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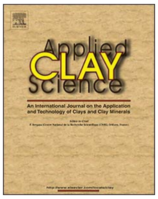

Research Paper

Water adsorption and its impact on the pore structure characteristics of shale clay

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ABSTRACT

Water is considered ubiquitous within the shale reservoirs and mainly stored in the hydrophilic clay minerals. The water distribution characteristics and its effect on pore structure are important for the gas-in-place of shale systems. In this work, water vapor adsorption on montmorillonite (Mt), kaolinite (Kaol) and illite (Il) were performed to investigate the behaviors of water adsorption on shale clay. Subsequently, the moisture-equilibrated samples were conducted with N_2 gas-adsorption techniques to investigate the effect of adsorbed water on pore structure characteristics, such as apparent pore size distribution (APSD), N_2 BET specific surface area (N_2-BET SSA) and pore volume (PV). The results show that the water uptake isotherms of our samples have the sigmoidal-shaped profiles and GAB model provides a good fit for the adsorption behavior. In addition, The APSD curves under different relative humidity (RH) conditions have validated the condensation effect and indicated that the small pores (approximately smaller than 5 nm) are blocked by the capillary water and will disappear on the APSD curves at RH of 98% while the large nanopores ($>$ 5 nm) are covered with water film, these effects will lead dramatically decrease of N_2-BET SSA. Taking Mt and Il samples as the examples, the N_2-BET SSA has declined to 33.51% and 33.66% compared with the dry conditions when S_w approaches to 50%. Meanwhile, these effects also indicate that the gas storage for clay minerals is massively overestimating under dry condition, the contribution to methane adsorption might be negligible in the actual shale reservoir.

1. Introduction

Shale gas, which is derived from thermogenesis or biogenesis during the thermal evolution process of kerogen, has attracted numerous attentions of individuals and companies in recent decades (Curtis, 2002; Chalmers and Bustin, 2008; Liu et al., 2013). Unlike conventional gas, the adsorption phase is one of the most important occurrences of shale gas, the proportion ranges from 20% to 85% (Curtis, 2002; Jarvie, 2012). Clay minerals, like montmorillonite (Mt), kaolinite (Kaol) and illite (Il), are widely distributed in shale reservoirs and play an important role in gas storage and gas transport dynamics (Merkel et al., 2015, 2016; Sun et al., 2017a, 2017b; Wu et al., 2015, 2016, 2017b). The pore structure information (apparent pore size distribution (APSD), pore volume (PV), specific surface area (SSA)) of dry clay samples have been extensively investigated with the N_2 sorption in published literatures, which have demonstrated that the abundance of nanopores result in large surface area and provide many adsorption sites for methane molecules second only to the kerogen (Ross and Bustin, 2009; Ji et al., 2012; Liu et al., 2013). However, water is considered omnipresent in shale formation and mainly stored in the clay minerals due to the stronger hydrophilicity than organic matter (Jarvie, 2012; Dehghanpour et al., 2012, 2013; Merkel et al., 2015; Li et al., 2016). Therefore, the water distribution characteristics and pore structure information under moist conditions are essential for estimating the contribution of clay minerals to gas storage, gas transport and production dynamics, but the correlational studies are rarely reported in published works.

In general, the water distribution and interaction of sorption system can be investigated with the water vapor adsorption isotherms, which describe the relationship between adsorbed water content and equilibrium relative humidity at a constant temperature (Do, 1998; Hatch et al., 2012). Tandanand (1985) used the water adsoption isotherms to investigate the mechanical strength degradation of shale, Wen et al. (2015) measured the water adsorption isotherms of shale to analyze the

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relationship between mineralogical composition and water activity. Nevertheless, the occurrence of functional groups in kerogen pores has a significant effect on water adsoption behaviors, which are not entirely consistent with the pure clay minerals (Gasparik et al., 2012, Gasparik et al., 2014). Meanwhile, the water uptake on other porous media (e.g., coal, cement paste and food) have been widely investigated and many isotherm models are proposed to describe the adsorption process in both theoretical and empirical way (Oswin, 2010; Halsey, 1948; Henderson, 1952; De Boer, 1953; Chung and Pfost, 1967; Do, 1998; Chirife and Iglesias, 2010; Hatch et al., 2012). However, there are few descriptions about water adsorption isotherms on pure clay minerals.

