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

Xu Tang^{*}, Nino Ripepi^{*,†}, Nicholas P. Stadie[‡], Lingjie, Yu^{§,¶}, Matthew R Hall^{#,||}

(^{*} Department of Mining and Minerals Engineering & [†] Virginia Center for Coal and Energy Research, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 24060, U.S.; [‡]ETH Zürich, Laboratory of Inorganic Chemistry, Vladimir-Prelog-Weg 1, 8093 Zürich, Switzerland; [§]Wuxi Research Institute of Petroleum Geology of Sinopec Exploration & Production Research Institute & [¶]Sinopec Key Laboratory of Petroleum Accumulation Mechanisms, Wuxi, Jiangsu, 214151, China; [#]Nottingham Centre for Geomechanics, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD UK, ^{||}British Geological Survey, Environmental Science Centre, Keyworth, Nottingham, NG12 5GG UK)

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.

Key words: Shale gas, methane, absolute adsorption, Langmuir

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% to 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, 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,

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

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 (equation 2),

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

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 $K(T) = A_0 \cdot \exp(-\frac{E_0}{RT})$, 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 equation (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,

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

where $V_{\max}$ is the volume of the adsorbed phase at maximum adsorption capacity. This unknown volume ($V_{\max}$) can be left as an independent fitting parameter and varies from system to system but often yields densities of the adsorbed phase that are close to that of the liquid adsorbate. Combining equations (1), (2) and (3), the excess adsorption uptake can be obtained as shown in equations (4)

$$n_e(P, T) = (n_{\max} - V_{\max} \cdot \rho_g) \cdot \frac{K(T)P}{1 + K(T)P} \quad (4)$$

However, this single-site Langmuir equation cannot sufficiently describe a large number of real gas-solid adsorption systems (31-32). For heterogeneous surfaces (as in almost all real-world materials), the adsorption energy at each site will vary, depending on the local chemistry and structure. The single site Langmuir model is limited in this application (31-32). The most favorable sites will be filled first, followed by the less favorable sites. In order to address heterogeneous adsorbents, the most simplified case is

where only two different adsorption sites are available. Each site can be modelled by a separate equilibrium constant, $K_1(T)$ and $K_2(T)$ ($K_1(T) = A_1 \cdot \exp(-\frac{E_1}{RT})$ and $K_2(T) = A_2 \cdot \exp(-\frac{E_2}{RT})$), weighted by a coefficient (α). Thus, the dual-site Langmuir equation can be written in the following form (equation 5), where α is the fraction of the second type of site ($0 < \alpha < 1$),

$$n_a(P, T) = n_{\max} \cdot \left[(1 - \alpha) \frac{K_1(T)P}{1 + K_1(T)P} + \alpha \frac{K_2(T)P}{1 + K_2(T)P} \right] \quad (5)$$

In the same way as for the single-site equation, the excess uptake in the dual-site equation can be obtained, shown in (6),

$$n_e(P, T) = (n_{\max} - V_{\max} \cdot \rho_g) \cdot \left[(1 - \alpha) \left(\frac{K_1(T)P}{1 + K_1(T)P} \right) + \alpha \left(\frac{K_2(T)P}{1 + K_2(T)P} \right) \right] \quad (6)$$

Both the single-site (equation 2, 4) and dual-site equations (equation 5, 6) shown herein are based on the assumption that the volume of the adsorbed layer increases linearly with the adsorbed amount, up to a monolayer completion ($V_{\max}$). Then, the absolute adsorption amount can be obtained from the measured adsorption data *via* a least-squares fitting analysis. It should be noted that the real-world material may have an abundance of different adsorption sites in actuality, but that a two-site model has often been found to be sufficient for describing such a system owing to the large number of independent fitting parameters (28-30), and when using a global fitting method (see: Section 3 Materials and methods) it is desirable to decrease the number of unnecessary such parameters (30).

3. Materials and methods

Shale samples from the Lower Silurian Longmaxi Formation (collected at a depth of 2400.8 m) were obtained from the Fuling #1 well in the Fuling region, Sichuan Province, China. The shale specimen was ground and sieved using 0.38-0.83 mm metal sifters and placed in a drying oven at 105 °C for 24 h to dehydrate. After dehydration, the prepared sample was stored in a desiccator prior to adsorption measurements. Methane adsorption measurements were conducted using a Rubotherm Gravimetric Sorption Analyzer (Rubotherm GmbH, Bochum, Germany) with research grade methane gas (99.99%). Detailed experimental procedures and physical parameters of the shale sample are given in the Supplemental Materials.

