



Investigations on the methane sorption capacity of marine shales from Sichuan Basin, China



Feng Yang^{a,b,c,*}, Zhengfu Ning^{a,b}, Rui Zhang^{a,b}, Huawei Zhao^{a,b}, Bernhard M. Krooss^c

^a State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum (Beijing), #18, Fuxue Rd, Changping, Beijing 102249, PR China

^b Ministry of Education Key Laboratory of Petroleum Engineering, China University of Petroleum (Beijing), #18, Fuxue Rd, Changping, Beijing 102249, PR China

^c Energy and Mineral Resources Group (EMR), Institute of Geology and Geochemistry of Petroleum and Coal, Lochnerstr. 4-20, RWTH Aachen University, 52056 Aachen, Germany

ARTICLE INFO

Article history:

Received 5 February 2015

Received in revised form 22 May 2015

Accepted 22 May 2015

Available online 28 May 2015

Keywords:

Shale gas

Sorption isotherm

Sorption capacity

Langmuir

Marine shale

ABSTRACT

High-pressure methane sorption isotherms measured at 30, 50 and 80 °C and pressure up to 20 MPa were measured on Lower Silurian marine shales from Sichuan Basin of China. The effect of total organic carbon content, temperature, thermal maturity, mineral composition, and pore structure on methane sorption capacity has been investigated. A linear combination approach has been developed to predict the Langmuir sorption capacity of shales based on the mass fractions of their organic and inorganic components. This information can be used to estimate the in situ sorption capacity of shale layers as a function of burial depth (formation pressure and temperature), and composition.

Methane sorption capacity of the dry shales shows a positive relationship with TOC and specific surface area. The Langmuir pressure decreases with increasing maturity, but the TOC-normalized Langmuir sorption capacity of over-mature shales also decreases with increasing thermal maturity. This may be related to the carbonization of highly over-mature organic matter. For the samples investigated, approximately 16.3%–46.7% (average 28.6%) of the methane sorption can be attributed to clay minerals and 46.5%–81.5% to (average 67.6%) organic matter in these shales, respectively. Using the linear combination approach, the calculated Langmuir sorption capacity function matches the measured values reasonably. Methane sorption capacity computed as a function of depth (for a mean hydrostatic pressure gradient of 0.01 MPa/m and a geothermal gradient of 0.03 °C /m) shows a rapid increase and reaches a maximum between 900 and 1800 m followed by a slow decrease with increasing depth. At shallow burial depths (<900–1800 m), the sorption capacity is controlled by the combination of hydrostatic pressure and geothermal gradients. At deeper burial (>900–1800 m) sorption capacity is controlled by the geothermal gradient. Higher geothermal gradients result in a steeper decline of sorption capacity.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Increasing demand, depletion of conventional hydrocarbon resources, increasing energy prices and new technological developments have led to a rapid development of exploration and production of unconventional gas resources such as tight gas, coalbed methane and shale gas in North America during recent years. Shale gas reservoirs are characterized as self-contained source–reservoir systems, with hydrocarbon gases dominated by methane derived from organic matter through biogenic and/or thermogenic processes (Krooss et al., 1995). Shale gas is stored as (1) adsorbed gas in organic matter and inorganic minerals, (2) free gas in pores and fractures, and (3) possibly dissolved gas in oil and water (Curtis, 2002; Zhang et al., 2012). The amount of free gas is associated with the porosity of shales, and the contribution of adsorbed gas to total gas capacity varies from 20% to 85% in some U.S. shale basins (Curtis, 2002; Montgomery et al., 2005).

Because physical adsorption contributes significantly to the gas storage capacity of shales, knowledge of gas sorption capacity is important for the accurate prediction of maximum gas in place quantities in shale gas reservoirs. Previous studies have shown that the sorption capacity of shales is influenced by total organic carbon (TOC) content, thermal maturity, organic matter type and pore structure (Chalmers and Bustin, 2007a, 2008; Gasparik et al., 2012, 2014; Rexer et al., 2014; Ross and Bustin, 2007, 2009; Wang et al., 2013; Zhang et al., 2012). Recent publications using advanced techniques such as field emission scanning electron microscopy (FESEM), small-angle neutron scattering and low pressure gas adsorption have revealed the complexity pore structure in shales, comprising micropores (diameter < 2 nm), mesopores (2 nm ≤ diameter ≤ 50 nm) and macropores (diameter > 50 nm) (Bernard et al., 2012; Bustin et al., 2008; Clarkson et al., 2013; Loucks et al., 2009; Milliken et al., 2013; Yang et al., 2013, 2014). Gas is adsorbed in micropores owing to large specific surface area and great adsorption potential in narrow pores. Several authors have found a positive relation between TOC, micropore volume and sorption capacity of shales, and concluded that microporosity associated

* Corresponding author.

