Evaluation of Gas Adsorption in Marcellus Shale

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Abstract

Production from shale gas reservoirs plays an important role in natural gas supply in the United States. Horizontal drilling and multi-stage hydraulic fracturing are the two key enabling technologies for the economic development of these shale gas reservoirs. It is believed that gas in shale reservoirs is mainly composed of free gas within fractures and pores and adsorbed gas in organic matter (kerogen). It is generally assumed in the literature that the monolayer Langmuir isotherm describes gas adsorption behavior in shale gas reservoirs. However, in this work, we have analyzed several experimental measurements of methane adsorption from the Marcellus Shale core samples that deviate from the Langmuir isotherm, but obey the BET (Brunauer, Emmett and Teller) isotherm. To the best of our knowledge, it is the first time to find that gas adsorption in a shale gas reservoir behaves like multilayer adsorption. Consequently, investigation of this specific gas desorption effect is important for accurate evaluation of well performance and completion effectiveness in shale gas reservoirs based on the BET isotherm. The difference in calculating original gas in place based on both isotherms is discussed. We also perform history matching with one production well from the Marcellus Shale and evaluate the contribution of gas desorption to the well’s performance. History matching shows that gas adsorption obeying the BET isotherm contributes more to overall gas recovery than gas adsorption obeying Langmuir isotherm, especially early time in production. This work provides better understanding of gas desorption in shale gas reservoirs and updates our current analytical and numerical models for simulation of shale gas production.

Introduction

In recent years, the boom of shale gas production was fueled by the improvements in horizontal drilling and multi-stage hydraulic fracturing technologies. As a result, shale gas has become an increasingly important source of natural gas supply in North America and around the world. In nature, gas shales are characterized by extremely small grain size, extremely low permeability on the order of nano-Darcy (10^-6 md), small porosity, and high total organic carbon (TOC). Shale can serve as both source and reservoir rock. The amount of gas in place in shale is strongly affected by the TOC, clays, and the adsorption ability of methane on the internal surface of solid (Martin et al., 2010). In general, complex fracture networks that are generated connect the shale formation and the horizontal well. Shale matrix has strong gas storage capacity but cannot transport the gas for long distance because it is very tight; a fracture network can transport the gas efficiently due to large hydraulic conductivity but has limited storage capacity (Lane et
Since a part of gas in shale reservoirs is adsorbed, investigation of gas adsorption can provide critical insights into evaluation of well performance, shale characterization, and optimization of fracture design in shale gas reservoirs.

Generally, natural gas in shale reservoirs is stored as free gas in both organic matter (kerogen) and larger mineral pores and natural fractures, as well as adsorbed gas within organic matter (Leahy-Dios et al., 2011). The adsorbed gas has a higher density than the surrounding free gas. Clarkson and Haghshenas (2013) presented five mechanisms for methane existence in shale gas reservoirs: (1) adsorption on internal surface area; (2) conventional (compressed gas) storage in natural and hydraulic (induced) fractures; (3) conventional storage in matrix porosity (organic and inorganic); (4) solution in formation water; (5) absorption (solution) in organic matter. The organic matter is nanoporous material primarily consisting of micropores (pore length less than 2 nm) and mesopores (pore length between 2 and 50 nm) (Kang et al., 2011). The organic matter occupies only a part of the bulk rock as connected clusters embedded in the rock or dispersion among mineral grains (Silin and Kneafsey, 2012). In the Appalachian Basin, the well performance from darker zones within Devonian Shale with higher organic content is better than that from organic-poor gray zones (Schmoker, 1980). Lu et al. (1995) showed that the relationship between gas adsorption capacity and TOC is approximately linear when the TOC is high; while for a very low TOC, illite plays an important role in gas storage in Devonian shales. The adsorption process in shale gas reservoirs is mainly physical adsorption, which means that the adsorption is fully reversible, allowing gas molecules to completely adsorb and desorb, and the interaction force between the solid surface and the adsorbed gas molecules is controlled by the weak van der Waals force. The specific surface area, defined as surface area per gram of solid, plays an important role in controlling the adsorption capacity. The rougher solid surface and the smaller pore sizes can contribute a larger specific surface area (Solar et al., 2010). The specific surface area can be calculated using the BET method (Brunauer et al., 1938). A rough solid surface with many nanometer-scale cavities can adsorb gas more strongly than an ideally polished surface (Rouquerol et al., 1999; Solar et al., 2010).