On the other aspect, clay minerals are the important components to shale gas reservoir space, especially at the low-mature stage of shale reservoirs containing a low content of organic matter, their pore structures have been widely characterized with N_2 gas sorption and ultra-/small angle neutron scattering (Ross and Bustin, 2009; Loucks et al., 2012; Wang et al., 2016). Liu et al. (2013) meausred the N_2 SSA of clay minerals (Mt, Kaol and Il) with the BET (Brunauer–-Emmett–Teller) method, the results indicated that the value ranges from 11.2 to 56.5m^2/g, and the methane adsorption capacity is 2.22 cm^3/g–6.01 cm^3/g; Ji et al. (2012) obtained the pore size information with the BJH (Barrett-Joyner-Halenda) method and demonstrated that shale clay is rich of micro and nano-size pores ranging from several to dozens of nanometers. Tang and Fan (2014) proposed that the contribution of clay minerals accounts for 44.12% of total adsorbed gas in Longmaxi shale of China. However, the experiments mentioned above are all conducted under dry condition. Generally, it has been widely reported that moisture has negative effect on methane adsorption of clay and shale samples (Ross and Bustin, 2009; Zhang et al., 2012; Gasparik et al., 2012, 2014; Merkel et al., 2015, 2016). The results from Ross and Bustin (2009) showed that the CH_4 adsorption capacity of moisture-equilibrated clay (Mt: 0.6 cm^3/g; Il: 0.4 cm^3/g) is far lower than that in dry condition (Mt: 2.9cm^3/g; Il: 2.1 cm^3/g). As for the shale samples, the methane adsorption capacity of Bossier shale and Haynesville shale could decrease by 78% and 68% at RH of 50–75%, the decreasing amplitude for clay-rich shales is more serious than organic-rich one (Merkel et al., 2015, 2016), the main reason for this phenomenon is the abundance of clay minerals, which have strong affinity to water molecules and result in more complicated interaction for methane adsorption (Chen et al., 2016; Pozo et al., 2017). Actually, the comparison of pore structure between dry condition and moist conditions may give a mechanism explanation for this phenomenon because the pore structure controls the gas storage mechanism and gas transport behaviors.

In this paper, the aim of our study is (1) to measure the water adsorption isotherms of commom shale clays (Mt, Kaol and Il) and to select an appropriate adsorption model to describe the adsorption process, (2) to analyze the water distribution characteristics by comparing the pore size distribution between dry and moist conditions, (3) to analyze the role of adsorbed water on pore structure characteristics and give a mechanism interpretation for the effect on methane adsorption of clay and shale.

2. Experiment and method

2.1. Samples characterization

In our work, the purified Mt, kaol and Il were obtained with the method of filtrating followed by the repeated separation and sedimentation from the clay-rich rocks, which were sourced from Yanchang mines in Ordos Basin of China. The XRF measurements were conducted on XRF-1800 with Rh K alpha radiation using a max voltage of 60 kV and max current of 150 mA, the measured chemical compositions on samples are showed in Table 1, the results show that the Mt in our work is apparently rich in magnesium, which may have influence on the water adsorption process (Cases et al., 1997). Heating treatment of samples were performed in a temperature-controlled oven at 200 °C for 48 h following the standard procedure; at this temperature, all the moisture (free water, loose bound water and strong bound water) could be removed without fearing the irreversible damage to clay structure (Wang and Li, 2006; Środoń and Macarty, 2008; Kuila and Prasad, 2013; Li et al., 2016), the lost moisture content of Mt, kaol and Il is 15.28%, 3.60% and 1.60%, respectively. The measured specific gravity of samples is 2.65 g/cm^3, 2.61 g/cm^3 and 2.72 g/cm^3.