E-mail address: feng.yang@emr.rwth-aachen.de (F. Yang).

with organic matter was the main control on methane sorption (Chalmers and Bustin, 2007a, 2008; Gasparik et al., 2014; Hu et al., 2015; Ross and Bustin, 2007, 2009). Organic nanopores develop during the thermal maturation of organic matter (Jarvie et al., 2007; Loucks et al., 2009). With increasing thermal maturity, TOC-normalized methane sorption capacity in organic-rich shales was observed to increase as a result of creation of organic microporosity (Ross and Bustin, 2009; Zhang et al., 2012). However, this trend may be reversed at very high maturities (Gasparik et al., 2014; Zhang et al., 2012). At the same time, there seems to be no general correlation between thermal maturity and organic matter-hosted porosity, and the absence of organic matter-hosted porosity in shales in the gas window has been observed (probably attribute to the limited resolution of SEM) (Curtis et al., 2012; Loucks et al., 2012; Milliken et al., 2013). The type of organic matter also plays a role in the sorption capacity of shales (Chalmers and Bustin, 2008; Zhang et al., 2012). The sorption capacity of type III kerogen has been shown to be higher than that of type II and type I kerogens and this was attributed to the higher sorption capacity of microporous vitrinite compared to other maceral types (Chalmers and Bustin, 2007b; Clarkson and Bustin, 1996). Furthermore, Zhang et al. (2012) suggest that the chemical structure of organic matter plays an important role in methane adsorption, and type III kerogen rich in aromatic structural units has a stronger affinity for methane than type II and type I kerogens, which contain more aliphatic organic matter. Besides, the clay minerals do contribute to the sorption capacity (Gasparik et al., 2012; Ji et al., 2012; Rexer et al., 2014). The specific surface areas of clay minerals, especially montmorillonite, are much higher than quartz. Ji et al. (2012) have found that the sorption capacity of clay minerals decreases in the order: montmorillonite > I-S mix-layer > kaolinite > chlorite > illite. However, the affinity of CH₄ to organic matter is stronger than to clay minerals. Zhang et al. (2013) have found that the heats of sorption for methane on clay minerals are considerably smaller than those on kerogen. In addition, sorption capacity of shales may be reduced significantly when moisture is present (Ross and Bustin, 2007). The sorption capacity of shales and coals decreases with increasing moisture content until a “critical moisture” content is reached. Once this “critical moisture” content is exceeded, the gas sorption capacity remains constant (Busch and Gensterblum, 2011; Day et al., 2008; Levy et al., 1997). Moisture is thought to preferentially occupy the polar sites, such as hydroxyl groups, on the coal surface and thus reduce the gas sorption capacity by physical displacement (Day et al., 2008), but blocking of microporosity and restricting access of methane to active sorption sites were also suggested (Chalmers and Bustin, 2007a; Ross and Bustin, 2009).

Since shale is a heterogeneous mixture of organic and inorganic matters, gas sorption on shales is complex. Published sorption data on shales are mainly limited to North American shales. Gas sorption experiments on European shales have been carried out recently (Gasparik et al., 2012, 2014; Rexer et al., 2013, 2014). China has abundant shale gas resources in several prospective basins: Sichuan, Tarim, Junggar, Songliao, the Yangtze Platform, Jiangnan and Subei. Technically recoverable shale gas resources in marine shales of the Sichuan Basin are estimated to amount to 626 Tcf, thus constituting half of China's total shale gas resources (1115 Tcf) (E.I.A., 2013). Shale gas exploration led by PetroChina, Sinopec, and Shell is underway in the Sichuan Basin and Yangtze Platform areas, and some shale gas field in this area have been developed for commercial production. However, only few studies have been performed on methane sorption on the marine shales of Sichuan Basin, which makes it difficult to evaluate their gas storage capacity. Furthermore, due to deep burial, the marine shales in Sichuan Basin usually have higher thermal maturities than gas shales in North America. The objective of the present work was to investigate the methane sorption capacity of selected marine highly mature shales from Sichuan Basin. Methane sorption isotherms were measured at 30, 50 and 80 °C and pressures up to 20 MPa on dried crushed shale samples. The controls of organic matter richness, thermal maturity, mineralogy,

and pore structure on methane sorption capacity are discussed. The temperature dependence of sorption capacity was analyzed based on multiple-temperature sorption isotherms for selected samples and a linear combination approach was developed to estimate the in situ sorption capacity of the shales. Finally, the evolution of methane sorption capacity as a function of depth has been analyzed.