A recent study conducted by the Energy Information Administration (EIA, 2014) concludes that the Marcellus Shale is one of six key tight oil and shale gas regions, which account for 95% of domestic oil production growth and all domestic natural gas production growth during 2011-2013. The Marcellus Shale is located in the Appalachian basin across six states, including Pennsylvania, New York, West Virginia, Ohio, Virginia, and Maryland. The Marcellus Shale covers a total area of more than 100,000 square miles, and the depth is in the range of 4,000 – 8500 ft with an average thickness of 50 ft to 200 ft (U.S. Department of Energy, 2013). The average estimated ultimate recovery (EUR) is about 2.325 bcf (billion cubic feet) per well and the average porosity is 8% and TOC is 12 wt% (EIA, 2011). The Marcellus Shale has 1,500 tcf (trillion cubic feet) of original gas in place (OGIP) with 141 tcf of technically recoverable gas (U.S. Department of Energy, 2013). Reservoir temperature in the Marcellus Shale is observed to be around 140 °F and bottom hole pressure is up to 6,000 psi (Williams et al., 2011). The kerogen type of Marcellus Shale is primarily Type II with a mixture of Type III (Weary 2000).

Most publications to-date have used the Langmuir isotherm to describe gas desorption in shale gas reservoirs. In this paper, we observe that the gas desorption in some areas of the Marcellus Shale follows the BET isotherm based on laboratory measurements. The Langmuir and BET isotherms are compared with experimental data. In addition, through history matching with one production well in the Marcellus Shale, we evaluate the effect of gas adsorption on well performance at short and long production times.

**Adsorption Model for Shale Gas Reservoirs**

Adsorption at the gas/solid interface is referred to as the enrichment of one or more components in an interfacial layer (Sing et al., 1985). The organic matter in shale has a strong adsorption potential due to the large surface area and affinity to methane. In order to simulate gas production in shale gas reservoirs, an accurate model of gas adsorption is very important. According to the International Union of Pure and
Applied Chemistry (IUPAC) standard classification system (Sing et al., 1985), there are six different types of adsorption, as shown in Fig. 1. The shape of the adsorption isotherm is closely related to the properties of adsorbate and solid adsorbent, and on the pore-space geometry (Silin and Kneafsey, 2012). The detailed description of the six isotherm classifications can be found in Sing et al. (1985).

The most commonly applied adsorption model for shale gas reservoirs is the classic Langmuir isotherm (Type I) (Langmuir, 1918), which is based on the assumption that there is a dynamic equilibrium at constant temperature and pressure between adsorbed and non-adsorbed gas. Also, it is assumed that there is only a single layer of molecules covering the solid surface, as shown in Fig. 2(a). The Langmuir isotherm has two fitting parameters:

$$v(p) = \frac{v_L p}{p + p_L}$$

where $v(p)$ is the gas volume of adsorption at pressure $p$; $v_L$ is Langmuir volume, referred to as the maximum gas volume of adsorption at the infinite pressure; and $p_L$ is Langmuir pressure, which is the pressure corresponding to one-half Langmuir volume. Instantaneous equilibrium of the sorbing surface and the storage in the pore space is assumed to be established for the Langmuir isotherm (Freeman et al., 2012).
2012). Gao et al. (1994) demonstrated that the instantaneous equilibrium is a reasonable assumption because the ultra-low permeability in shale leads to very low gas flow rate through the kerogen component of shale.

