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Development and Current Situation of Study on Theory of Methane Adsorption on Coal

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Abstract

From aspects of the adsorption mechanism, adsorption experiment method and standards, application of adsorption isotherm method, the paper has summarized and appraised the theory research course and achievement of methane adsorption on coal at home and abroad and analyzed existing problems in China's coal reservoir adsorption theoretical research and experiment method. Finally the paper probed into the study of the development trend and problems need to be resolved.

Key words: coalbed methane; adsorption; mechanism; appraisal

1. Introduction

The study on the adsorption problem could be traced back as early as to 1800s, it was centralized in the chemical industry field, and the research results played the important roles in the aspects such as the purification, drying, separation, decolorization and catalysis, etc. The early study on the coal adsorption behavior was developed in order to resolve the mine gas outburst problem; started from the aspects of the mine safety and mine gas geology, a lot of experiment studies and application studies on gas adsorption-desorption properties of single component of dry coal sample were developed.

Beginning from 1970s, with the development of the exploration and development of the coalbed methane (CBM) resources, CBM is considered as a kind of resource, the importance about the

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understanding on the coal reservoir adsorption capacity is outstanding. In order to understand the storage regurality of the mine gas, the study on the coal adsorption theory is deepened further, and many results are obtained.

2. Mechanism of methane adsorption on coal

Coal is a kind of porous medium; it has the large internal surface area, so it has the capacity for gas adsorption. The adsorption refers to a kind of process in which the gas as the coagulating state or liquid-like state is contained by the porous medium, and the adsorption process could be divided into two types: physical adsorption and chemical adsorption. The acting force of the physical adsorption is the van de Waals force, of which, the most primary one is the dispersive power. The feature of the physical adsorption is that there has not the charge transfer between the adsorbate and adsorbent, without the generation and destruction of the chemical bond, and without the adomic rearrangement and so on. Compared with the chemical adsorption, the physical adsorption has the fast speed, low adsorption heat and could be desorbed. With regard to the coal isotherm adsorption features, a lot of research works were conducted at home and abroad[1] – [11]. Although about the features and mechanism of methane adsorption on coal there also have different understandings and recognizations, the common recognizations were discovered by the researches of Moffat and Weale (1985) [1], Yang and Saunders (1985) [2], the methane adsorption on coal belongs to the physical adsorption, its reason is that the adsorption heat of the methane is lower by 2 – 3 times than the vaporization heat, the adsorption of helium and hydrogen is like as the methane, and it indicates that the gas adsorption on coal has not the selective. A lot of the adsorption experiments of Daines (1968) [3], Mavor et al (1990) [4] proved that the coal adsorpting gas such as methane is fast and reversible. Therefore, it can use the physical adsorption model to approach the mechanism of gas adsorption on coal.

In the low-temperature infrared spectroscopy experiment of the interaction between methane gas and coal surface, Chen Changguo (1995)[5] had discovered that the interaction between methane gas and coal surface is anisotropy, when the methane appears as the normal triangular cone overlapping, the energy is the lowest, the interaction potential is the largest, and within the scope of –100 ~ 30℃ the existence of the chemical adsorption state had not been discovered. Based on the quantum chemistry calculation, Sun Peide (1998)[6] concluded that when the methane is adsorbed on the coal d002 face, the largest adsorption potential only is 2.65kJ/mol, and obviously, it belongs to the physical adsorption process, i.e., the surface coagulating. The diameter of the typic methane molecule is between 0.20 ~ 0.36nm. The functional analysis on the potential energy of the methane adsorption on coal revealed that in the place about 0.5nm apart from the coal pore surface the potential energy already trends to zero, i.e., the coal pore surface adsorpting methane is mainly the single-layer adsorption.

The coal isothermal adsorption test is conducted generally under the reservoir temperature, the coal reservoir temperature is largely in the scope of 10 ~ 50℃, this temperature is far higher than the critical temperature of the methane (–82.57℃), so it is not easy to happen the multiple-layer adsorption, and within the coal the occurrence form of methane is the gas. Coal is a kind of porous medium with more complicated pore structure and uncentralized pore diameter distribution, and it is impossible that the adsorption is happened only in the microporous structure with the particular pore diameter (Ailuni, 1992)[7], that is, the adsorption is not the process which is mainly the microporous infill. Therefore, the viewpoint that the methane isothermal adsorption on coal is the single molecule layer adsorption is recognized by many research persons. Gray (1987)[8], Mavor and Owen (1990)[4] considered that under the reservoir condition the adsorption of gas-phase medium on coal conforms to the Langmuir single molecule adsorption theory. Utilizing the Langmuir equation it can better describe the majority of the coal

isothermal adsorption processes, it can meet its requirements when it is used for engineering application [9], although it has a definite of error.

