c \) is the critical pressure of methane, 4.62 MPa; \( T_c \) is the critical temperature of methane, 190.6 K. Then the calculated saturated vapor pressure is 11.68 MPa under conditions of 298 K temperature and pressure range from 0 to 12 MPa.

The adsorption potential can not reflect coal adsorbance but coal adsorption capacity on the view of thermodynamics. As different coal sample has different adsorbance, adsorption potential is calculated using same adsorbance (2.5 m³/t), the results can be seen in Table 2.
<table>
<thead>
<tr>
<th>Coal sample</th>
<th>$B$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry sample</td>
<td>0.26042</td>
<td>10.8464</td>
</tr>
<tr>
<td>Equilibrium moisture sample</td>
<td>0.477697</td>
<td>8.623737</td>
</tr>
<tr>
<td>8 MPa injection water sample</td>
<td>0.348532</td>
<td>9.984286</td>
</tr>
<tr>
<td>16 MPa injection water sample</td>
<td>0.384205</td>
<td>9.431831</td>
</tr>
<tr>
<td>20 MPa injection water sample</td>
<td>0.372538</td>
<td>10.48536</td>
</tr>
</tbody>
</table>

The results show that surface adsorption potential of dry sample is biggest and that of equilibrium moisture sample is smallest, which suggests that adsorption capacity of dry sample is highest and that of equilibrium moisture sample is lowest. However, adsorption capacity of water injection sample is higher than that of equilibrium moisture sample (Fig.1).

**Fig.1.** Surface adsorption potential of different coal sample

### 5. Analyses of intermolecular force of methane

Virial equation is always used in supercritical adsorption analysis[8-9], which describe the relationship between gas pressure and adsorption volume in the form of polynomial, so compressibility factor is expressed in form of pressure power series in virial equation

$$z = \frac{PV}{RT} = 1 + BP + CP^2 + \cdots$$

Where $B$ and $C$ depend on temperature and have nothing with pressure or density, and can be regarded as constant for the invariable experimental temperatures (298 K). Two-dimension virial equation can be deduced based on Gibbs equation

$$\ln V = RT(c_0 + c_1P + c_2P^2) + \ln P$$

Then the simplification virial adsorption isotherm equation is given

$$V = aP\exp(c_0 + c_1P + c_2P^2)$$

Where, $B = c_1/c_0$, $C = c_2/c_0$.

The significance of virial coefficient is the direct relationship with intermolecular force. For ideal gas, there are no forces between molecules. In fact, the intermolecular distance between gas molecules is so far that the gas is regarded as ideal gas. The intermolecular force is low under the condition of low gas density because the intermolecular force decreases with the increase of intermolecular distance. With the increase of gas density, the intermolecular distance decreases and the interaction increases which relates with virial coefficient. The physical significance of coefficient $B$, the second virial coefficient, is the deviation to ideal gas about the collision or interaction of two gas molecules. If adsorption capacity of coal is low, intermolecular distance of methane gas is small and interaction is big, then the second virial coefficient is big, which coincide with Langmuir volume of adsorption isotherm experiment.
The second virial coefficient can be calculated by fitting results of adsorption isotherm using Data Processing System. The results show in Table 2.

![Graph showing second virial coefficients of different coals](image)

Fig. 2. Second virial coefficients of different coal samples

The results show that (Fig.2), the second virial coefficient of equilibrium moisture sample is biggest and that of dry sample is smallest, because water content make coal adsorption capacity decrease and intermolecular force increases. The second virial coefficient of water injection sample is lower than that of equilibrium moisture sample; therefore adsorption volume of water injection sample are higher than those of equilibrium moisture sample.

6. Conclusions

1) Long range force of wetted coal matrix is lower than that of dry coal matrix, which proves adsorption capacity of water injection sample is lower than that of dry coal sample.

2) Surface adsorption potential of water injection sample is higher than that of equilibrium moisture sample but lower than that of dry sample, which proves adsorption capacity of water injection sample is higher than equilibrium moisture sample but lower than that of dry sample. It is suggest that adsorption capacity of wetted coal matrix is higher than that of dry coal matrix adsorbing gaseous water.

3) Second virial coefficient of water injection sample is lower than that of equilibrium moisture sample but higher than that of dry sample, which proves adsorption volume of water injection sample is higher than equilibrium moisture sample but lower than that of dry sample. It is suggest that water injection sample provide more effective adsorption site than equilibrium moisture sample.

In a word, surface adsorption potential, long range force and second virial coefficient are all prove the theoretical hypothesis on physical chemistry mechanism of liquid water influence coal methane adsorption: liquid water wets coal matrix and forms a monolayer water film, and methane absorbs on the surface of water film by the force from wetted coal matrix.

Acknowledgements

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