



Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Research papers

The effect of moisture on the methane adsorption capacity of shales: A study case in the eastern Qaidam Basin in China

Lu Wang, Qingchun Yu *

School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 10083, China

ARTICLE INFO

Article history:

Received 27 January 2016

Received in revised form 19 August 2016

Accepted 6 September 2016

Available online xxxxx

This manuscript was handled by L. Charlet, Editor-in-Chief, with the assistance of Fereidoun Rezanezhad, Associate Editor

Keywords:

Methane adsorption

Moisture

Shale

Qaidam Basin

ABSTRACT

This study investigated the effects of moisture on high-pressure methane adsorption in carboniferous shales from the Qaidam Basin, China. The shale characteristics, including the organic/inorganic compositions and pore structure (volume and surface) distribution, were obtained using various techniques. Gibbs adsorption measurements were performed over a pressure range up to 6 MPa and temperatures of 308.15 K on dry samples and moisture-equilibrated samples to analyze the correlations between organic/inorganic matter, pore structure, and moisture content on the methane sorption capacity.

Compared to dry samples, the sorption capacity of wet samples (0.44–2.52% of water content) is reduced from $19.7 \pm 5.3\%$ to $36.1 \pm 6.1\%$. Langmuir fitting is conducted to investigate moisture-dependent variations of adsorbed methane density, Langmuir pressure, and volume. By combining the pore volume and surface distribution analyses, our observations suggested that the main competition sites for $\text{CH}_4\text{-H}_2\text{O}$ covered pores of approximately 2–7 nm, whereas the effective sites for methane and water were predominantly distributed within smaller (<4 nm) and larger pores (>10 nm), respectively. Regarding the compositional correlations, the impact of moisture on the amount of adsorbed methane shows a roughly linearly decreasing trend with increasing TOC content ranging from 0.62 to 2.88%, whereas the correlation between the moisture effect and various inorganic components is more complicated. Further fitting results indicate that illite/smectite mixed formations are closely related to the methane capacity, whereas the illite content show an evident connection to the pore structural (volume and surface) variations in the presence of moisture.

© 2016 Published by Elsevier B.V.

1. Introduction

The gas storage capacity of shale, an uncontroversial reservoir rock, is largely influenced by its compositional and structural characteristics (Bruant et al., 2002; Lu et al., 1995; Chalmers and Bustin, 2007). With regard to composition, organic matter (for example, bitumen and remaining kerogen) has traditionally been suggested to play a critical role in gas generation and storage because of the large internal surface area. (Gan et al., 1972; Beamish and Crosdale, 1995; Zhang et al., 2012). One interesting issue addressed in an investigation of the organic matter was the controversial finding of porosity during the thermal pyrolysis process. Jarvie (1991) and Modica and Lapiere (2012) confirmed the presence of porosity resulting from the thermal maturation of kerogen, while Milliken et al. (2013) stated that there seems to be no general correlation between thermal maturity and the abundance of pores in organic matter. Since total organic content (TOC) played a first order role

in the adsorptive capacity for methane, classifying the generation of the potential effective sites within interleaved organic matter is a critical issue during research for interactions of shale and CH_4 .

Zhang et al. (2012) proposed that physical sorption is a dominant process in CH_4 sorption in both organic-rich shales and clay minerals. The authors found that the Brunauer-Emmett-Teller (BET) surface area of the investigated samples was linearly correlated with the CH_4 sorption capacity regardless of the sample composition. However, fewer studies have examined the adsorption of methane and other hydrocarbon gases on clays because mineral matter is conventionally believed to be essentially non-adsorptive for methane (Crosdale et al., 1998). In fact, clay minerals were found to strongly affect CH_4 adsorption in clay-rich rocks (Wang et al., 2004). These authors determined that clay minerals can adsorb gas into their internal structures and that the amount of gas that is adsorbed depends on the clay type. This may be because that inorganic material influences the pore size, total porosity, and sorption characteristics of shales (Ross and Bustin, 2008). The experimental results of Ji et al. (2012) further demonstrated that under experimental conditions, the clay mineral type

* Corresponding author.

E-mail address: yuqch@cugb.edu.cn (Q. Yu).

affects the CH₄ sorption capacity in the following order: montmorillonite > illite/smectite mixed layer > kaolinite > chlorite > illite.

In terms of pore structure, the extremely low porosity and poor connectivity of the pore network strongly promotes pore characteristics as the key role of in gas sorption and transport. In an attempt to better understand the pore shape and scale, [Curtis et al. \(2010\)](#) introduced focused ion beam/scanning electron microscopy (FIB/SEM) technology, which enabled the imaging of these nano scale pore structures in three dimensions (3D). In their work, three different shale samples (125 μm) were imaged, and the pore systems were computationally reconstructed. [Klaver et al. \(2015\)](#) tested four Haynesville Shale and four Bossier Shale samples using a combination of Scanning Electron Microscopy (SEM) and Broad Ion Beam (BIB) polishing. The relative roles of the TOC, thermal maturity, mineralogy and grain size on the porosity were discussed based on these tests, and the authors found that the pore morphology and porosity were related to the composition of the shales. Thus, the evidence was proposed for the statement that increasing TOC and maturity linearly increased the porosity, whereas the effects of mineral components were less obvious.