Applying the quantum chemistry calculation method MP2, Jiang Wenping (2007)[10] studied the action energy between the coal matrix with different metamorphic degree and methane molecule, it is discovered that with the increase of the coal matrix diameter, the action energy between the coal matrix and methane molecule also increase gradually; combined with the space physical property of the coal with different metamorphic degree, the isothermal adsorption results of different coals were explained from the microcosmic angle. In the evolution process of the coal, the buried depth of the coal is varied continuously, and it reflects that the reservoir temperature and pressure are a kind of the dynamic variation process. Combined with the coal seam buried history, geotemperature variation course, coal metamorphism course and gas-generating process and so on, how to reproduce the gas storage in coal seam and the reservoir features in current stage, it is a difficult problem existed in the study on the CBM-storage mechanism. Zhang Qingling (2008)[11] simulated the temperature and pressure corresponded to the coal reservoir with different depth, established the temperature-variable and pressure-variable adsorption experiment method of the coal. The variation features of the adsorption quantity of the coal with different coal ranks under the combined impact of the temperature and pressure are put forward, it is considered that the adsorption on coal in depth suffers the double action of the higher fluid pressure and higher suffered temperature, the impact on the coal adsorption quantity appears as the binary relation, and the increase or decrease of the adsorption quantity is different due to the different metamorphosed degree of the coal.

3 Method and standard of coal isothermal adsorption experiment

The coal isothermal adsorption experiment is the indispensable important component in the CBM test technique, its objective is mainly to determine the technical parameters such as the Langmuir volume, Langmuir pressure, isothermal adsorption curve and so on, and these parameters play the important roles in the CBM resource assessment and development. In the early period the test on methane adsorption on coal measured mainly the isothermal desorption line with the objective to simulate audio-visually the gas release process by the pressure reducing. With the deepening of the CBM exploration and development, it is recognized that the test condition should simulate the reservoir condition, i.e., the reservoir temperature, pressure and moisture and so on, lets the test results more conform to the real situations, and are more reliable. Because the reservoir temperature and pressure are knowable commonly, therefore, the main difficulty encountered in the isothermal adsorption test is the resume of the moisture in coal under the reservoir condition. The moisture has the very important impact on the coal adsorption process; the existence of the moisture can reduce the adsorption quantity of methane adsorption on coal. The water is the polar molecule, compared with the methane, it is even easier adsorbed by the coal, then it occupies the position of the methane. Especially, in the coal with low coal rank, the moisture is higher, and this phenomenon is more obvious. The studies of Joubert et al (1973, 1974)[12] discovered that when the coal does not attain to the critical moisture, the increase of the moisture lets the adsorption quantity of methane on coal is reduced, and after the critical moisture is exceeded, the adsorption quantity of methane is no longer reduced with the increase of the moisture. Based on the experiment about the impact of temperature, grain size and time on balanced moisture, Zhang Qingling (1999)[13] put forward the measure method of balanced moisture under the coal reservoir condition. And in 2008, the coal industry standard “Measure method of balanced moisture in isothermal adsorption test of coal” was drawn up [14].

At present, the better method describing the adsorption property is the volumetric method, and it also is the universally adopted method in CBM industry at home and abroad [15]. In recent years, the coal, petroleum and geology and mineral departments introduced successively the isothermal adsorption

apparatus from USA, but these apparatus all belong to the non-finalized products, the properties of various sets of apparatus themselves are differentiated, without the unified operation rule, and it is unfavorable for the exchange and management. Based on the system condition experiment and on the base of analyzing test results of lots of samples, Zhang Qingling et al (2004)[16] [17] conducted the overall study on various factors having the impacts on the measured results of isothermal adsorption tests of coal, and found out the optimal test conditions. In 1998 the technical specification (Industrial standard) of the isothermal adsorption test by high pressure volumetric method was put forward, in 2004 the "Isothermal adsorption test method of coal by high pressure volumetric method" (State standard) was drawn up, and in 2008 this state standard was revised [18]. In the standard, the grain size, balanced moisture, test temperature, pressure, balanced time, data processing all are stipulated in detail, lets the operations can obey the regulations, and the test results could be compared at home.

