Research Article

Apparent Permeability Model for Shale Gas Reservoirs Considering Multiple Transport Mechanisms

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Shale formation is featured in nanopores and much gas adsorptions. Gas flow in the shale matrix is not a singular viscous flow, but a combination of multiple mechanisms. Much work has been carried out to analyze apparent permeability of shale, but little attention has been paid to the effect of unique gas behavior in nanopores at high pressure and adsorbed layer on apparent permeability. This work presents a new model considering multiple transport mechanisms including viscous flow (without slip), slip flow, Knudsen diffusion, and surface diffusion in the adsorption layer. Pore diameter and mean free path of gas molecules are corrected by considering the adsorption layer and dense gas effect, respectively. Then the effects of desorption layer, surface diffusion, and gas behavior on gas apparent permeability in nanopores of shale are analyzed. The results show that surface diffusion is the dominant flow mechanism in pores with small diameter at low pressure and that the effect of adsorbed layer and dense gas on apparent permeability is strongly affected by pressure and pore diameter. From the analysis results, the permeability value calculated with the new apparent permeability model is lower than in the other model under high pressure and higher than in the other model under low pressure, so the gas production calculated using the new permeability model will be lower than using the other model at early stage and higher than using the other model at late stage.

1. Introduction

Much attention has been paid to shale due to the considerable volume of natural gas trapped in it. Over the past decades, technology advances in horizontal drilling and hydraulic fracturing have enabled profitable production of shale gas. However, because of the unique deposit character and flow mechanisms of shale gas, controversy still exists on how much gas can be produced from shale [1].

Compared with conventional reservoirs, shales are characterized with pores between 1 and 100 nm, of which the dominant diameter is in nanoscale [2], making it difficult to get accurate shale permeability. Both experimental methods and theoretical methods were proposed to solve the problem. Due to overlarge time consumption, constant-pressure steady-state-flow measurement is not applicable to shale [3]. As a result, other approaches such as TED [4] and crushed rock method [5] were commonly adopted. However,

flow regimes could not be well characterized with experimental methods. Therefore, different theoretical models were proposed to investigate gas flow behavior in shale, among which apparent permeability models are the most prevailing and can be divided into two categories. The first category is correcting intrinsic permeability with a function of Knudsen number. Empirical parameters are included in most of the models, and gas flow regimes (viscous flow, slip flow, transition flow, and Knudsen diffusion) in a single capillary are classified based on Knudsen number and viscous flow slip flow and diffusion are mutually exclusive. Beskok and Karniadakis [6] conducted many experiments and presented a correction factor, and Florence et al. [7] simplified the correction factor. Many other correlations are also provided in apparent gas permeability in tight porous media [8–11]. The second category is weighted models, in which flow and diffusion are not mutually exclusive and their weight in apparent permeability is different at different Knudsen

numbers. When the Knudsen number is small, collision between gas molecules is dominant and gas flow is characterized by viscous flow and slip flow. When the Knudsen number is large, however, collision between gas molecules and the pore surface becomes dominant and gas flow is characterized by transition flow or Knudsen diffusion. In most cases, these two regimes coexist in nanopore in shale and account for different weights. Ertekin et al. [12] provided the weights for slip flow and Knudsen diffusion; apparent permeability is calculated by a weighted average of slip flow and Knudsen diffusion. Many new weighted models are also proposed by Liu et al. [13], Javadpour et al. [14, 15], Darabi et al. [16], and Shahri et al. [17]. These models have a relatively comprehensive analysis of gas flow in nanopores with the pore scale effect; however, some other unique properties of shale affecting gas apparent permeability are not considered.

The first characteristic of shale formation affecting apparent permeability is that there are a lot of organics and clay minerals with much gas adsorption in the shale matrix [18]. Gas adsorption in shale is generally believed to be single-layer physical adsorption [19]. It is suggested by Akkutlu and Fathi [20] that surface diffusion exists in the adsorption layer, and it is driven by a concentration gradient. Experiments of core permeability tests, pressure decay tests, and numerical calculation show that the permeability measured and calculated with adsorptive gas is much larger than that with nonadsorptive gas and indicate that the high permeability is caused by surface diffusion of adsorptive gas [21–23]. Many theories have been presented to describe surface diffusion in porous media, in which the hopping model is most widely used for surface diffusion [24–27]. If enough energy is acquired by the adsorbed gas molecule and it bounces to the nearest adsorption site, activation process and surface diffusion happen. It is verified that it is reasonable to use Langmuir isotherms to study surface diffusion [28]. Wu et al. [29–31] proposed a surface diffusion model which takes account of coverage of adsorbed gas at high pressure. Although surface diffusion is incorporated in these models, the effect of the adsorbed layer on gas retention and flow capacity is often neglected, which is not negligible as the radius of shale nanopores is in the same order with that of methane molecules. Another impact factor of shale formation is that gas in shale nanopores is dense gas rather than rarefied gas [32]. In shale nanopores, the storage and transport space for gas molecules is in the same order with size of gas molecules and therefore makes the assumption of rarefied gas no longer valid and need correction. The intrinsic size of molecules and the interaction between molecules are negligible for ideal gas. Wang et al. [33, 34] build a multiscale scheme to capture both slip and nonideal gas effects and considered the Enskog equation to cover the dense gas effect in the nanochannel. However, the effects of the adsorption layer, surface diffusion, and dense gas in formation conditions are not all considered in most of the existing models, and an apparent permeability model is needed to incorporate all these impact factors.