At high reservoir pressures, one can expect that natural gas sorbed on the organic carbon surfaces forms multi-molecular layers. In other words, the Langmuir isotherm may not be a good approximation of the amount of gas sorbed on organic carbon-rich mudrocks. Instead, multilayer sorption of natural gas should be expected on organic carbon surfaces, and the gas adsorption isotherm of Type II should be a better choice. Type II isotherm often occurs in a non-porous or a macroporous material (Kuila and Prasad, 2013). In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller (BET) published their theory in the Journal of the American Chemical Society (Brunauer et al., 1938). The BET isotherm model is a generalization of the Langmuir model to multiple adsorbed layers, as shown in Fig. 2(b). The expression is shown as follows:

$$v(p) = \frac{v_m C p}{(p_o - p)\left[1 + (C-1)\frac{p}{p_o}\right]}.$$  \hspace{1cm} (2)

where $p_o$ is the saturation pressure of the gas; $v_m$ is the maximum adsorption gas volume when the entire adsorbent surface is being covered with a complete monomolecular layer; and $C$ is a constant related to the net heat of adsorption, which is defined as below:

$$C = \exp\left(\frac{E_1 - E_L}{RT}\right).$$ \hspace{1cm} (3)

where $E_1$ is the heat of adsorption for the first layer, and $E_L$ is that for the second and higher layers and is equal to the heat of liquefaction. The assumptions in the BET theory include homogeneous surface, no lateral interaction between molecules, and the uppermost layer is in equilibrium with gas phase.

A more convenient form of the BET adsorption isotherm equation is as follows:

$$\frac{p}{v(p_o-p)} = \frac{1}{v_m C} + \frac{C-1}{v_m C} \times \frac{p}{p_o}.$$ \hspace{1cm} (4)

A plot of $p/v(p_o-p)$ against $p/p_o$ should give a straight line with intercept of $1/v_m C$ and slope of $(C-1)/v_m C$. Based on $v_m$, the specific surface area can be calculated using the following expression:

$$S = \frac{v_m Na}{22400},$$ \hspace{1cm} (5)

where $S$ is the specific surface area in m$^2$/g, $N$ is Avogadro constant (number of molecules in one mole, $6.023 \times 10^{23}$), $a$ is the effective cross-sectional area of one gas molecule in m$^2$, 22400 is the volume occupied by one mole of the adsorbed gas at standard temperature and pressure in mL.

The standard BET isotherm assumes that the number of adsorption layers is infinite. But, in the case of $n$ adsorption layers in some finite number, then a general form of BET isotherm is given below:

$$v(p) = \frac{v_m C \frac{p}{p_o}}{1 - \frac{p}{p_o} \left[1 - (n+1)\left(\frac{p}{p_o}\right)^n + n\left(\frac{p}{p_o}\right)^{n+1}\right]}.$$ \hspace{1cm} (6)

When $n = 1$, eq. (6) will reduce to the Langmuir isotherm, eq. (1). When $n = \infty$, eq. (6) will reduce to eq. (2).

Here $v(p)$ is the specific volume of gas adsorbed at the reservoir pressure and temperature per unit mass of bulk rock, reference to a standard pressure and temperature (stock tank condition (ST) in the oil
industry). The customary cubic fields are the standard cubic feet of sorbed gas per ton of bulk rock (scf/ton), or the standard cubic centimeters of gas per gram of rock. The conversion factor is

\[ \frac{\text{scf}}{\text{ton of bulk rock}} = \frac{1}{32} \left( \frac{\text{standard cm}^3}{\text{g of bulk rock}} \right) \]

Fig. 3 compares shapes of the Langmuir and BET isotherms: gas desorption along the BET isotherm contributes more significantly at early time of production than that with the Langmuir isotherm curve. This is because the slope of the BET isotherm curve at high pressure is larger than that of the Langmuir isotherm curve, resulting in more adsorbed gas releasing at early production times. In addition, under the same pressure drop from the initial reservoir pressure to the bottomhole pressure (BHP), the amount of released adsorbed gas with the BET isotherm curve is larger than that with the Langmuir isotherm curve.

