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Study on the Controlling Factors of Shale Gas Adsorption

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Shale gas refers to the natural gas storing in shale formation (mainly dark mudstone, carbon-rich mudstone, or containing thin sand), which is typical "in-situ" reservoir (Zhang, 2003). Portion of shale gas store in intergranular pore and natural fractures as free state, others store on the surface of organic matter (kerogen) and minerals as adsorbed state (Ross and Bustin, 2009); the proportion of adsorbed gas is high, generally between 40% to 85% (Curtis, 2002; Mavor, 2003).The methane sorption capacity, affected by many factors such as temperature, pressure, moisture content, maturity, gas composition, etc, is one of the key parameters of shale gas reservoir evaluation. Therefore, studying on the controlling factors of shale gas adsorption/desorption and pore characteristics contribute to understand the microscopic pore structure of shale，storage capacity，it is also helpful to find the favorable area of shale gas exploration and has important significance on the late prediction of yield.

We get through a series of parallel experiments to reveal the effects of the factors of maturity, moisture content and gas composition on shale gas adsorption, also carrying on CO_2, N_2 adsorption isothermal experiment of shale,which use different theoretical models to reveal its pore structure and pore size distribution.

Studies suggest that:

(1) Methane sorption capacity of matured sample has greatly improved, and the higher degree of maturation, the stronger sorption capacity will be. At 120℃ under water equilibrium condition, Methane sorption capacity of matured sample to 500℃ is 2.58 times as primary sample (Fig.1a). Because the precess of maturing samples occur obvious hydrocarbon generation and expulsion, TOC of the sample result in lower, if we normalize the sample according to the content of organic carbon, methane sorption capacity of matured sample to 500℃ will be 5.98 times as primary sample (Fig.1b).

(2) The experiment of shale CO_2 adsorption isothermal is useful for characterizing microporosity (<2nm), while N_2 adsorption isothermal use to reveal pore size distribution of meso- and macro-porosity (2nm-100nm). CO_2 adsorption data were interpreted using Dubinin-Astakhov model analysis for pore size distribution ,we can realise that the distribution of miscroporosity become more centralized and uniform in the process of thermal evolution of organic, with a large number of microporosity generation (Fig.2). N_2 adsorption data were generally interpreted using Barrett–Joyner–Halenda (BJH) , Density function theory (DFT), HK and SF methods analysis for pore size distributions, while （NL）DFT method have high calculate precision involving more complex algorithm; BJH method can reach requirement of the precision on the analysis of mesoporosity and involves simple algorithm (Jin, 2001), It is worth noting that if we choose the desorption branch to interpreted, the influences of tensile strength effect, adsorbate phase transition and pore structure may lead a false peak at about 3.8nm (Groen, 2003). The adsorption branch interpreted using BJH method and DFT method substantially exhibited the same pore size distribution characteristics, so choosing the adsorption branch to interpret is more suitable (Fig.3).

(3) Different humidity shale adsorption experiments show that methane sorption capacity of shale affected by moisture. with increasing of moisture content, the sorption capacity decline, which may be due to water-filled pore throats, water molecular l molecules occupying the surface of clay minerals and kerogen ,then adsorption sites decline and thereby reduce the gas adsorption capacity (Krooss et al., 2002; Tian et al., 2007；Ross and Bustin, 2007, 2009)。

(4) Temperature and pressure are important factors of impacting the shale adsorption capacity, shale adsorption curve showed that with increasing pressure, the adsorption capacity increases until it reaches saturation; temperature rise is not conducive to gas adsorption, due to the physical