After the drying process, the XRD measurements of samples were conducted on Bruker D8 Advance diffractometer using CuKα radiation ($\lambda = 0.154$ nm), the scan rate was 1°(2θ)/min with each step of 0.02°(2θ). As shown in Fig. 1, the XRD patterns of clay samples show the main phases of the highly ordered crystalline of Mt, Kaol and Il. The reflections appearing at approximately 6.04°, 12.42° and 9.10°(2θ) are attributed to the (001) characteristic diffraction reflection of Mt, kaol and Il; the corresponding d_{001} value obtained with the Bragg equation ($2d\sin\theta = \lambda$) is 1.462 nm, 0.712 nm and 0.971 nm, respectively. Meanwhile, quartz impurity are found in all clay minerals and the reflection appears at approximately 22° or 27°(2θ); besides, the weak reflection at approx. 30°(2θ) in Kaol is attributed to the very few calcite impurity. Furthermore, the interlayer distances of Mt and Il can be estimated by subtracting the thickness of structural TOT layer unit (0.96 nm) from the basal spacing (d_{001} value), yielding value of 0.502 nm and 0.011 nm, respectively; while 0.012 nm for Kaol by subtracting the thickness of the structural TO layer unit (0.71 nm). Therefore, the interlayer distance of Kaol and Il are negligible. Of cource, this interlayer space is not a constant value, especially for the Mt minerals, which will extend as the moisture (relative humidity) increases (Liu et al., 2013; Hyun and Hayes, 2015; Deng et al., 2017).

Meanwhile, the SEM images were taken with field emission scanning electron microscope (FESEM) to characterize the micro-structure of clay samples. Before the experiments, spraying gold and vacuum treatment are necessary, in such condition, the adsorbed gas and moisture will be evacuated. The SEM images are a good indication of micro-morphology and the enrichment degree of nanopores. Fig. 2(A, C, E) demonstrate the clay particles are highly variable in shape and size, the Mt (Fig. 2A) and Kaol (Fig. 2C) samples display granular shape while Il (Fig. 2E) presents a flake morphology; the SEM images also show that all three clays have average particle size diameters > 1 μm. Fig. 2(B, D, F) demonstrate the smaller microstructure of clay minerals, they show that the laminated structure of Il (Fig. 2F) aligns more tightly, indicating less micro-mesopores; the basal layer structure of Mt (Fig. 2B) is adhered with much smaller debris, resulting in the richer of nanopores.

2.2. Water uptake measurements at controlled relative humidity

After the drying process, 10 g clay samples were picked to obtain the water adsorption isotherms. In order to achieve the moisture equilibrium, clay samples were placed in a sealed vessel with the saturated salt solutions at 298 K to establish a defined relative humidity, the RH% was as following: ZnCl for 10%, CH_3COOK for 23%, $MgCl_2$ for 32%, K_2CO_3 for 44%, $MnCl_2$ for 56%, NH_4NO_3 for 67%, NaCl for 75%, KCl for 85%, KNO_3 for 94%, K_2SO_4 for 98% (Li et al., 2016; Zolfaghari et al., 2017a, 2017b). Water adsorption experiments lasted for 72 h to ensure the clay minerals equilibrated adequately. During this period, the amount of pre-adsorbed water was measured at regular intervals with a high precision balance (FA2204B). The moisture M% (in wt%) was calculated as following:

$$M = \frac{m_{moist} - m_{dry}}{m_{dry}} \tag{1}$$

where M% is the water content adsorbed in clay minerals; m_{moist} is the weight of moist samples, g; m_{dry} is the weight of dry samples, g.