**Gas Flow Model in Shale**

An equation to describe mass balance of gas flow in shale gas reservoirs by considering the gas desorption effect is given below (Patzek et al., 2013; Yu et al., 2014a):

\[ \frac{\partial}{\partial t} \left[ \rho_g S_g \phi + \left( 1 - \phi \right) \rho_a \right] = - \left[ \frac{\partial}{\partial x} (\rho_g u_g) + \frac{\partial}{\partial y} (\rho_g u_g) + \frac{\partial}{\partial z} (\rho_g u_g) \right], \]

where \( u_g \) is Darcy velocity of gas, \( S_g \) is initial gas saturation, \( \rho_g \) is the free gas density, and \( \rho_a \) is the adsorbed gas density.

The final governing nonlinear equation of transient gas flow in shale gas reservoirs, considering the gas desorption effect, is shown below, and more details about the derivation can be found in our previous work (Yu et al., 2014a):

\[ \frac{\partial}{\partial x} \left( \frac{\rho_g k}{\mu_g} \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{\rho_g k}{\mu_g} \frac{\partial p}{\partial y} \right) + \frac{\partial}{\partial z} \left( \frac{\rho_g k}{\mu_g} \frac{\partial p}{\partial z} \right) = \left[ \phi S_g + (1 - \phi) K_a \right] c_g \rho_g \frac{\partial p}{\partial t}, \]

where \( k \) is reservoir permeability, \( c_g \) is the isothermal gas compressibility factor, \( K_a \) is the differential equilibrium partitioning coefficient of gas at a given temperature (Patzek et al., 2013), defined as follows:

\[ K_a = \left( \frac{\partial \rho_a}{\partial \rho_g} \right)_T \]
The mass balance of adsorbed gas in one unit bulk volume is described as
\[ \rho_a (1 - \phi) = \rho_g \left( p_{ST}, T_{ST} \right) \rho_b \nu, \] (11)

where \( \rho_b \) is bulk density of shale; \( \nu \) is the specific volume of gas adsorbed at the reservoir pressure and temperature per unit mass of bulk rock; and \( \rho_g (p_{ST}, T_{ST}) \) is the stock tank gas density.

The adsorbed gas density at the standard condition can be calculated as follows:
\[ \rho_a = \frac{\rho_g \left( p_{ST}, T_{ST} \right) \rho_b \nu}{1 - \phi} \] (12)

The differential equilibrium partitioning coefficient of gas can be expressed by
\[ K_a = \left( \frac{\partial \rho_a}{\partial \rho_g} \right)_T = \frac{\rho_g \left( p_{ST}, T_{ST} \right) \rho_b \nu}{1 - \phi} \frac{\partial \nu}{\partial p} \frac{\partial p}{\partial \rho_g} \] (13)

The isothermal gas compressibility factor can be determined as
\[ c_g = \frac{1}{\rho_g} \left( \frac{\partial \rho_g}{\partial p} \right)_T \] (14)

The equation of states for real gas is given by
\[ \rho_g = \frac{pM}{Z(p)RT}, \] (15)

where, \( p \) is pressure in kPa, \( M \) is the molecular weight of the gas (\( M = \gamma_g M_{air} \), where \( M_{air} = 29 \) kg/kmol is the molecular weight of air), \( R \) is the ideal gas constant with 8.3145 kPa m³/(kmol K), \( T \) is absolute temperature (K), and \( Z(p) \) is the gas compressibility factor.