This paper presents a comprehensive apparent permeability model in which all the flow mechanisms, including viscous flow, slip flow, Knudsen diffusion, adsorption layer,

FIGURE 1: Langmuir adsorption isotherm.

surface diffusion, and dense gas effect, are taken into account. Then the effects of the desorption layer, surface diffusion, and dense gas in shale nanopores with different diameters are analyzed.

2. Apparent Permeability Model for Shale Nanopores

2.1. Adsorption Layer. The Langmuir isothermal adsorption equation is widely used to describe the adsorption and desorption of coal bed methane [32] and also introduced into the study of the transport regime of shale gas. It is based on instantaneous phase equilibrium; that is, adsorption or desorption due to pressure change is completed instantaneously. As the permeability of the shale matrix is extremely low, desorption time is negligible compared with gas flow in nanopores and the assumption made by Langmuir is also valid in shale gas reservoirs. The equation is as follows:

$$V = \frac{V_L \cdot p}{P_L + p}, \quad (1)$$

in which V is the volume of adsorbed gas per unit mass of shale, m^3/t ; V_L is the Langmuir volume, m^3/t , denoting the maximum adsorption capacity of the shale matrix at a certain temperature; and P_L is the Langmuir pressure, MPa , denoting the pressure at which the actual adsorption is half of the maximum adsorption on the adsorption isotherm, as shown in Figure 1.

As the radius of shale nanopores is in the same order with that of methane molecules, the effect of the adsorbed layer on gas retention and flow capacity is not negligible. For example, a pore whose diameter is 4 nm cannot allow 10 methane molecules at most to pass at the same time. In a single capillary, the adsorbed layer reduces the capacity of fluid flow, as shown in Figure 2. However, the effect of the adsorbed layer varies with different pore diameters: for pores whose diameter is larger than 100 nm, the effect

FIGURE 2: The effect of the adsorbed layer on the effective sectional flow area of pores of different diameters.

FIGURE 3: Hopping model for surface diffusion.

is negligible; for pores whose diameter is smaller than 10 nm, the adsorbed layer accounts for a large portion of the shale pores and narrows the flow channel significantly, as shown in Figure 2.

The adsorbed layer is taken into account in this paper with the assumption of single-layer adsorption. As adsorption molecules do not exist on all adsorption sites, coverage of adsorption molecules is introduced to calculate the thickness of the adsorbed layer; the effective pore diameter is [11]

$$d = d_0 - 2d_M\theta, \quad (2)$$

in which d_0 is the actual pore diameter, m; d_M is the diameter of gas molecules, m; and θ is the coverage of adsorbed gas based on (1), dimensionless, and it is defined as

$$\theta = \frac{p}{p_L + p}. \quad (3)$$

The effective pore radius is

$$r = \frac{d}{2}. \quad (4)$$

The hopping model is used in this paper to characterize surface diffusion in shale gas reservoirs, as shown in Figure 3. According to the hopping model, if enough energy is acquired by the adsorbed gas molecule and it bounces to the nearest adsorption site, activation process and surface diffusion happen. The surface diffusion model in this paper is based on the model of Wu et al. [29], and the assumptions are as follows:

- (1) A local equilibrium exists between bulk gas and adsorbed gas.

- (2) Surface transport takes place by activated diffusion, that is, site hopping.
- (3) The surface diffusion coefficient at higher pressure can be corrected by that at lower pressure with coverage of adsorbed gas defined in (3).

A surface diffusion coefficient at higher pressure is offered by correcting the coefficient at lower pressure, considering the effect of gas coverage on surface diffusion [26]:

$$D_s = D_s^0 \frac{(1 - \theta) + (\kappa/2)\theta(2 - \theta) + \{H(1 - \kappa)\}(1 - \kappa)(\kappa/2)\theta^2}{(1 - \theta + (\kappa/2)\theta)^2}, \quad (5)$$

in which D_s is the surface diffusion coefficient, m^2/s ; D_s^0 is the surface diffusion coefficient at low pressure, m^2/s ; $H(1 - \kappa)$ is the Heaviside function, dimensionless; θ is the coverage of adsorbed gas defined in (3), dimensionless; and κ is the ratio of the rate constant for blockage to the rate constant for forward migration, dimensionless. According to Xiong et al. [11], D_s^0 can be calculated with (6); $H(1 - \kappa)$ is defined in (7) and (8).

$$D_s^0 = (8.29 \times 10^{-7}) T^{0.5} \exp\left(-\frac{\Delta H^{0.8}}{RT}\right), \quad (6)$$

$$H(1 - \kappa) = \begin{cases} 0, & \kappa \geq 1, \\ 1, & 0 \leq \kappa \leq 1, \end{cases} \quad (7)$$

$$\kappa = \frac{\kappa_b}{\kappa_m}, \quad (8)$$

where T is the reservoir temperature, K; ΔH is the isosteric adsorption heat at the gas coverage of zero, J/mol; R is the

FIGURE 4: The effect of dense gas on the mean free path of gas molecules ($T = 360$ K).

gas universal constant, $8.314 \text{ J}/(\text{mol}\cdot\text{K})$; κ_m is the rate constant for forward migration, m/s; and κ_b is the rate constant for blockage, m/s. κ is set to 0.5 in this paper according to Wu et al. [29].