The isothermal adsorption curve of coal seam describes the adsorption capacity of methane gas on coal and the relation between adsorption quantity and pressure, it reflects the gas storage capacity of coal , and is the function of the coal chemical property, reservoir pressure, formation temperature, mineral matter in coal, moisture and coal-petrological component. Mavor (1990)[4] and Rice (1993)[19] indicated that the isothermal adsorption features of coal could be used to assess the gas-bearing saturation of coal reservoir, predict the gas content in coal seam, determine the critical desorption pressure of coal reservoir (Fig.2-1) and estimate the CBM recovery rate, and provide the needed parameters for the aspects such as the resource quantity calculation, reservoir simulation and productivity prediction, etc.

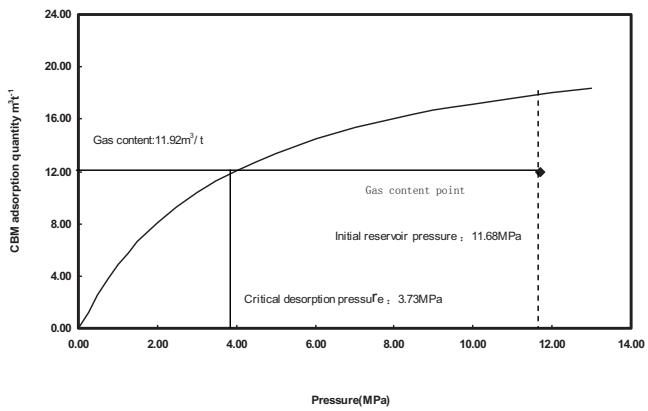

Fig.2-1 The schematic map showing the isothermal adsorption curve of coal and critical desorption pressure

Zhang Qing-ling (2004)[20] studied the adsorption features of the coals in main coal-forming periods, various coal ranks and with balanced moisture, and the variation regularities of their Langmuir volume and Langmuir pressure, analyzed the relationships among the Langmuir constants and the coal-petrological macerals, mineral matter content and porosity, and the inherent causes of the impacts of various factors on adsorption capacity of coal. It is considered that the impacts of the macerals on the adsorption capacity of coals with various coal ranks are differentiated, in the brown coal stage, the adsorption capacity of coal is increased with the increase of the inertinite content, and is reduced with the increase of the vitrinite content; in the long-flame coal stage, the relationship between the adsorption capacity of coal and the macerals is unobvious. In the gas coal, fat coal, coking coal, lean coal, meagre coal and anthracite III stages, the adsorption capacity of coal is reduced with the increase of the inertinite

vontent, and is increased with the increase of the vitrinite content. In the anthracite II stages, under the situations that the maceral content is identical, the adsorption capacity of coal is varied largely. With the increase of the ash yield, the Langmuir volume of the air-dry coal is reduced, and both appear as the negative correlation; with the increase of the vitrinite reflectivity, the porosity of coal is increase; with the increase of the porosity, the Langmuir volume is increased and the Langmuir pressure is reduced. Based on the Langmuir adsorption model, Ye Jianping and Qin Yong (1998) [21] assessed concretely the CBM adsorption features and regional distribution in our country.

4 The problems existed in theoretical research of methane adsorption on coal and the prospects

Although the related researches on the theory of methane adsorption on coal and the isothermal adsorption experiment already obtain many achievements, but the overall and systematic summaries on some problems are still insufficient. With respect to the current research on the theory of methane adsorption on coal in our country, several following problems still need to study thoroughly.

4.1 Multiple- component t adsorption

The CBM is dominated by the CH4, and companied with the combination gas of N2, CO2 and other hydrocarbon gases, although the quantity of these non-CH4 components is lesser, but they could produce the obvious impact on CBM adsorption and desorption behaviors. Therefore, utilizing the pure CH4 gas to measure the coal isothermal adsorption curve, the obtained coal adsorption-desorption properties cannot represent really the coal adsorption features under the reservoir condition [7]. If the CBM resource quantity is predicted and the productivity is assessed on this base, it will result in the wrong conclusions, and even mislead the investors. Under the condition that the multiple-component gas is existed, due to the different adsorption capacities of coal on various gases in the combination gas, it results in the mutual competition among the adsorption actions, various gas components in the multiple- component gas and the coal as adsorbent all happen the adsorption with different degrees, after that it has the impact on the overall adsorption quantity and the adsorption quantities of various components. Because in the multiple-component experiment from the beginning to end, the components of the combination gas in the free phase could occur the variation, thus, the test technique and data processing of the multiple-component adsorption experiment are relatively more complicated than the single component adsorption experiment [22]. Up to date, the adsorption features of the multiple- component gas have not conducted the thorough and systematic researches at home and abroad.