Mahmoud (2014) developed a new correlation for calculating the real gas compressibility as follows:
\[ c_g = \frac{c_{pr}}{p_c}, \] (16)

\[ c_{pr} = \frac{1}{p_{pr}} \left[ \frac{1}{Z(p)} \left( 1.404e^{-2.5T_{pr}} \right) p_{pr} - \left( 5.524e^{-2.5T_{pr}} \right) \right], \] (17)

\[ p_{pr} = \frac{p}{p_c}, \] (18)

\[ T_{pr} = \frac{T}{T_c}, \] (19)

where \( p_c \) is the gas critical pressure, \( c_{pr} \) is the reduced gas compressibility, \( p_{pr} \) is the reduced pressure, and \( T_{pr} \) is the reduced temperature.

Substituting eq. (14) into eq. (13) yields
\[ K_a = \left( \frac{\partial \rho_a}{\partial \rho_g} \right)_T = \frac{\rho_g \left( p_{ST}, T_{ST} \right) \rho_b \nu}{1 - \phi} \frac{\rho_g c_g}{\partial p} \] (20)
Consequently, for the Langmuir isotherm equation, the differential equilibrium partitioning coefficient of gas can be expressed as follows:

\[ K_a = \left( \frac{\partial \rho_a}{\partial \rho_g} \right)_{T_f} = \frac{\rho_a (p_{ST}, T_{ST}) \rho_b}{1 - \phi} \frac{v_i p_i}{(p_i + p)^2} = \frac{\rho_a (p_{ST}, T_{ST}) \rho_b}{1 - \phi} \frac{v_i^2 p_i}{(1 - \phi) c_\rho \rho_g} \frac{v_i p_i}{v_i^2 p_i} \]  

(21)

For the BET isotherm, the differential equilibrium partitioning coefficient of gas can be expressed as

\[ K_a = \left( \frac{\partial \rho_a}{\partial \rho_g} \right)_{T_f} = \frac{\rho_a (p_{ST}, T_{ST}) \rho_b}{1 - \phi} \frac{v_i^2 p_i}{C_v m p_o \left( \frac{p_o^2}{p^2} + C - 1 \right)} \]  

(22)

Gas Adsorption Measurements in Marcellus Shale

In this work, we have analyzed gas adsorption laboratory measurements on four samples from the lower Marcellus Shale, as shown in Fig. 4. It can be seen that the adsorption measurements do not obey the Langmuir isotherm but obey the BET isotherm. We employed both the Langmuir and BET isotherms to fit the experimental measurements, as shown in Fig. 5. The fitting parameters of Langmuir and BET isotherms are listed in Tables 1 and 2, respectively. The coefficient of determination, also known as $R^2$, is used to evaluate goodness of fit. The measurements are better approximated by the BET isotherm than by the Langmuir isotherm.

The relationship between the TOC and gas storage capacity at the reference pressure of 5000 psi is shown in Fig. 6, illustrating a good linear relationship. Based on eq. (5), the specific surface area for the four samples is calculated by assuming the diameter of methane to be 0.4 nm, see Fig. 7. The range of specific surface area for the Marcellus Shale is 3.38-14.16 m$^2$/g.
Comparison of Free Gas and Adsorbed Gas

It can be seen from eq. (9) that \((1-\phi)K_a\) and \(\phi S_g\) represent the contributions of adsorbed gas and free gas in shale. The actual reservoir properties of Marcellus Shale are used. Porosity of 0.142 and initial gas saturation of 90% are employed for calculation. We calculated the \((1-\phi)K_a\) of four samples using eqs. (21) for the Langmuir isotherm and eq. (22) for BET isotherm, respectively, as shown in Fig. 8. For the Langmuir isotherm, Fig. 8(a) shows that gas desorption is comparable to free gas at low reservoir pressure, while gas desorption is less important at high reservoir pressure. However, for the BET isotherm, Fig. 8(b) illustrates that gas desorption is significant at both high and low reservoir pressure.

Calculation of Original Gas in Place

The traditional method for calculating the original gas in place for free gas is expressed below (Ambrose et al., 2010):

\[
v_f = 32.0368 \times \frac{\phi S_g \rho_b}{\rho_s B_g}, \tag{23}\]

where \(v_f\) is the free gas volume in scf/ton, \(\phi\) is reservoir porosity, \(S_g\) is the initial gas saturation, \(\rho_b\) is the bulk rock density, \(\text{g/cm}^3\), and \(B_g\) is the gas formation volume factor in reservoir volume/surface volume.