Eqs. (7) and (8) show that when $\kappa_m > \kappa_b$, there is a net forward movement even when the next site is occupied. When $\kappa_b > \kappa_m$, a nearly total blockage occurs. However, pore blockage cannot cause a negative movement; rather, the activated sorbate molecule stays at its original site.

2.2. Dense Gas Effect

2.2.1. Mean Free Path of Gas Molecules. The intrinsic size of molecules and the interaction between molecules are negligible for ideal gas. In this scenario, the mean free path of gas molecules can be expressed as [21]

$$\lambda = \frac{k_B T}{\sqrt{2} \pi P d_M^2}, \quad (9)$$

in which k_B is the Boltzmann constant, $1.3805 \times 10^{-23} \text{ J/K}$; T is the absolute temperature, K; P is the pressure, Pa; and d_M is the diameter of the gas molecule, m.

However, the size of the gas molecule is not negligible in actual shale formations. On the other hand, due to high pressure and short distance between gas molecules, the gas should be viewed as dense gas. According to the dense gas theory presented by Enskog [21], the mean free path of gas molecules is expressed as

$$\lambda = \frac{k_B T}{\sqrt{2} \pi \chi(\eta) P d_M^2}, \quad (10)$$

in which $\chi(\eta)$ is the collision correction factor defined by Cowling [33], dimensionless; η is a function of gas density

$$\eta = \frac{2}{3} \pi n d_M^3, \quad (11)$$

in which $n = P/k_B T$, which is the number of molecules.

2.2.2. Collision Correction Factor. According to the dense gas theory of Enskog [21], as the gas density increases, the percentage of gas molecules in the total volume is no longer negligible. Therefore, the gas molecules cannot be simplified as point particles any more, and the effect of molecular size on collision should be considered [33]

$$\Gamma' = \frac{\Gamma}{V'}, \quad (12)$$

in which $V' = 1 - 4\pi n d_M^3/3$, and Γ is the collision rate.

As the collision rate increases, a tertiary collision between molecules and the blocking effect are introduced. The rectified collision rate [33] is

$$\Gamma' = \chi(\eta) \Gamma \quad (13)$$

in which the collision correction factor [33] is

$$\chi(\eta) = \frac{1 - 11\pi n d_M^3/12}{1 - 4\pi n d_M^3/3} = \frac{1 - 11\eta/8}{1 - 2\eta}. \quad (14)$$

Eq. (12) is a function of η with first-order accuracy and is relatively accurate when $\eta < 0.03$. If a quaternary and higher collision is considered, a more accurate collision correction factor is acquired by numerical calculation [35]:

$$\chi(\eta) = 1 + 0.625\eta + 0.2869\eta^2 + 0.115\eta^3 + 0.0386\eta^4. \quad (15)$$

Figure 4 shows the variation of the mean free path of gas molecules of methane at formation pressure and a temperature of 360 K. We can see that the difference between the mean free path of gas molecules of the ideal gas and that of the dense gas effect is not significant at low pressure. However, as pressure increases, the difference becomes increasingly significant; that is, the dense gas effect is more significant at higher formation pressure. In addition, considering that nanopores are well developed

FIGURE 5: Three gas transport mechanisms in shale nanopores.

in the shale matrix and the fact that the diameter of gas molecules is in the same order as that of the pore diameter, methane molecules should not be viewed as point particles and the effect of intrinsic size of molecules should be considered.

2.3. Apparent Permeability Model. There are three transport mechanisms for gas flow in shale nanopores (see Figure 5): surface diffusion of adsorbed gas, viscous flow and slip flow caused by collision between bulk gas molecules, and Knudsen diffusion caused by collision between bulk gas molecules and the pore surface.

Based on the surface diffusion coefficient in 5, the surface diffusion permeability of the adsorbed phase in a single nanopore is acquired:

$$k_s^0 = -\frac{J_s \mu}{\rho_{\text{ads}} (\partial P / \partial x)} = \frac{D_s C_s \mu}{\rho_{\text{ads}} P}, \quad (16)$$

in which k_s^0 is the surface diffusion permeability of the adsorbed phase, mD; ρ_{ads} is the density of the adsorption gas, kg/m^3 , which is a fitting parameter of experiment data based on the Langmuir theory, which can be calculated with SLD models [36]; μ is the viscosity of the adsorption gas, mPa-s; P is the pressure; C_s is the concentration of the adsorbed gas, kg/m^3 ; and M is the gas molar mass, kg/mol .

According to Wu et al. [29], C_s can be calculated as

$$C_s = \frac{4\theta M}{\pi d_M^3 N_A}. \quad (17)$$

However, surface diffusion is the transport regime for adsorbed gas and is irrelevant to free gas in the bulk phase. Therefore, in order to get total apparent permeability, surface diffusion permeability of the adsorption layer should be corrected and combined with apparent permeability of the bulk phase. For surface diffusion, the flow section is made up by the molecules in the adsorption layer and should be converted to the effective flow section for the whole

pore, so the weighting coefficient of surface diffusion ζ_{ms} is introduced [30]:

$$\zeta_{ms} = \frac{\phi}{\tau} \left[\left(1 - \frac{d_M}{r} \right)^{-2} - 1 \right], \quad (18)$$

in which ϕ is the shale porosity and τ is the tortuosity.