In this work, four methane adsorption isotherms were obtained at 303.15 K, 318.15 K, 333.15 K and 355.15 K. All isotherms were measured up to 27 MPa and fluctuations in temperature during a given isotherm were $< 0.2^\circ\text{C}$. The data were processed using a previously developed Mathematica script (28-30); the four Gibbs excess adsorption isotherms were fitted simultaneously to the dual-site Langmuir model (equation 6) by a least-squares residual minimization algorithm based on the Differential Evolution method. Each data point was given the same weight and none were discarded. The density of the bulk fluid as a function of temperature and pressure was obtained from the NIST REFPROP database. The seven independent fitting parameters were varied to achieve the global minimum of the residual-squares value within the following limits: $0 < n_{\max} < 100 \text{ mmol/g}$, $0 < V_{\max} < 10 \text{ cm}^3/\text{g}$, $0 < \alpha < 1$, $0 < E_1 < 100 \text{ kJ/mol}$, $0 < E_2 < 100 \text{ kJ/mol}$, $A_1 > 0$, $A_2 > 0$). Minimization was performed in excess of 100 unique times by changing the random seed in order to assure that a global minimum was achieved. Once the seven fitting parameters were determined, absolute and excess adsorption uptake could be easily calculated at any temperature and pressure by use of equations 5 and 6.

4. Results and discussions

4.1 Modeling of observed Gibbs excess adsorption at high pressures

Equilibrium excess adsorption uptake of methane measured on Longmaxi shale between 303-355 K and 0.1-27 MPa is shown in Figure 1. In all isotherms, the observed Gibbs excess adsorption uptake increases with increasing pressure up to a maximum value and then decreases. At pressures below the Gibbs excess maximum, the excess adsorption is always lower at higher temperatures. However, at a point somewhere beyond the Gibbs excess maximum, the isotherms crossover and higher temperatures now result in higher excess uptake at equivalent pressures. As seen in Figure 1, the observed maximum Gibbs excess adsorption quantities are 0.0893 mmol/g, 0.0813 mmol/g, 0.0786 mmol/g and 0.0719 mmol/g at 303.15 K (8 MPa), 318.15 K (10 MPa), 333.15 K (12 MPa) and 355.15 K (12 MPa), respectively. As the isotherm temperature increases, higher pressure is needed to reach the Gibbs excess maximum. This is a well-known phenomenon of supercritical gas adsorption (33). The dual-site Langmuir adsorption model (equation 6) gives a good global fit to the observed data, and the corresponding best-fit parameters are: $n_{\max}=0.1715$ mmol/g, $V_{\max}=0.0097$ mL/g, $\alpha=0.2640$, $E_1=16.706$ kJ/mol, $A_1=0.0002$ 1/MPa, $E_2=15.592$ kJ/mol, $A_2=0.0032$ 1/MPa. It should be emphasized that these seven parameters apply to all the isotherms measured, and that by performing a single global fit to all the data at once, a most general understanding of the properties of the adsorbent-adsorbate system can be achieved.

Figure 1 Gibbs excess adsorption isotherms of methane on Longmaxi shale (symbols) and dual-site Langmuir model fits (lines)

An explanation of the Gibbs excess maximum phenomenon can be made by examining the change in the volume of the adsorbed phase as compared to the volume-density product, as shown in Figure 2. The volume of the adsorbed methane phase changes with pressure and temperature following a dual-site equivalent of equation 3. Higher temperature decreases the adsorbed quantity of methane, which results in a decreased volume of the adsorbed phase. As pressure increases, the volume-density term ($V_a \cdot \rho_g$) of equation (6) always increases but the difference of ($V_a \cdot \rho_g$) at different temperatures becomes more pronounced. The ($V_a \cdot \rho_g$) term at low temperature is always higher than that at high temperature and the maximum absolute adsorption quantity ($n_{\max}$) is constant, which results in the crossover of the Gibbs excess adsorption isotherms. Therefore, the observation of the crossover phenomenon in the measured data (Fig. 1) supports the assumption that the volume of adsorbed methane changes with

temperature and pressure following a dual-site Langmuir-type equation. This is in distinct contradiction to the approximation that the adsorbed phase is constant, an often used approximation in other work.