However, SEM-based studies are limited when the distribution of pores of less than 50 nm needs to be quantified, as SEM fails to provide an accurate description for pores of this size range. However, growing emphasis has been placed on the distribution of pores within this diameter range (<50 nm) due to the recognition that micro-pores and meso-pores play essential roles in gas storage ([Mosher et al., 2013](#)). To draw a comprehensive picture of the pore size distribution in shales, researchers have utilized low-pressure N₂ sorption and Hg porosimetry as reliable methods to elucidate the complex pore volume and surface distributions of meso-pores and macro-pores ([Katsube and Williamson, 1994](#); [Strapoc et al., 2010](#); [Clarkson et al., 2013](#)). For micro-pores, carbon dioxide sorption was later determined to be more accessible as a measurement ([Clarkson et al., 2012](#)). However, although the pore structure was well analyzed, their geometric (shape and size) contribution to methane adsorption still calls for intensive studies.

Furthermore, water plays a synthetic role in methane adsorption in shales. Although broad, detailed studies have stressed the impact of moisture on methane adsorption in clay and coal ([Krooss et al., 2002](#); [Clarkson and Bustin, 2000](#); [Crosdale et al., 2008](#)), only a limited number of studies have debated how moisture in shales influences methane adsorption. [Hatch et al. \(2012\)](#) determined the water adsorption capabilities of kaolinite, illite, and montmorillonite clays as a function of relative humidity (RH) at room temperature (298 K) using horizontal attenuated total reflectance (HATR) Fourier transform infrared (FTIR) spectroscopy with a flow cell. These authors treated the water content as a function of RH and found that Freundlich adsorption isotherm models could provide complementary multilayer adsorption analyses of the water uptake in clays. They also found that the water contents of illite and montmorillonite are similar and approximately 3 times larger than that of kaolinite. As confirmed by multilayer adsorption, the moisture content is negatively correlated with the methane capacity of clays. On the other aspect, the adsorbed water-organic matter interaction influences the methane adsorption. Conventional wisdom has stated that water molecules reduce the volume of sorption sites for methane ([Joubert et al., 1974](#); [Levy et al., 1997](#)). Controversially, experiments have examined the effects of moisture on methane adsorption on cretaceous gas shales, demonstrating a general increase in gas sorption with the total organic carbon (TOC) content in high-pressure CH₄ isotherms for dried and moisture-equilibrated shales ([Chalmers and Bustin, 2008](#)); additionally, moisture has been suggested to act as a diluent for gas sorption ([Yee et al., 1993](#)). Actually, the effects of moisture cannot be easily isolated ([Ross and Bustin, 2008](#)). [Hu et al. \(2014\)](#) performed simulations to demonstrate that with oxygenated

functionalized groups within the kerogen body, water molecules favorably stay inside the pore because of surface activation. However, higher maturity also leads to a loss of functional groups, making the previously mentioned correlation valid for only immature to early mature organic matter. Experimental measurements have clearly suggested that only adsorbed water affects the equilibrium capacity of a coal for methane; excessive water has no effect on methane sorption ([Joubert et al., 1974](#)). Comparably, evidence of the moisture behavioral impact on methane around inorganic matters is sparse, with most of the literature focusing on the moisture-clay interaction. In particular, discussions about the relevant effects on methane are very limited. [Jin and Firoozabadi \(2013\)](#) performed a series of simulations to suggest that methane sorption in dry clay nano-pores is dominated by surface adsorption. When water is added, however, water molecules have a strong affinity to clay surface atoms due to their strong dipole moment, which reduces methane adsorption accordingly. However, those authors suggested that the effect depends on the pore structure. In small pores (1 nm), water, CO₂, and methane adsorb in the same layer. In large pores (>2 nm), water molecules adsorb onto the first layer, whereas CO₂ and methane adsorb weakly onto the second layer. However, that pore system analysis was completed in shales with mixed organic/inorganic components, making it nearly impossible to draw conclusions from the coal and clay samples directly to explain the effects of moisture on the methane adsorption capacity of shales.

For a better understanding of organic/inorganic composition and moisture effect on shale pore structure alternation and methane capacity, in this work, shales samples from the Qaidam Basin in China were investigated for their pore characteristics and methane adsorption capacities under dry and wet conditions, respectively. Primarily, the types and content of organic and inorganic matter were analyzed using rock pyrolysis, fluorescence microscopy, and X-ray diffraction (XRD). The distributions of the pore volume and surface area were obtained for pores ranging in size from 0 to 200 μm using mercury intrusion and the N₂ and CO₂ adsorption methods, and increasing pore size variations were observed in macro-pores when influenced by moisture. The methane adsorption capacities were measured using a manometric analytical method, and a Langmuir fitting model was established to analyze the optimized parameters (adsorbed density, Langmuir pressure, and volume). Interestingly, the adsorbed methane density distinctively decreased in the presence of water. Further comparisons of the isotherms suggested that CH₄-H₂O interactions mainly occurred in pores that were smaller than 7 nm and differed in terms of their organic and inorganic composition. The ambiguity of the role that water plays in hydrocarbon generation and storage drives our efforts toward a better understanding of the influence of moisture on shale pores and the corresponding methane adsorption capacities.

2. Methodology

2.1. Samples and geological setting

The investigated shale samples were extracted from the Carboniferous Keluke Group Formation in the eastern Qaidam Basin, China. The basin is located in western China and is rich in natural resources such as mineral deposits, oil and coal ([Li et al., 2015](#)). The study area underwent transgression and accepted extensively coaly continental-littoral deposits. These deposits date to the Carboniferous Period and are exposed in regional mountains at a depth of 280–2500 m. [Fig. 1](#) shows the lithology log for the 900–1050 m range of the drilling strata; the samples extracted from the Chaie-2 core-drilling well in the Shihuigou region are

Download English Version:

<https://daneshyari.com/en/article/6409276>

Download Persian Version:

<https://daneshyari.com/article/6409276>

[Daneshyari.com](https://daneshyari.com)