In summary, surface diffusion permeability in a single capillary can be expressed as

$$k_s = \frac{\zeta_{ms} D_s C_s \mu}{\rho_{\text{ads}} P}. \quad (19)$$

For the viscous/slip flow and Knudsen diffusion of the bulk phase, the weighting coefficients are [31]

$$\omega_v = \frac{1}{1 + \text{Kn}}, \quad (20)$$

$$\omega_k = \frac{1}{1 + 1/\text{Kn}}, \quad (21)$$

in which Kn is the Knudsen number, which is defined as

$$\text{Kn} = \frac{\lambda}{d}. \quad (22)$$

For a single capillary, the viscous flow and slip flow permeability of the bulk phase can be expressed as

$$k_{\infty} = \frac{\phi r^2}{8\tau}. \quad (23)$$

Despite the fact that the generalized model cannot cover all the flow regimes, it is completely applicable to viscous flow and slip flow when $\text{Kn} \leq 1$. Therefore, the correction factor for permeability can be introduced to characterize the pressure-driven viscous flow and slip flow. The viscous flow or slip flow permeability of the bulk phase driven by pressure difference can be expressed as

$$k_v^0 = \frac{\phi r^2}{8\tau} f(\text{Kn}). \quad (24)$$

TABLE 1: Parameters for the validation case.

Parameter	Symbol	Unit	Value
Formation temperature	T	K	300
Porosity	ϕ	Dimensionless	0.048
Tortuosity	τ	Dimensionless	1.35
Gas type	CO ₂	—	—
Gas molecule diameter	d_M	m	4.64×10^{-10}
Gas molar mass	M	kg/mol	4.4×10^{-2}
Universal gas constant	R	J/(mol·K)	8.3145
Boltzmann constant	K_B	J/K	1.3805×10^{-23}
Molar volume of gas under standard condition	V_{std}	m ³ /mol	0.0224
Avogadro's constant	N_A	1/mol	6.02×10^{23}
Langmuir pressure	P_L	MPa	1.8
*Isosteric adsorption heat at the gas coverage of zero	ΔH	J/mol	203,000
*The ratio of the rate constant for blockage to the rate constant for forward migration	κ	Dimensionless	0.21
*Pore diameter	d_0	nm	2.8

The parameters highlighted with asterisk (*) are matched with the experimental data.

The viscous flow and slip flow permeability without considering the weighting coefficient can be expressed as [6]

$$k_v^0 = \frac{\phi r^2}{8\tau} [1 + \alpha \text{Kn}] \left[1 + \frac{4\text{Kn}}{1 + \text{Kn}} \right], \quad (25)$$

in which α is the rarefaction coefficient for ideal gas; its expression is shown in (26) by Beskok and Karniadakis [6] based on lots of experiments.

$$\alpha = \frac{128}{15\pi^2} \tan^{-1} [4\text{Kn}^{0.4}]. \quad (26)$$

The viscous flow and slip flow permeability in a single capillary driven by pressure difference considering the weighting coefficient defined in (20) is

$$k_v = \frac{\phi r^2}{8\tau} \frac{1 + \alpha \text{Kn}}{1 + \text{Kn}} \left[1 + \frac{4\text{Kn}}{1 + \text{Kn}} \right]. \quad (27)$$

The Knudsen diffusion permeability of the bulk phase is [16]

$$k_k^0 = \frac{2\phi}{3\tau} r V_{\text{std}} \mu \left(\frac{8}{\pi R T M} \right)^{0.5}, \quad (28)$$

in which V_{std} is the volume of a mole of gas under standard conditions, 0.0224 m³/mol.

The Knudsen diffusion permeability of the bulk phase, considering the weighting coefficient defined in (21), becomes

$$k_k = \frac{2\phi}{3\tau} r V_{\text{std}} \mu \left(\frac{8}{\pi R T M} \right)^{0.5} \frac{1}{1 + 1/\text{Kn}}. \quad (29)$$

The total apparent permeability of shale nanopore is

$$k_t = k_s + k_v + k_k. \quad (30)$$

FIGURE 6: Validation of the proposed model with experimental data (from [37]).

In the apparent permeability model shown in (28), the permeability contribution of the bulk gas and the adsorption layer is calculated with an effective pore diameter, and viscous/slip flow and Knudsen diffusion are weighted as shown in (20) and (21), respectively.

3. Results and Discussion

3.1. Model Validation. To validate the model proposed in this paper, experimental data for CO₂ from [37, 38] is applied. This experiment used extremely accurate differential-pressure transducers to measure the flow of gas passing

FIGURE 7: The effect of different factors on total apparent permeability (pore diameter = 4 nm).

through the core sample under in situ conditions. And the laboratory set-up is fully automated to avoid human error and maintain the temperature stable. In the experiments, organic-rich shale samples from Marcellus shale are used and CO_2 is used as absorbent gas. Therefore, the experiment data is applied to validate the model with surface diffusion considered in this study. The detail of the experiment is presented in [38].