Figure 2 Modelled values of the volume of adsorbed methane (V_a) (solid lines, filled symbols, left major axis) and the volume-density term ($V_a \cdot \rho_g$) (dotted line, hollow symbols, right minor axis) on Longmaxi shale as a function of pressure

The crossover of the excess uptake isotherms is not observed when the isotherms are plotted as a function of bulk gas density instead of pressure (Figure 3). The measured isotherms show the same temperature dependence at all pressures, *i.e.* increasing excess uptake with decreasing temperature. This behavior is also inherently predicted by the dual-site Langmuir equation (see the fits in Figure 3). The small deviations from this trend in the measured data at 318.15 K can be attributed to experimental error, and the overall trend remains clear. The same phenomenon (seen when plotting excess uptake as a function of bulk fluid density) was also reported for carbon dioxide, methane and nitrogen adsorption in different materials (15, 17, 21).

Figure 3 Gibbs excess adsorption isotherms of methane on Longmaxi shale (symbols) and dual-site Langmuir equation fits (lines) as a function of bulk methane density

4.2 Prediction of absolute adsorption and extrapolation to higher temperatures

Absolute adsorption isotherms of methane on Longmaxi shale based on equation 5 are shown in Figure 4. As is characteristic of the Langmuir equation, the adsorption quantity increases monotonically up to 27 MPa, which is consistent with the physical nature of adsorption. The absolute adsorption quantity is significantly higher than the observed Gibbs excess quantity, especially at 27 MPa. This implies the significant contribution of the adsorbed phase volume of methane in shale toward the absolute adsorption content, which is neglected in the observed Gibbs excess adsorption isotherms. Figure 4 also shows that at higher temperatures, this contribution becomes less pronounced.

Predicting adsorption isotherms at different temperatures is of fundamental interest for shale GIP estimations in the deep subsurface, typically reservoirs at a depth over 1000 m. It is impractical to measure a large number of isotherms at different temperatures for shale gas resource estimation. Thus, another feature of the dual-site Langmuir model used herein is that it can be used to predict isotherms at arbitrary temperatures near the measured isotherms. This is very notably not possible when each isotherm is fitted individually, as is often the case in other studies, and a global fit across numerous isotherms is therefore an extremely desirable feature of a particular model. Interpolation of the measured data (i.e., predictions at temperatures between the measured isotherms) is expected to be highly accurate, though extrapolation to higher or lower temperatures than measured, while also possible, should be performed with caution. Nevertheless, extrapolation can often shed valuable light on conditions outside of the region where measurement is possible.

Estimated absolute adsorption isotherms of methane on Longmaxi shale are also shown at different temperatures up to 415.15 K in Figure 4. The predicted Gibbs excess adsorption isotherms exhibit similar properties as the observed isotherms and therefore the extrapolation is determined to be reasonably dependable. As the temperature increases, the contribution of the adsorbed phase volume for the absolute adsorption gradually becomes less pronounced. Notably, the negative effect of temperature on methane adsorption on shale remains clear at all temperatures.

Figure 4 Gibbs excess adsorption (solid lines, filled symbols) and absolute adsorption (dashed lines) isotherms of methane on Longmaxi shale as fitted by a dual-site Langmuir equation (measured up to 355.15 K), extrapolated up to 415.15 K (gradual grey lines)

4.3 Accurate shale gas-in-place estimations from adsorption measurements

Equilibrium methane adsorption measurements in shale can be used to estimate the geological gas-in-place (GIP) content of subsurface shale formations. It is important to note that this method does not take into account any moisture present in the shale which can reduce the methane adsorption capacity. In addition, this GIP content does not include any contribution from dissolved methane in the liquid hydrocarbon or brine, and also does not consider the presence of other gaseous components of natural gas (e.g., higher alkanes and hydrogen sulfide).

The geological GIP is estimated herein as the total amount of methane present in the gaseous and adsorbed phases in a homogeneous formation of shale. Conceptually, this amount is accessible via the sum of the free gas phase content, n_{free} , and the absolute adsorbed phase content, n_a .

$$GIP = n_{free} + n_a \quad (7)$$

The amount of gaseous methane is equal to the bulk methane density multiplied by the volume of the gas phase alone (excluding the volume of the adsorbed phase) as shown in Figure 5. However, the volume accessible to the free gas is not the same as the entire empty volume of the shale since the adsorbed phase occupies a finite volume itself, which is significant at high pressure.

