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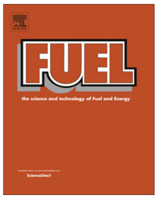

Full Length Article

A dual-site Langmuir equation for accurate estimation of high pressure deep shale gas resources

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ABSTRACT

Adsorbed methane makes up a large portion of the total shale gas-in-place (GIP) resource in deep shale formations. In order to accurately estimate the shale GIP resource, it is crucial to understand the relationship between the adsorbed methane quantity and the free methane quantity of shale gas in shale formations (under high pressure conditions). This work describes and accurately predicts high pressure methane adsorption behavior in Longmaxi shale (China) using a dual-site Langmuir model. Laboratory measurements of high pressure methane adsorption (303–355 K and up to 27 MPa) are presented. Our findings show that for depths greater than 1000 m (>15 MPa) in the subsurface, the shale gas resources have historically been significantly overestimated. For Longmaxi shale (2500–3000 m in depth), classical approaches overestimate the GIP by up to 35%. The ratio of the adsorbed phase compared to the free gas has been significantly underestimated. The methods used herein allow accurate estimations of the true shale GIP resource and the relative quantity of adsorbed methane at *in situ* temperatures and pressures representative of deep shale formations.

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1. Introduction

Shale gas resources are globally abundant and shale gas production has continuously increased over the past ten years as a result of horizontal drilling and hydraulic fracture techniques [1–7]. It is now recognized as a promising unconventional natural gas resource, and many countries have attempted to accurately estimate their shale gas resources in an effort to meet their future energy demands [4,7,8]. For example, shale gas production has grown very rapidly in the United States, reaching nearly 40% of total natural gas production in 2013 [6]. Despite its widespread importance, substantial uncertainties exist in assessing the quantity of recoverable shale gas, and current resource estimates should be treated with considerable caution [9,10]. This large and continuing uncertainty significantly impacts the total gas-in-place (GIP) estimation at a majority of sites, especially in terms of the often-neglected effects of high pressure and temperature in deeper shale formations, e.g. Barnett shale. The future of the shale gas industry and worldwide energy policy therefore depends on the development of a more accurate shale gas resource estimation methodology. In addition, with the development of non-aqueous fracturing fluids such as carbon dioxide in the hydraulic fracturing technique, deep shale formations may become a viable option for carbon dioxide sequestration [11,12]. A reasonable assessment of the carbon dioxide adsorption capacity of shale at high pressure and temperature geological conditions is of parallel interest [13,14].

Shale gas trapped within shale formations is different from conventional natural gas since the shale formation is often both the source and the reservoir of the natural gas itself. Shale gas exists in three different phases within the shale formation: (i) as free compressed gas, (ii) as adsorbed fluid on the surface, and (iii) as a dissolved component in the liquid hydrocarbon and brine. The most widely used approach for estimating shale GIP is to sum these three components. The adsorbed phase accounts for 20–85% of the total amount based on current studies in five major shale formations in the United States [1]. Thus, the estimation of the adsorbed amount of natural gas, the largest component of which is methane,

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significantly influences the final determination of the geological GIP quantity and the working life of the shale gas producing well [9].

Unlike coalbed methane which usually occurs in shallow coal seams (at depths of <1000 m), shale formations are typically much deeper and under significantly different geological conditions. For example, the Barnett shale completions are up to 2500 m deep, where reservoir pressures can reach 27 MPa and the reservoir temperature can be up to 360 K [1]. Unfortunately, the effects of these high pressure and temperature conditions on the quantity of adsorbed methane available in shale gas reservoirs have rarely been appropriately considered in both academia and industry. The standard practice for estimating shale GIP is to use methane adsorption measurements at intermediate pressure conditions (10–15 MPa) to predict the methane adsorption behavior in the higher pressure region (>15 MPa) [1,2,4,5,8]. However, the methodology used in the standard practice does not account for the difference between observed and absolute adsorption quantities. This misinterpretation can significantly affect the shale GIP estimation, especially the contribution of the adsorbed methane at high pressure geological conditions (high pressure refers to reservoir pressures above 15 MPa in this work) [9] where the Gibbs excess adsorption phenomenon is very pronounced. Even though this phenomenon has been observed and acknowledged in numerous cases [15–24], several fundamental problems still remain to be addressed. These include the development of physically reasonable methods to (i) accurately describe the observed (excess) adsorption isotherms, (ii) predict the corresponding absolute adsorption isotherms, and (iii) predict adsorption isotherms at pressures and temperatures beyond the measured data. Several adsorption models have been proposed [15,17–19,21–23], but these models do not give a satisfactory interpretation of the experimental data and excess adsorption phenomena, and the assumptions used are unphysical in nature. Most notably, a common assumption is to treat the adsorbed layer as having a constant volume independent of the adsorbed amount and/or pressure of the bulk phase [15–19,21–23]. Although in some cases this volume is allowed to vary with temperature [15,16], it is generally not valid to assume that the volume will not change as the adsorbed phase increases in occupancy. The simplified, homogeneous pore structures used in the computational approach can also not be used to reasonably portray the heterogeneous properties of shale or coal [24–26]. In addition, all of these proposed methods cannot predict adsorption isotherms at arbitrary conditions in a robust and rational way, which inhibits their application for shale gas resource estimation as a function of specific location (e.g., subsurface depth). All of these shortcomings are compounded by a lack of measured data under high pressure conditions (well beyond the Gibbs excess maximum). Therefore, both high-pressure adsorption measurements and an optimized adsorption model are needed to accurately describe the adsorption behavior of methane in shale under relevant subsurface conditions. This will in turn allow an accurate shale GIP estimation for a plethora of worldwide shale resources under actual *in situ* conditions.