The parameters are shown in Table 1, in which the parameters highlighted with asterisk (*) are matched with the experimental data. The density of bulk gas is calculated in (31); gas viscosity and the z -factor are calculated with the numerical approximate method proposed by Lee et al. [39] and Dranchuk and Abou-Kassem [40]. The density of adsorption gas can be a fitting parameter of experiment data based on the Langmuir theory; it can be calculated with SLD models [36] more accurately.

$$\rho = \frac{pM}{zRT}. \quad (31)$$

In this study, three models are used to match the experiment data as shown in Figure 6. In the first model, gas slippage is considered; we could find that the matching result is not good. In the second model, both slippage and Knudsen diffusion are considered; the result shows that this model has a better fit than the first model. In the third model, all the effects are considered, and we got the best fit here. On the other hand, we could find that the fitting average pore diameter differs from each other. If more flow mechanisms are considered, the fitting average pore diameter would be

smaller. At the same time, we could find that the fitting average pore diameter using the third model is far smaller than the other two models; this is because surface diffusion has a great impact on gas transport for this case (the pressure is quite low and the pore size is in nanoscale). The effects of different flow mechanisms and pore diameter on transient behavior will be discussed later in this study.

3.2. Applicability of the Model. The apparent permeability model of shale nanopores presented in this paper is compared with previous models, as shown in Figure 7. Parameters used in the model are shown in Table 2.

Figure 7 shows the total apparent permeability of shale (pore diameter = 4 nm) at different pressures, in which various factors are considered. We can see that the effect of the adsorption layer and dense gas on total apparent permeability is not significant, when compared with Beskok's model, while surface diffusion increases total apparent permeability considerably. As pressure increases, the improvement of total apparent permeability due to surface diffusion decreases, the dense gas effect reduces total apparent permeability, and the effect of the adsorption layer on total apparent permeability is still insignificant; therefore, the increment of total apparent permeability due to all three factors decreases with increased pressure.

Figure 8 shows total apparent permeability of shale (pore diameter = 50 nm) at different pressures, in which various factors are considered. We can conclude from the figure that the effect of the adsorption layer on total apparent permeability is still insignificant compared with Beskok's model [6]. In

TABLE 2: Parameters for modeling results and discussion.

Parameter	Symbol	Unit	Value
Formation temperature	T	K	368
Porosity	ϕ	Dimensionless	0.05
Tortuosity	τ	Dimensionless	3.5
Gas type	CH_4	—	—
Gas molecule diameter	d_M	m	3.8×10^{-10}
Gas molar mass	M	kg/mol	1.6×10^{-2}
Universal gas constant	R	J/(mol·K)	8.3145
Boltzmann constant	K_B	J/K	1.3805×10^{-23}
Molar volume of gas under standard condition	V_{std}	m^3/mol	0.0224
Avogadro's constant	N_A	1/mol	6.02×10^{23}
Langmuir pressure	P_L	MPa	5.82
Isosteric adsorption heat at the gas coverage of zero	ΔH	J/mol	16,000
The ratio of the rate constant for blockage to the rate constant for forward migration	κ	Dimensionless	0.5
Pore diameter	d_0	nm	2/4/10/20/50/100/200

FIGURE 8: The effect of different factors on total apparent permeability (pore diameter = 50 nm).

addition, surface diffusion is smaller at high pressure, when compared with Figure 7.

3.3. Composition of Apparent Permeability. Parameters used in this section are shown in Table 2. Figure 9 shows surface diffusion permeability and its percentage in total apparent permeability at different pressures. We can see that surface

diffusion permeability is higher at low pressure and contributes more to total apparent permeability, and it considerably decreases with increasing pressure, because the desorption of the adsorbed phase reduces the coverage rate and thus decreases the concentration of adsorbed gas, which is unfavorable for surface diffusion; however, the decrement of the coverage rate increases the vacancy rate of adsorption sites,

FIGURE 9: Surface diffusion permeability and its percentage in total apparent permeability.

FIGURE 10: Viscous flow and slip flow permeability and their percentage in total apparent permeability.

which is favorable for adsorbed gas molecules to jump from one adsorption site to another. Consequently, surface diffusion permeability at low pressure is larger.

Meanwhile, in smaller pores, the percentage of the adsorption layer in pore space is larger and the surface diffusion effect is more significant: when the pore diameter is no more than 10 nm, the contribution of surface diffusion to total apparent permeability is more than 60% even when formation pressure is up to 40 MPa; when the pore diameter is more than 50 nm, the percentage of surface diffusion permeability is smaller than 10% even when pressure is as low as 5 MPa.

Figure 10 shows viscous flow and slip flow permeability driven by pressure difference and its percentage in total

apparent permeability at different pressures. From the figure, we can see that the viscous flow and slip flow permeability are higher at lower pressure and decrease with increasing pressure. The explanation is that as pressure increases, the mean free path of gas molecules and the Knudsen number increase, the correction factor of permeability becomes smaller, the transport mechanism transits from slip flow to viscous flow, the gas slip effect becomes weaker, and apparent permeability driven by pressure difference approaches a constant.