Ambrose et al. (2010) proposed a new method to calculate the free gas volume by considering the volume occupied by the adsorbed gas on the surface based on the Langmuir isotherm equation. The porosity occupied by adsorbed gas based on the Langmuir isotherm is:

\[
\phi_{a,\text{Langmuir}} = 1.318 \times 10^{-6} M \frac{\rho_b}{\rho_s} \left( \frac{v_f p}{p + p_L} \right), \tag{24}\]
The final governing expression is shown below:

$$v_{f, \text{Langmuir}} = \frac{32.0368}{B_g} \left[ \frac{\phi(1 - S_w)}{\rho_b} - \frac{1.318 \times 10^{-6} M}{\rho_s} \times \left( \frac{v_f p}{p + p_f} \right) \right],$$  \hspace{1cm} (25)

where $S_w$ is the initial water saturation; $\rho_s$ is the adsorbed gas density, g/cm$^3$; and $M$ molecular weight of natural gas, lbm/lbmole.

The total original gas in place can be obtained by summation of free gas volume and adsorbed gas volume:

$$v_{t, \text{Langmuir}} = v_{f, \text{Langmuir}} + v_{a, \text{Langmuir}},$$  \hspace{1cm} (26)

where $v_{f, \text{Langmuir}}$ is the free gas volume based on the Langmuir isotherm, scf/ton, $v_{a, \text{Langmuir}}$ is the adsorbed gas volume based on the Langmuir isotherm, scf/ton, and $v_{t, \text{Langmuir}}$ is the total gas volume based on the Langmuir isotherm, scf/ton.

In this work, we modified the model for calculating original gas in place proposed by Ambrose et al. (2010) by considering the BET isotherm. The porosity occupied by adsorbed is modified as follows for the BET isotherm:

$$\phi_{a, \text{BET}} = 1.318 \times 10^{-6} M \frac{\rho_b}{\rho_s} \times \left\{ \frac{v_a Cp}{(\rho_o - p)[1 + (C-1)p/p_o]} \right\}$$  \hspace{1cm} (27)

The governing equation is obtained below:
The total original gas in place can be obtained by summation of free gas volume and adsorbed gas volume:

\[ V_{f,\text{BET}} = \frac{32.0368}{B_g} \left( \frac{\phi(1 - S_a)}{\rho_b} + \frac{1.318 \times 10^{-6} M}{\rho_s} \right) \left( \frac{v_m C_p}{(p_o - p) \left[ 1 + (C - 1) \frac{p}{p_o} \right]} \right) \]

The total original gas in place can be obtained by summation of free gas volume and adsorbed gas volume:

\[ V_{t,\text{BET}} = V_{f,\text{BET}} + V_{a,\text{BET}}, \]

where \( V_{f,\text{BET}} \) is the free gas volume based on the BET isotherm in scf/ton, \( V_{a,\text{BET}} \) is the adsorbed gas volume based on the BET isotherm in scf/ton, and \( V_{t,\text{BET}} \) is the total gas volume based on the BET isotherm in scf/ton.

The actual reservoir properties of Marcellus Shale are used for the calculation of original gas in place, as shown in Table 3. Using eqs. (24)-(27), the porosities of gas adsorption, free gas in place, adsorbed gas in place, and the total original gas in place are calculated, as summarized in Tables 4 and 5. As shown, the average total original gas in place is 519 scf/ton, calculated using the BET isotherm, which is larger than the 507 scf/ton calculated using the Langmuir isotherm. Hence, characterizing the gas adsorption isotherm is important for quantifying the total original gas in place and evaluating the economic potential of gas shales.

