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The role of pre-adsorbed water on methane sorption capacity of Bossier and Haynesville shales

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ABSTRACT

Methane in unconventional shale gas reservoirs is partially stored as sorbed gas. Water, which is omnipresent in gas shales, decreases methane sorption and gas storage capacity. However, the exact controls and mechanism for this are still not sufficiently understood. Therefore, we measured high-pressure methane sorption isotherms of Bossier and Haynesville shales as a function of pre-adsorbed water content at 318 K (45 °C) and 348 K (75 °C) and pressures up to 25 MPa.

Pre-adsorbed water content significantly decreases methane excess sorption capacity. Dry maximum methane sorption capacities of 0.110 mmol/g for the Bossier Shale and 0.104 mmol/g for the Haynesville Shale at 318 K (45 °C) decrease by 78% and 68% upon moisturizing the sample to 97% relative humidity (RH). Decrease in methane excess sorption capacity linearly correlates with increasing water content up to a critical threshold of 0.6–1 mmol/g (app. 50–75% RH). Additional pre-adsorbed water content has no further impact on methane excess sorption.

Dry methane sorption isotherms can be approximated as the sum of the sorption behavior of individual constituents. The main sorption sites are located on clays (mostly illite) and organic matter in approximately equal proportions.

Illite clays are responsible for the main loss in methane sorption with increasing water content. All of the methane sorption sites of clay minerals are lost at water saturations of 32 and 50% for the Haynesville and Bossier shales, respectively. This makes the clays methane excess sorption on the reservoir scale negligible, where comparable or higher water saturations prevail. Consequently, the hydrophobic part of the organic matter alone makes up the residual methane excess sorption.

The reduction in methane excess sorption for the analyzed samples can be as high as 54 and 72% for reservoir water saturation values for Haynesville and Bossier shales, respectively. This research demonstrates how methane storage capacity calculations for the reservoir scale might be grossly over-estimated when the significant impact of water and its interaction with the mineralogical and organic parts of the shale is not properly accounted for.

1. Introduction

Water is considered ubiquitous in unconventional shale gas systems (Jarvie, 2012). However, the effect of water on the sorption behavior of methane on the reservoir scale, hence also on gas in place calculations, is still not sufficiently understood. The ratio of sorbed and free gas is strongly dependent on the water saturation of the shale but quantitative impact analyses are not available in literature.

While methane sorption studies on moisture-equilibrated coals are numerous (Day et al., 2008; Gensterblum et al., 2013; Joubert et al., 1973, 1974; Krooss et al., 2002; McCutcheon et al., 2003; Yee et al., 1993), studies on moisture-equilibrated shales are few and do not dealt with the topic of water in much detail (Gasparik et al., 2013; Ross and Bustin, 2007a,b; Tan et al., 2014; Yuan et al., 2014). However, all authors stress the negative effect of water vapor on methane sorption.

In recent studies on the methane sorption of shales, variations in sorption capacity have been mostly ascribed to the Total Organic Carbon (TOC) content (Chalmers and Bustin, 2008; Gasparik et al., 2013; Ross and Bustin, 2009; Wang et al., 2013; Weniger et al., 2010). However, Schettler and Parmely (1991) point out that the efficiency of organic carbon as an adsorbant might vary by as much as a factor of 4. They found that the methane sorption capacity of shales with low TOC content was similar to the one of the samples rich in TOC, indicating a significant sorption capacity of clay minerals. Several investigators found positive correlations between clay content and sorption capacity (Gasparik et al., 2012; Ji et al., 2012; Schettler and Parmely, 1991), whereas others found no correlation (Gasparik et al., 2014; Wang et al., 2013). Zhang et al. (2012) investigated the impact of organic

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matter on the methane sorption capacity of immature shales (0.56–0.58% VR_r) by isolating and measuring isotherms on kerogen extracts. The isolated kerogen showed higher sorption capacities than their source shales indicating that sorption capacity is not only a simple function of rock composition, TOC or mineralogy. Transport, pore accessibility, texture of clay minerals, relationship between organic matter and clay minerals, blockage and availability of sorption sites, which are mostly found in the micropores of the rock have to be considered as well (Hao et al., 2013; Ross and Bustin, 2009; Schettler and Parmely, 1991). Most authors agree that the controls and mechanisms of gas storage in shale reservoirs are complex and most likely a function of various rock properties rather than the organic fraction alone. However, the organic matter is prevalent concerning methane sorption and might mask other geological controls (Chalmers and Bustin, 2008).

In this study, we experimentally analyzed the impact of pre-adsorbed water on the methane sorption capacity of Bossier and Haynesville Shale to achieve an improved understanding of the interaction between water and gas in a competitive sorption environment for shales and their individual constituents.

2. Geology

The Bossier and Haynesville shales comprise a number of different Upper Jurassic marine lithofacies ranging from argillaceous to carbonate-dominated as well as organic-rich to organic-poor mudrocks (Hammes and Frébourg, 2012). Typical TOC contents of the Haynesville shale are 3%, with porosity values ranging between 8 and 12%, ranging in vitrinite reflectance (VR_r) between 2.2 and 3% (Jarvie, 2012; Williams, 2009). The Bossier Shale has an average TOC of 1.6% with porosities of 4 to 10% and an average thermal maturity of 2.06% VR_r (Hammes et al., 2011; Jarvie, 2012). BIB-SEM investigations found that the majority of the visible porosity (>10 nm) is associated with inorganic and not with organic matter for these two shales (Klaver et al., 2015). The productive intervals are between 9700 and 15,300ft (3000–4600 m) and the main exploration and production efforts for these heterogeneous shales are focused in an area situated roughly along the center of the Texas and Louisiana border in the U.S. (Hammes and Frébourg, 2012).