The viscous flow and slip flow permeability and surface diffusion permeability are in the same magnitude and decrease with increasing pressure, but the decline rate of the former is significantly smaller than that of the latter,

FIGURE 11: Knudsen diffusion permeability and its percentage in total apparent permeability.

FIGURE 12: Apparent permeability of shale nanopores of different diameters.

and the percentage of viscous flow and slip flow in total apparent permeability increases with increasing pressure. For pores whose diameter is larger than 50 nm, viscous flow and slip flow permeability is dominant and even when pressure decreases to 5 MPa, the contribution is more than 70%; for pores whose diameter is no more than 10 nm, even when pressure reaches 40 MPa, the percentage of viscous flow and slip flow in total apparent permeability is smaller than 15%.

Figure 11 shows Knudsen diffusion permeability and its percentage in total apparent permeability at different pressures. We can see from the figure that Knudsen diffusion permeability is higher at low pressure and it decreases rapidly

with pressure, because as pressure increases, the mean free path of gas molecules decreases, the Knudsen number becomes smaller, and the collision between gas molecules and the pore surface becomes smaller and even negligible. At low pressure, smaller diameter means larger Knudsen number and the collision rate of gas molecules and the pore surface is high and therefore makes Knudsen diffusion permeability larger.

The percentage of Knudsen diffusion permeability in total apparent permeability depends on both formation pressure and pore diameter. For pores whose diameter is larger than 50 nm, the percentage of k_v is dominant, while k_v/k_t increases with increasing pressure and therefore makes the

FIGURE 13: The effect of the adsorbed layer on apparent permeability of shale (pore diameter = 2 nm).

percentage of Knudsen diffusion permeability decrease with increasing pressure; for pores whose diameter is no more than 10 nm, the percentage of k_s is dominant and k_s/k_t decreases with increasing pressure and therefore makes the percentage of Knudsen diffusion in total apparent permeability increase with increasing pressure; for pores whose diameter is around 20 nm, k_k/k_t increases and then decreases with increasing pressure.

Figure 12 shows total apparent permeability of a single capillary at different pressures. We can see from the figure that total apparent permeability decreases with increasing pressure and there is a plateau when the pressure is larger than 10 MPa, which is the Klinkenberg permeability. At low pressure, however, as the mean free path of gas molecules and the pore surface (Knudsen diffusion) and hopping of the adsorbed phase dramatically improve total apparent permeability, and this effect is more significant for a smaller diameter. As shown in Figure 9, the surface diffusion effect is more significant in small pores and particularly significant at low pressure, while

viscous and slip flow are more significant at large pores. Therefore, there is an intersection for the curves of total apparent permeability of a single capillary of different grades of diameter. And when ΔH and κ are larger, the contribution of surface diffusion will decrease; the intersections will happen at lower pressure. For example, when pressure is lower than 2.5 MPa, the total apparent permeability of a single capillary whose diameter is 100 nm is smaller than that whose diameter is 4 nm. However, this does not mean that the flow rate in a 4 nm tube can be larger than that of a 100 nm tube, because the flow section for a 100 nm tube is more than 500 times that of a 4 nm tube.

3.4. Sensitivity Analysis. In this section, the effect of the adsorbed layer, Knudsen diffusion, dense gas effect, and pore size distribution on apparent permeability is analyzed; the parameters of the model are shown in Table 2.

3.4.1. Adsorbed Layer. The effect of the adsorption layer on total apparent permeability of shale (pore diameter = 2 nm)

FIGURE 14: The effect of adsorbed layer on apparent permeability of shale (pore diameter = 50 nm).

is shown in Figure 13. Figure 13 indicates that the effect of the adsorption layer on three kinds of permeability is significant, because the adsorption layer reduces the effective flow space in nanopores and thus intensifies surface diffusion but reduces viscous flow and slip flow permeability as well as Knudsen diffusion permeability. As a result, despite that total apparent permeability is mainly affected by surface diffusion, the adsorbed layer improves total apparent permeability.

The effect of the adsorption layer on total apparent permeability of shale (pore diameter = 50 nm) is shown in Figure 14. Figure 14 indicates that the effect of the adsorption layer on three kinds of permeability and total apparent permeability is insignificant, because the percentage of the adsorption layer in the 50 nm pore is negligible. The adsorption layer reduces the effective flow space in nanopores and intensifies surface diffusion permeability but reduces viscous flow and slip flow permeability and Knudsen diffusion permeability. However, total apparent

permeability in the 50 nm pore is predominantly affected by viscous flow and slip flow; therefore, the adsorption layer reduces total apparent permeability.

In order to characterize the effect of the adsorption layer on total apparent permeability, the improvement factor of total apparent permeability due to adsorption layer is defined as

$$\varepsilon_{\text{ads}} = \frac{k_{t(\text{considers adsorbed layer})} - k_{t(\text{does not consider adsorbed layer})}}{k_{t(\text{does not consider adsorbed layer})}} \times 100\%. \quad (32)$$

Figure 15 shows the improvement factor of total apparent permeability due to the adsorption layer at 20 MPa. From the figure, we can see that for pores whose diameter is smaller than 20 nm, as total apparent permeability is dominated by surface diffusion, the introduction of the adsorption layer improves total apparent permeability; for pores whose diameter is larger than 20 nm, as total apparent

FIGURE 15: The effect of the adsorbed layer on total apparent permeability (formation pressure = 20 MPa).