Figure 5 Schematic depiction of the quantities relevant to gas-solid adsorption in two distinct regimes: in the dilute limit (left) and at high pressures (right) of the bulk gas

The total GIP amount can also be derived in a much simpler way as the sum of the excess adsorbed amount and a product of the entire free volume of the empty shale with the bulk gas phase density, because of the Gibbs definition (from equation 1):

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$$GIP = n_{free} + n_e + V_a \cdot \rho_g = V_{tot} \cdot \rho_g + n_e \quad (8)$$

287 All three of the quantities in the final expression of equation 8 are directly measurable: the total empty
 288 volume accessible to gas in the shale formation (V_{tot}), the density of pure gaseous methane at the
 289 equilibrium conditions of the formation (ρ_g), and the excess adsorbed amount under these conditions
 290 (n_e). In practice, the excluded space within the shale ($V_{tot}=V_{bulk}-V_{skeletal}$) and/or its skeletal density ($\rho_{shale} =$
 291 $m_{shale}/V_{skeletal}$) are generally measured using pycnometry with a probe gas such as helium, which is
 292 assumed to be non-adsorbing, or by other indirect approaches such as well logging. This measurement is
 293 required in order to make adsorption measurements, for which the experimental outcome is the excess
 294 adsorbed amount (n_e). It must therefore be emphasized that the simplest and most accurate approach
 295 to estimate the total shale GIP is *via* equation 8. This is demonstrated in Figure 6 where the adsorption
 296 isotherm of methane on Longmaxi shale measured in this work is directly converted to GIP content as a
 297 function of pressure at 355.15 K. No adsorption model is necessary to arrive at the total GIP content in
 298 this way.

299

300 **Figure 6 Directly calculated shale GIP content as a function of pressure using the measured data at**
 301 **355.15 K**

302 Historically, the precise definition of the measured adsorbed amount has been a matter of confusion. In
 303 some reports, the volume of the adsorbed layer is accounted for twice owing to the incorrect method of
 304 summing the “free gas content” in the entirety of the empty pore and the absolute adsorption content
 305 (9, 34,35), corresponding to:

306

$$GIP_{incorrect} = V_{tot} \cdot \rho_g + n_a \quad (9)$$

307 In this approach, where the absolute adsorption isotherms are used in place of the excess quantity for
 308 estimating GIP, the total shale gas content will be significantly overestimated.

309 This may suggest that the effort to extract the absolute adsorption isotherm from the measured data is
 310 unnecessary for understanding and estimating total GIP since only the excess adsorption data are
 311 required (9, 34, 35). However, in order to determine the relative amount of adsorbed methane versus
 312 gaseous methane in this total figure, the absolute adsorption isotherm is required.

4.4 Geological gas-in-place resource estimation of a shale gas reservoir in Fuling, China

Generally, coal seams are shallower than shale formations (usually within depths up to 1000 m below the surface), and therefore the pressure (below 10-15 MPa) is low enough that the contribution of the volume of the adsorbed methane phase toward absolute adsorption content has little influence. In this case, employing either the absolute adsorbed amount (equation 9) or the measured Gibbs excess quantity (equation 8) is reasonable to estimate the total GIP content, though it is still simpler to use the directly measured quantity. Methane in deep shales, on the other hand, are in a different geological situation. For example, the Barnett shale completions are up to 2500 m deep, where the reservoir pressure reaches up to 27 MPa and the reservoir temperature can be up to 360 K (1). Therefore, both pressure and temperature effects on the adsorbed methane content cannot be neglected. In addition, the large difference between the observed adsorption uptake and the absolute adsorption uptake at these pressures demonstrates the importance of using an accurate model of methane content in subterranean shale formations. In other reports, the absolute adsorbed amount is estimated by simply fitting the excess adsorption quantities along a single isotherm to a single site (classical) Langmuir isotherm (1, 2, 4, 5, 8), which cannot accurately describe the changing volume of the adsorbed phase that is taking place. In these cases, regardless of whether equation 7 or 9 is used, the estimated GIP will be significantly incorrect. This result is demonstrated in Figure 7. Logically, there is undeniably a large contribution to the adsorbed amount at high pressures that is undetected by experiment since the bulk gas density approaches that of the adsorbed phase and the excess adsorption quantity is no longer accurate.

Figure 7 Comparison of the Gibbs excess adsorbed methane content (solid line) to two estimates of absolute adsorbed methane (dashed lines) on Langmaxi shale, at geological conditions of one completion well (353.15 K and up to 37.69 MPa (34)).