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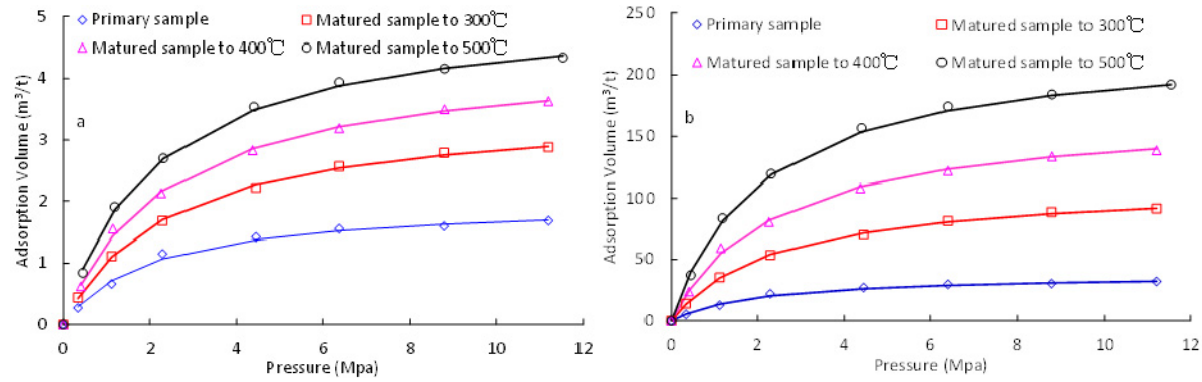

Fig.1. Isothermal adsorption curves and simulation of Langmuir model per unit mass of rock (a) and total organic carbon (b).

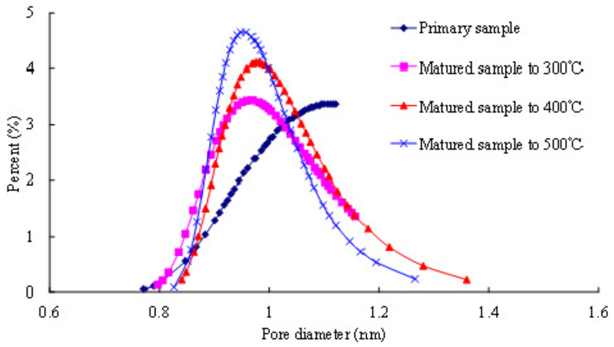

Fig.2. CO_2 adsorption experiments showing the diameter distribution of micropores based on Dubinin-Astakhov equation.

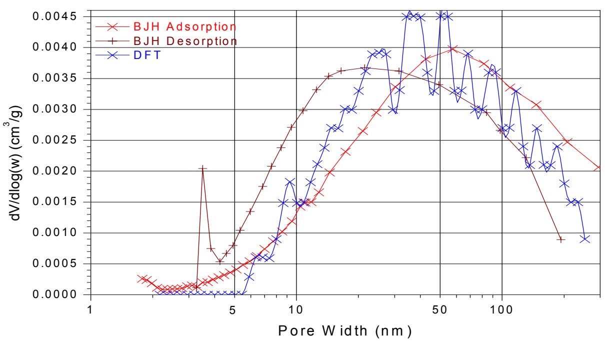

Fig.3. pore size distributions of sample using BJH and DFT methods analysis for N_2 adsorption data.

adsorption is exothermic and the higher temperature increases the thermal motion of gas molecules,which is unfavorable for adsorption(Ross and Bustin, 2009). Under geological conditions, temperature and pressure gradually increase with depth deepening, they play opposite effect on shale gas adsorption. Just to consider the impact of temperature and pressure using adsorption potential model for geological application discovery that methane sorption capacity exhibits increasing at first then decreasing, and the free gas increases constantly but gradually trend to be slow down.

(5) In addition to methane, shale gas also contains small amount of heavy hydrocarbons (C_2-C_6) and non-hydrocarbon gases (CO_2, N_2), while the presence of these gases inevitably occur competitive adsorption, therefore, the gas component will affect the total amount of adsorbed gas. Recent studies on different gas sorption capacity of coal show that each gas component adsorption capacity and adsorption rate is: CO_2>CH_4>N_2>H_2, but shale adsorption experiments show that CO_2>N_2> CH_4, probally due to organic carbon of shale is less then coal.Therefore CO_2 can be injected to improve shale gas recovery during shale exploitation.

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