In this work, methane adsorption in a sample of Longmaxi shale from China was measured using a gravimetric method at four temperatures (303.15 K, 318.15 K, 333.15 K and 355.15 K) and high pressures (up to 27 MPa). A dual-site Langmuir adsorption model is introduced to describe both the observed and absolute isotherms at high pressure, utilizing the assumption that the volume of the adsorbed phase changes constantly with the number of adsorbed molecules following a dual-site Langmuir-type equation. These results shed light on the true quantity of shale GIP that can be applied over a large range of temperature and pressure, relevant to the geological conditions of actual shale gas resources.

2. Dual-site Langmuir adsorption model

In any pure gas-solid adsorption system, the observed adsorption quantity, also called the Gibbs excess adsorption uptake, is given by the Gibbs equation,

$$n_e = n_a - V_a \cdot \rho_g = n_a \cdot \left(1 - \frac{\rho_g}{\rho_a}\right) \tag{1}$$

where the excess adsorption quantity (n_e) refers to the difference between the absolute adsorption quantity (n_a) and the quantity of adsorbate that would be present in the same volume (V_a) of the adsorbed phase at the density of the bulk gas phase (ρ_g). When V_a is very low or the density of the adsorbed phase (ρ_a) is much higher than the bulk gas phase density (ρ_g), the excess adsorption quantity is approximately equal to the actual adsorbed amount. However, this relation is invalid at high pressure where the density of the adsorbed phase is similar to the density of the bulk fluid, the point at which the observed adsorption quantity reaches a maximum and then decreases. Under such conditions, the conventional adsorption models that neglect the real volume of the adsorbed phase cannot reasonably explain such adsorption behavior. Therefore, it is imperative to use a more sophisticated approach to obtain the absolute isotherms from observed Gibbs excess isotherms at high pressures. The absolute adsorbed amount (n_a) should always be a monotonically increasing quantity with increasing pressure for a physical adsorption system. A simple description of such a system is the widely used Langmuir equation (Eq. (2)),

$$n_a = n_{\max} \cdot \frac{K(T)P}{1 + K(T)P} \tag{2}$$

where n_a is the absolute adsorption quantity under equilibrium temperature (T) and pressure (P), n_{max} is the maximum adsorption capacity, K(T) is the temperature-dependent equilibrium constant, which can be expressed as $K(T) = A_0 \cdot \exp\left(-\frac{E_0}{RT}\right)$, E_0 is the energy of adsorption, A_0 is the pre-exponential coefficient and R is the ideal gas content (where both E_0 and A_0 are independent of temperature).

In order to obtain the absolute adsorption amount from the observed Gibbs excess adsorption isotherms, V_a or ρ_a must be known. However, it is not possible to measure either of these quantities directly. Therefore, the most widely used approach is to estimate the density of the adsorbed layer based on one of numerous empirical relationships [15,17–23]. It is common to assume that the volume of the adsorbed phase is always constant as a function of adsorption uptake, or in some cases only dependent on temperature. This assumption does not have a basis in the physical understanding of adsorption where the volume of the adsorbed phase must increase as uptake increases.

An alternative approach is to assume that the adsorbed phase has a constant density and that its volume is therefore a linear function of adsorbed amount. In this case, the fact that different researchers use different values for the density of the adsorbed phase (e.g., that of the liquid adsorbate) to obtain absolute isotherms from observed Gibbs excess isotherms is a significant issue, and these values cannot be directly validated through laboratory approaches [15–23]. The most general approach is to allow the adsorbed density to be an independent parameter of the adsorption model. This is adopted herein as shown in Eq. (3), by treating the adsorbed layer as constantly increasing as a function of uptake up to a fitted maximum adsorbed phase volume [14,27–30]. This can be expressed as,

$$V_a = V_{\max} \cdot \frac{K(T)P}{1 + K(T)P} \tag{3}$$

where V_{max} is the volume of the adsorbed phase at maximum adsorption capacity. This unknown volume (V_{max}) can be left as

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