3. Experimental methods

3.1. Water sorption isotherm measurements at controlled relative humidity

Water sorption isotherms were measured on 2–5 g of crushed sample material with a grain size of 0.1–0.3 mm. Sample material was dried overnight at 378 K (105 °C) in a vacuum oven before measuring the dry mass of three aliquots. For moisture equilibration the samples were placed inside a desiccator together with a container holding one of the five saturated salt solutions at constant temperature 296 K (23 °C) to establish a defined water vapor pressure: LiCl for 11%, $MgCl_2 \cdot 6H_2O$ for 33%, $Mg(NO_3)_2 \cdot 6H_2O$ for 53%, NaCl for 75%, and K_2SO_4 for 97% RH (relative humidity) (DIN EN ISO 483:2006–02, 2006). The shale samples were placed inside the desiccator for at least 48 h although a fraction of the time is often considered sufficient for moisture equilibration (White and Pichler, 1959). The resulting water uptake at a defined vapor pressure was measured using a high precision balance (Kern Model ABJ 320–4).

3.2. Methane sorption measuring procedure

Methane excess sorption isotherms at 318 K (45 °C) and 348 K (75 °C) and pressures up to 25 MPa were measured using a manometric sorption setup (Fig. 1). The experimental setup consists of a stainless steel sample cell, a set of automated valves and a high-precision pressure transducer (30 MPa max. pressure with a precision of 0.05% of full scale value). The volume between the two valves (V1 and V2) inside the heating cabinet was calibrated by helium expansion and used as the reference cell (RC). A 0.5 μm in-line filter prevents particulate matter from entering and damaging the valves. At the beginning of the measurement the reference cell is filled with methane. After pressure and temperature equilibration is reached, V2 is opened to expand methane into the sample cell. The recorded decrease in pressure over time is an effect of volume expansion and methane sorption. As soon as no more decrease in pressure can be recorded the sample and reference cell are separated by closing V2 and the reference cell's pressure is increased. The process is started again thereby continuously increasing the pressure in the sample cell until the desired pressure of 25 MPa is reached. Details of the measuring procedure have been reported previously (Busch et al., 2004; Gasparik et al., 2012; Krooss et al., 2002; Weniger et al., 2010).

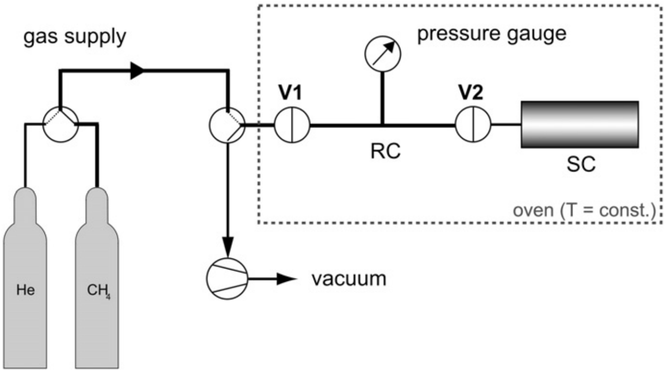

Fig. 1. Manometric high-pressure sorption setup scheme (modified after Gasparik et al. (2012)). Reference cell (RC) and sample cell (SC) are placed inside a temperature regulated oven.

3.3. Gas storage calculations

In a manometric sorption measurement, the excess sorbed amount of substance (n_{excess}) is calculated as the difference between the total amount of gas transferred into the sample cell ($n_{transferred}$) and the volumetric storage capacity of the void volume (V_{void}) determined by helium expansion (Eq. (1)).

$$n_{excess} = n_{transferred} - \overline{\rho}_{gas}(p,T) \cdot V_{void}. \tag{1}$$

Here $\overline{\rho}_{gas}$ is the molar gas density calculated by the GERG equation of state (Kunz et al., 2007). Helium is used for the determination of the void volume under the assumption that it is a non-adsorbing gas or its adsorption can be neglected (Sakurovs et al., 2009). The experimental excess sorption isotherms are fitted with the following function (Eq. (2)) (Gasparik et al., 2012):

$$n_{excess} = n_{\infty} \frac{p}{p + p_L} * \left(1 - \frac{\rho_{gas}(p,T)}{\rho_{sorb}}\right) \tag{2}$$

where n_{∞} is the maximum amount of sorbed gas at complete occupancy of all sorption sites (corresponding to the "monolayer" sorption capacity of the Langmuir model), p is the pressure of the free gas phase, p_L is the Langmuir pressure, corresponding to the pressure at which half of all sorption sites are occupied, ρ_{gas} and ρ_{sorb} are the density of the free gas and the sorbed gas phase, respectively. The density of the sorbed phase cannot be measured experimentally. It can either be estimated by theoretical considerations or used as a free fitting parameter. At low gas pressures the gas density/sorbed phase density ratio in Eq. (2) becomes negligible and the equation approaches the conventional Langmuir formula. Every mention of gas sorption in the following text refers to excess sorption, even if not explicitly stated.