Therefore, based on the components and concentrations of CBM in different areas and different coal seams, to conduct the adsorption experiments of the multiple- component gas, then it can obtain the real and reliable properties of the coal reservoir [23]. At the same time, the CO2 sequestration technique [24] in coal seam also takes the multiple- component gas adsorption on coal as the base, therefore, the study on the adsorption of multiple- component gas has the important significances for recognizing the CBM storage mechanism, assessing the CBM development potential and effectively controlling the CO2 emission having the impact on the natural ecologic environment.

4.2 The volume of the adsorption phase

The volume of the adsorption phase refers to the methane volume in the adsorbed state in the isothermal adsorption experiment. In every balanced pressure point, when the adsorption quantity is calculated, one of the focal points with the larger divergence at home and abroad currently is whether the volume correction of the adsorption phase is needed or not. At present, the adopted correction equation is

advanced early by Sommen (1995) [25] , Moffat et al (1995) [26] . Rupple et al (1974) [27] discovered that after correction it cannot let the result more conform to the Langmuir isothermal line, especially, because the expression of the isothermal adsorption (Langmuir equation) is really drived from the absolute adsorption. Based on the data analysis of lots of isothermal adsorption experiments, and combined with the data such as the measured gas content and reservoir pressure, etc., in multiple CBM exploration wells, Zhang Qing-ling et al (2003) [28] considered that the isothermal adsorption experiment data without the correction of the adsorption phase volume more conform to the real situation, after correction the Langmuir volume and Langmuir pressure are increased by 30% - 40% than the uncorrected values, and seriously deviated from the true situations. It is considered that the adsorption phase volume only is the microphenomenon, is the volume occupied between the molecules, and it is insignificant compared with the macroscopic volume of the methane free gas. Therefore, in the isothermal adsorption experiment, if it conducts the artificial correction, it can result in the considerable error to the experiment result.

Because the current recognization on the adsorption phase is yet imperfect, although the adsorption phase is existed objectively, how mush volume is occupied by the adsorption phase methane, and how to calculate the methane density at every adsorption balance point are the problems waiting for discuss.

4.3 The adsorption mechanism of brown coal

The isothermal adsorption test of the coal samples indicated that the adsorption capacity of the brown coal is very low, and the matching degree of the isothermal adsorption line of the brown coal and the Langmuir equation is also low, therefore, it raises the even higher demands on the sensitivity and inspection limit of the adsorption experiment apparatus for the low rank coal sample. The low rank coal molecules are irregularly arranged, the structure is loosed, on the specific internal surface the carbon atom density is little, and there are many oxygen-bearing functional group and many adsorbed moisture, and the adsorption potential on gas is low, therefore, the capacity of its specific internal surface adsorpting gas is weak, and the Langmuir volume is on the low side overally. When the pressure is 8MPa, the adsorption quantity on methane is about 4cm^3/g generally, and it is obviously lower than the bituminous coal and anthracite [29]. With regard to the adsorption features of brown coal, it is only the description on the tested phenomena currently. With respect to the adsorption mechanism of the brown coal, it needs to conduct further the thorough study, to develop the study from the aspects such as the organic molecule structure, porous structure and adsorption dynamics and so on. On the bases of the tests and mechanism study, to establish the mathematical equation describing the isothermal adsorption line of the brown coal.

To sum up, the theoretical study and experiment method on the methane adsorption on coal have obtained the sufficient advance; however, the systematic expounding of the gas storage mechanism of the in-situ coal seam is faced with both the theoretical difficult problem and the practical problem. With the application of the new methods and new techniques, as well as the continuous advance of the CBM adsorption research, it will provide the more overall theoretical support for resolving the CBM storage and production mechanism, and promote further the CBM exploration and development course in our country.

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