### Numerical Simulation Methods

In this work, a compositional simulator is used to model multiple hydraulic fractures and gas flow in Marcellus Shale reservoirs (CMG, 2012). In our simulation model, local grid refinement (LGR) with logarithmic cell spacing is used to accurately model gas flow from shale matrix to hydraulic fractures. Non-Darcy flow is considered for which the non-Darcy Beta factor, used in the Forchheimer number, is determined using a correlation proposed by Evans and Civan (1994). This approach has been extensively used to model transient gas flow in hydraulically fractured shale gas reservoirs (Rubin, 2010; Yu and Sepehmoori, 2014a, 2014b; Yu et al., 2014b). In the simulation model, the Langmuir isotherm is used to model gas desorption. Also, the adsorption data can be entered as a table form. Increase in gas recovery is used to assess the contribution of gas desorption in this work, and it is defined by

\[ \text{Increase in gas recovery} = \frac{Q_{\text{GasDesorption}} - Q_i}{Q_{\text{GasDesorption}}}, \]

where \( Q_{\text{GasDesorption}} \) is cumulative gas production with gas desorption effect, whereas \( Q_i \) is cumulative gas production without gas desorption effect.
Basic Reservoir Model

A Marcellus Shale area of about 207 acres was simulated by setting up a basic 3D reservoir model with dimensions of 6,000 ft \times 1,500 ft \times 130 ft, which corresponds to length, width, and thickness, respectively, as shown in Fig. 9. The reservoir has two shale layers. Porosity of bottom and upper layers is around 14.2% and 7.1%, respectively. The horizontal well are stimulated in the bottom layer with 16 fracturing stages and four perforation clusters per stage with cluster spacing of 50 ft. The total well length is 3,921 ft. There are almost 190 days of production data available for performing history matching and evaluating the effect of gas desorption on well performance.

Table 6 summarizes the detailed reservoir and fracture properties of this well. The reservoir is assumed to be homogeneous and the fractures are evenly spaced, with stress-independent porosity and permeability. The flowing bottom hole pressure in Fig. 10 is used to constrain the simulation and cumulative gas production is the history-matching variable. Table 7 lists reservoir permeability and fracture properties with a good history match without considering the gas desorption effect, as shown in Fig. 11.
In the subsequent simulation studies, we have performed history matching by considering gas desorption from the four shale samples and production forecasting for a 30-year period by gradually dropping the bottom hole pressure at 190 days to 2000 psi within one month and then maintaining 2000 psi until 30 years. The comparisons of gas desorption effect between the Langmuir and the BET isotherms for the four shale samples are shown in Figs. 12-15. It can be seen that gas desorption with the BET isotherm contributes more significantly to gas recovery than that with the Langmuir isotherm at the early time of production (190 days). The range of increase in gas recovery after 190 days of production with
the BET isotherm is 6.3%-26%, while the range with the Langmuir isotherm is 1.1%-4.7%. At 30 years of production, the range of increase in gas recovery with the BET isotherm is 8.1%-36.5%, while the range with the Langmuir isotherm is 4.3%-15.1%. Hence, it can be suggested that the gas desorption effect with the BET isotherm plays an important role in performing history matching at early time of production and predicting the ultimate gas recovery.

Conclusions
We have analyzed the laboratory measurements of gas adsorption from four shale samples in the Marcellus Shale using the Langmuir and BET isotherms. The effect of gas adsorption on calculation of original gas in place and well performance has been investigated. The following conclusions can be drawn from this work:

1. The measured gas adsorption in four samples from the lower Marcellus Shale is better described by the BET isotherm, rather than by the Langmuir isotherm.
2. A good linear relationship between gas storage capacity and TOC is obtained.
3. The range of specific surface areas for the Marcellus shale is 3.38-14.16 m²/g.
4. Gas desorption obeying the BET isotherm is comparable to the free gas at low and high reservoir pressure.
5. The average total original gas in place is 519 scf/ton when calculated using the BET isotherm, and 507 scf/ton calculated using the Langmuir isotherm.
6. For the horizontal well investigated in this study, the range of increase in gas recovery at 190 days of production with the BET isotherm is 6.3%-26%, while the range with the Langmuir isotherm is 1.1%-4.7%. After 30 years of production, the range of increase in gas recovery with the BET isotherm is 8.1%-36.5%, while the range with the Langmuir isotherm is 4.3%-15.1%.