FIGURE 16: The effect of gas density on apparent permeability of shale (pore diameter = 2 nm).

FIGURE 17: The effect of gas density on apparent permeability of shale (pore diameter = 50 nm).

permeability is dominated by Darcy flow or slip flow, the adsorption layer reduces total parent permeability. In addition, both improving and reducing effect becomes weaker as pore diameter increases.

3.4.2. Dense Gas Effect. Figure 16 shows the effect of dense gas on total apparent permeability of shale (pore diameter = 2 nm). From the figure, we can see that the effect of dense gas on all kinds of apparent permeability is insignificant in spite of pressure change. As dense gas effect reduces the mean free path of gas molecules and therefore reduces the Knudsen number, slip flow and Knudsen diffusion permeability are reduced, while surface diffusion permeability keeps constant. Therefore, the dense gas effect reduces total apparent permeability.

Figure 17 shows the effect of dense gas on total apparent permeability of 50 nm pores. The trend of Figure 17 is similar to that of Figure 16, with the difference that the effect is even more insignificant in this scenario.

Similarly, in order to characterize the effect of dense gas on total apparent permeability, the improvement factor

of total apparent permeability due to dense gas effect is defined as

$$\varepsilon_{\text{ads}} = \frac{k_{t(\text{considers dense gas effect})} - k_{t(\text{does not consider dense gas effect})}}{k_{t(\text{does not consider dense gas effect})}} \times 100\%. \quad (33)$$

Figure 18 shows the improvement factor of total apparent permeability of pores of different diameters due to dense gas effect. From the figure, we can see that the dense gas effect reduces total apparent permeability. For pores whose diameter is smaller than 20 nm, total apparent permeability is dominated by surface diffusion permeability, which is barely affected by the dense gas effect, so the effect of dense gas on total apparent permeability is insignificant when the pore diameter is very small. As the pore diameter increases, the percentage of surface diffusion permeability in total apparent permeability gradually decreases and therefore the decline rate of total apparent permeability increases with increasing pore diameter. For pores whose diameter is larger than 20 nm, total apparent permeability is generally affected by

FIGURE 18: The effect of gas density on total apparent permeability (20 MPa).

FIGURE 19: Schematic of capillary bundle.

Darcy flow or slip flow, which is reduced by introduction of the dense gas effect. As the pore diameter increases, the effect of dense gas on the mean free path decreases and therefore the decline rate of total apparent permeability decreases.

3.4.3. Pore Size Distribution. Gas retention and transport mechanism in shale nanopores is closely related to the pore diameter. However, pore size distribution of the shale core is in a wide range, the effect of the adsorption layer on pores of different diameters varies, and consequently the Knudsen number at the same temperature and pressure is different. Therefore, pore size distribution should be considered in the characterization of total apparent permeability of actual shale formation to make it more feasible.

Based on the transport mechanism for a single capillary in shale gas reservoirs, the storage space in shale is simplified as ideal rock which is made up by a bundle of capillaries of various diameters, as shown in Figure 19. Pore distribution of a shale formation of interest is used for calculation of apparent permeability, as shown in Figure 20 (the data is from [41]). Total apparent permeability k_{ta} can be expressed as

$$k_{ta} = \frac{\sum_{i=1}^N k_{ti} (d_i/2)^2 \chi_i}{\sum_{i=1}^N (d_i/2)^2 \chi_i}, \quad (34)$$

where d_i is the effective pore diameter of capillary i , m; χ_i is the percentage of capillary i , %; and k_{ti} is the total apparent permeability of capillary i , m.

FIGURE 20: Pore size distribution curves of typical shale in Barnett (from [41]).

FIGURE 21: Total apparent permeability of type shale.

In the capillary bundle model, the tortuosity of each capillary is 3.5, which is an assumption in this case. Actually, this value may be higher than its truth, and different capillaries are of different tortuosity.

The model is used to analyze the apparent permeability of typical shale at different pressure, as shown in Figure 21. The figure shows that pore size distribution of the typical shale makes it equivalent to a single capillary, whose diameter is between 8 nm and 45 nm. In addition, when the pressure is larger than 20 MPa, the apparent permeability of shale approaches a constant, that is, Klinkenberg permeability, because the mean free path of gas molecules and Knudsen number are small and make the percentage of Knudsen diffusion and surface diffusion small.

3.5. Permeability Calculation Procedure and Model Limitations. If a certain shale field is given, the apparent permeability can be calculated with the procedure shown in Figure 22. The parameters should be obtained beforehand

FIGURE 22: Procedure for apparent permeability calculation.

including formation temperature, porosity, pore diameter, gas type, and its physical and thermodynamic parameters as shown in Table 2. Formation temperature, porosity, and pore diameter can be obtained by geological analysis. Gas molecule diameter and molar mass are determined if a certain type of gas is given. Langmuir pressure should be obtained with isothermal adsorption tests, and isosteric adsorption heat can be calculated with the Clausius-Clapeyron equation [42]. The ratio of the rate constant for blockage to the rate constant for forward migration κ is a constant which should be evaluated, which can be set as 0.5 for flow in nanopores referring to Wu et al. [29].