Herein, the geological GIP content of shale gas resources in the Fuling region in China is estimated as an example to determine the magnitude of the difference between conventional methods and those employed in this work. The shale gas wells in the Fuling region are the first commercialized shale gas resource in China (36, 37). The Longmaxi shale formation of the Fuling region is between 2000 to 3000 m deep; the pressure and temperature conditions as a function of depth can be estimated by the pressure coefficient (15 MPa/km) and the geothermal gradient (27.3°C/km). The average porosity and density of the shale rock are 4.5% and 2.4 g/mL, respectively (36, 37).

Figure 8 Comparison of methane adsorption capacity in Fuling region shale formations under geological temperature and pressure conditions as they vary with depth. Predictions are based on the following adsorption quantities: observed Gibbs excess adsorption, modeled absolute adsorption uptake (this work) and the “Conventional Absolute Prediction” (refer to Supplemental Materials).

Figure 9 Shale GIP content in Fuling region shale formations under geological conditions, where temperature and pressure are varied as a function of depth. The Correct Method uses Eq. 8 where n_e is calculated using Eq. 6; Incorrect Method 1 uses Eq. 9 where n_a is calculated using Eq. 5; Incorrect Method 2 uses Eq. 9 where n_a is calculated using the Conventional Absolute Prediction (refer to Supplemental Materials).

In this case, both the temperature and the pressure of the actual shale reservoir at maximum depth are out of the range of data measured in this work. Nevertheless, the dual-site Langmuir model can be used to predict both the Gibbs excess adsorption isotherms and the absolute adsorption isotherms under different temperature and pressures, as previously discussed. Figure 8 shows that there are significant differences between the observed Gibbs excess adsorption quantity, true absolute adsorption quantity (as determined by the dual-site Langmuir model), and a common oversimplified approach to predict the absolute quantity, especially for formations over 1000 m deep. The oversimplified prediction of absolute adsorption is two times larger or more than the Gibbs excess adsorption amount, and the best estimate

of absolute adsorption is three times larger or more. This is because the Gibbs excess adsorption amount and the oversimplified prediction (the “Conventional Absolute Prediction”, see Supplemental Materials) are always less than the true (absolute) adsorption amount. When equation 9 is used to incorrectly predict GIP, this leads to a significant overestimation of geological GIP content under real geological conditions as shown in Figure 9. The correct method to estimate GIP content as a function of depth is *via* equation 8. Using the incorrect method 1 and method 2 (shown in Figure 9), shale gas resources at a depth of 3000 m are overestimated by 35% and 16%, respectively.

To accurately determine the ratio of adsorbed methane to gaseous methane in the total GIP resource, one must employ an accurate absolute adsorption quantity. If either the measured excess adsorption quantity or an oversimplified absolute adsorption prediction (as in Figure 7) is used, the result will be a significant underestimation of the contribution to the total GIP from adsorbed methane. The correct method is to consider the absolute adsorption quantity as the total adsorbed amount, modeled by a physically robust method such as the dual-site Langmuir equation used herein. This is shown as a function of formation depth in Figure 10. The actual adsorbed methane amount still accounts for 46% of the total GIP content at a depth of 4000 m. If only the excess adsorption quantity is taken, the result is a very large underestimation of the contribution of adsorbed methane to the total GIP content: less than 12% at a depth of 3000 m.

Figure 10 Comparison of the estimated contribution to total GIP content by adsorbed methane in Longmaxi shale by three methods: where the actual adsorbed amount is estimated as the excess uptake (solid red), absolute uptake (by a dual-Langmuir fit, dashed red), and by a conventional prediction of absolute uptake (dashed black). For demonstration purposes, the correct total GIP content is used in all cases (via Eq. 8).

5 Conclusions

In this work, laboratory measurements of high pressure methane adsorption (303 - 355 K and up to 27 MPa) are presented. Then, the dual-site Langmuir model is applied to describe and accurately predict high pressure methane adsorption behavior in Longmaxi shale (China). Finally, the shale GIP resources in deep high pressure shale formation are accurately predicted. Several preliminary conclusions can be made,

- (1) The crossover of the adsorption isotherms under high pressures and high temperatures are observed and reasonably interpreted.
- (2) Dual-site Langmuir model can not only accurately describes observed adsorption isotherms but also can extrapolate adsorption isotherms beyond test data without using any empirical relationship.
- (3) For depths greater than 1000 m (> 15 MPa) in the subsurface, the shale GIP resources have historically been significantly overestimated, and the ratio of the adsorbed phase compared to the free gas has been significantly underestimated.
- (4) On the basis of the dual-site Langmuir model, the proposed method allows 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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