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Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>TOC</td>
<td>Total organic content</td>
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<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
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<tr>
<td>BHP</td>
<td>Bottom hole pressure</td>
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</table>
IUPAC = International Union of Pure and Applied Chemistry
CMG = Computer Modeling Group
LGR = Local grid refinement
EIA = Energy Information Administration
DOE = Department of energy
OGIP = Original gas in place, tcf
MMSCF = $10^6$ standard cubic feet, ft³
$p$ = Pressure, psi
$v(p)$ = Gas volume of adsorption at pressure $p$, scf/ton
$v_L$ = Langmuir volume, scf/ton
$p_L$ = Langmuir pressure, psi
$p_o$ = Saturation pressure of the gas, psi
$v_m$ = Maximum adsorption gas volume for a complete unimolecular layer, scf/ton
$C$ = Constant related to the net heat of adsorption
$E_1$ = Heat of adsorption for the first layer
$E_L$ = Heat of the second and higher layers
$S$ = Specific surface area, m²/g
$n$ = Maximum number of adsorption layers
$u_g$ = Darcy velocity of gas, m/s
$S_g$ = Initial gas saturation
$\rho_g$ = Free gas density, g/m³
$\rho_a$ = Adsorbed gas density, g/m³
$k$ = Reservoir permeability, m²
$c_g$ = Isothermal gas compressibility factor
$K_a$ = Differential equilibrium portioning coefficient of gas at a given temperature
$\rho_b$ = Bulk density of shale, g/cm³
$Z(p)$ = Gas compressibility factor
$p_c$ = Gas critical pressure, psi
$c_{pr}$ = Reduced gas compressibility
$p_{pr}$ = Reduced pressure
$T_{pr}$ = Reduced temperature
$\phi$ = Reservoir porosity
$B_g$ = Gas formation volume factor
$\phi_{a,\text{Langmuir}}$ = Porosity of adsorbed gas based on Langmuir isotherm
$\rho_s$ = Adsorbed gas density, g/cm³
$\phi_{a,\text{BET}}$ = Porosity of adsorbed gas based on BET isotherm
$v_{f,\text{Langmuir}}$ = Free gas volume based on the Langmuir isotherm, scf/ton
$v_{a,\text{Langmuir}}$ = Adsorbed gas volume based on the Langmuir isotherm, scf/ton
$v_{t,\text{Langmuir}}$ = Total gas volume based on the Langmuir isotherm, scf/ton
$v_{f,\text{BET}}$ = Free gas volume based on the BET isotherm, scf/ton
$v_{a,\text{BET}}$ = Adsorbed gas volume based on the BET isotherm, scf/ton
$v_{t,\text{BET}}$ = Total gas volume based on the BET isotherm, scf/ton
$Q_{\text{GasDesorption}}$ = Cumulative gas production with gas desorption effect, MMSCF
$Q_i$ = Cumulative gas production without gas desorption effect, MMSCF
SI Metric Conversion Factors

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion Factor</th>
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<tbody>
<tr>
<td>ft</td>
<td>3.048 m</td>
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<tr>
<td>ft³</td>
<td>0.02832 m³</td>
</tr>
<tr>
<td>°F</td>
<td>(°C - 32)/1.8</td>
</tr>
<tr>
<td>psi</td>
<td>6.895 kPa</td>
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<tr>
<td>ton</td>
<td>9072 kg</td>
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<tr>
<td>acre</td>
<td>0.0016 m²</td>
</tr>
<tr>
<td>scf/ton</td>
<td>0.00312 m³/ton</td>
</tr>
</tbody>
</table>

References