2. Samples

The shale samples investigated in this study are black shales from Sichuan Basin, Southwest China, deposited in marine environment (Fig. 1). The Sichuan Basin, located in the west of the Yangtze platform, extends over a wide area from Sichuan province to Chongqing municipality. The Longquanshan Mountain Fault and the Huaying Mountain Fault subdivide the Sichuan Basin into three tectonic zones: The Northwest Sichuan depression zone, the Central Sichuan uplift zone, and the Southeast fold belt (Liu et al., 2005). Sichuan Basin is a prolific hydrocarbon province, and both conventional and unconventional reservoirs have been developed. There are mainly four sets of hydrocarbon source rocks: the Lower Cambrian marine shale, Upper Ordovician–Lower Silurian marine shale, Lower Permian marine carbonate source rocks, and Upper Permian coal-bearing mudstone (Liang et al., 2008). Details of the stratigraphy, petrographic analyses, and potential evaluations of these marine source rocks have recently been published (Liang et al., 2008; Liu et al., 2005; Pu et al., 2010; Yang et al., 2013). A generalized Paleozoic stratigraphy (from Cambrian Series to Silurian Series) for the Southeast Sichuan Basin is shown in Fig. 2. The fourteen Lower Silurian shale samples studied were collected from the Longmaxi Formation: eight black shale samples come from a well drilled in the Changning shale gas demonstration area, located in Southern Sichuan Basin, while the other six samples are outcrops obtained from Chongqing area (Fig. 1).

The Longmaxi Formation of Lower Silurian age was deposited in deep-water shelf environment, and is widely distributed throughout Sichuan Basin with thicknesses varying from a few meters to 400 m. The lithology of Longmaxi Formation is dominated by black carbonaceous shales and silty mudstones. The source organic matter in these marine shales consists mainly of algae, zooplankton, and fungi. Although there are differences in the reported maceral types, the Lower Silurian

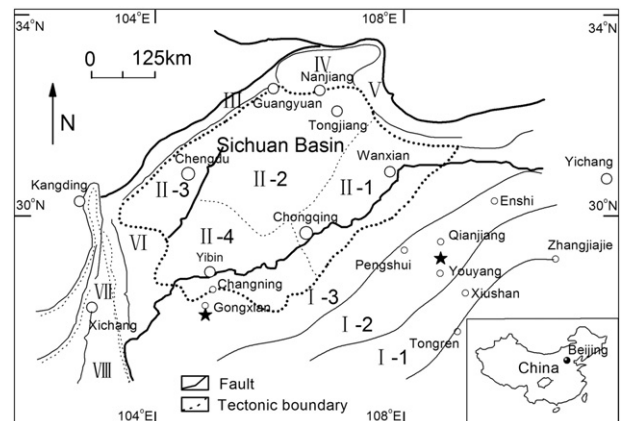


Fig. 1. Geological structure of the Sichuan Basin (modified after Liu et al., 2005) and the locations (★) of the samples investigated in this study (I: Sichuan–Hubei–Hunan–Guizhou fold belt; I-1: Xuefeng Mountain fold subzone; I-2: Western Hubei–Eastern Chongqing–Northern Guizhou fold subzone; I-3: Qiyue Mountain–Jinfou Mountain–Lou Mountain fold subzone; II-1: Eastern Sichuan fold belt; II-2: Central Sichuan fold belt; II-3: Western Sichuan fold belt; II-4: Southern Sichuan fold belt; III: Longmen Mountain depression fold belt; IV: Michang Mountain depression fold belt; V: Daba Mountain depression fold belt; VI: Emei Mountain–Liang Mountain block-fault belt; VII: Xichang basin; VIII: Kangdian tectonic belt).

Download English Version:

<https://daneshyari.com/en/article/1752923>

Download Persian Version:

<https://daneshyari.com/article/1752923>

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