However, there are still some limitations for this model. The pore size will change at high pressure because of the reduction of effective stress [43]. This apparent permeability model is based on a single nanopore, while the permeability in core scale should be given in reservoir simulation and rate/pressure transient analysis. Based on pore structure characterization [44], a pore network model is needed to accomplish this based on the apparent permeability model proposed in this paper, and this is our future work.

4. Conclusions

An apparent permeability model is presented in this paper, in which multiple flow mechanisms, including viscous flow, slip flow, Knudsen diffusion, adsorption layer, surface diffusion, and dense gas effect are taken into account. The main findings can be summarized as follows:

- (1) The effect of the adsorption layer and dense gas on apparent permeability of shale nanopores is characterized and surface diffusion of adsorbed gas is introduced to establish an apparent permeability model for the shale matrix.

- (2) Apparent permeability of the shale matrix is composed of three parts: surface diffusion permeability of the adsorbed phase, Darcy flow and slip flow permeability of the bulk phase, and Knudsen diffusion permeability of the bulk phase. The percentage of permeability caused by various mechanisms in total apparent permeability depends on pore diameters: when the pore diameter is larger than 50 nm, Darcy flow and slip flow of the bulk phase are dominant transport mechanisms; when the pore diameter is no more than 10 nm, surface diffusion of the adsorbed phase is the dominant transport mechanism; when the pore diameter is between 10 and 50 nm, especially when the pore diameter is around 20 nm, the percentage of surface diffusion of the adsorbed phase, Darcy flow, and slip flow of the bulk phase and Knudsen diffusion of the bulk phase is equivalent.
- (3) If pressure is more than 20 MPa, for pores whose diameter is smaller than 20 nm, the adsorption layer improves total apparent permeability; for pores whose diameter is larger than 20 nm, the adsorption layer reduces total apparent permeability.
- (4) If pressure is less than 20 MPa, for pores whose diameter is smaller than 20 nm, the dense gas effect makes the declining rate of total apparent permeability increase with pore diameter; for pores whose diameter is larger than 20 nm, the dense gas effect makes the declining rate of total apparent permeability decrease with pore diameter.

Disclosure

This study was once presented in “China Shale Gas 2015 (International Conference)”.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References

- [1] I. Urbina, *Insiders Sound an Alarm Amid a Natural Gas Rush*, New York Times, New York, NY, USA, 2011.
- [2] V. Swami and A. Settari, "A pore scale gas flow model for shale gas reservoir," in *SPE Americas Unconventional Resources Conference*, Pennsylvania, USA, 2012.
- [3] A. J. Mallon and R. E. Swarbrick, "How should permeability be measured in fine-grained lithologies? Evidence from the chalk," *Geofluids*, vol. 8, no. 1, 45 pages, 2008.
- [4] J. Billiotte, D. Yang, and K. Su, "Experimental study on gas permeability of mudstones," *Physics and Chemistry of the Earth Parts A/B/C*, vol. 33, Supplement 1, pp. S231–S236, 2008.
- [5] D. L. Luffel, C. W. Hopkins, and P. D. Schettler, "Matrix permeability measurement of gas productive shales," in *SPE Annual Technical Conference and Exhibition*, Houston, TX, USA, October 1993.
- [6] A. Beskok and G. E. Karniadakis, "Report: a model for flows in channels, pipes, and ducts at micro and nano scales," *Micro-scale Thermophysical Engineering*, vol. 3, no. 1, pp. 43–77, 1999.
- [7] F. Florence, J. Rushing, K. Newsham, and T. Blasingame, "Improved permeability prediction relations for low permeability sands," in *Rocky Mountain Oil & Gas Technology Symposium*, Denver, CO, USA, April 2007.
- [8] F. Civan, "Effective correlation of apparent gas permeability in tight porous media," *Transport in Porous Media*, vol. 82, no. 2, pp. 375–384, 2010.
- [9] F. Civan, C. S. Rai, and C. H. Sondergeld, "Shale-gas permeability and diffusivity inferred by improved formulation of relevant retention and transport mechanisms," *Transport in Porous Media*, vol. 86, no. 3, pp. 925–944, 2011.
- [10] F. Civan, C. Rai, and C. Sondergeld, "Determining shale permeability to gas by simultaneous analysis of various pressure tests," *SPE Journal*, vol. 17, no. 3, pp. 717–726, 2012.
- [11] X. Xiong, D. Devegowda, G. G. Michel Villazon, R. F. Sigal, and F. Civan, "A fully-coupled free and adsorptive phase transport model for shale gas reservoirs including non-Darcy flow effects," in *SPE Annual Technical Conference and Exhibition*, San Antonio, TX, USA, October 2012.
- [12] K. Ertekin, G. A. King, and F. C. Schwerer, "Dynamic gas slippage: a unique dual-mechanism approach to the flow of gas in tight formations," *Spe Formation Evaluation*, vol. 1, no. 1, pp. 43–52, 1986.
- [13] Q. Liu, P. Shen, and P. Yang, "Pore scale network modelling of gas slippage in tight porous media," *Fluid Flow & Transport in Porous Media Mathematical and Numerical Treatment*, vol. 295, pp. 367–375, 2001.
- [14] F. Javadpour, D. Fisher, and M. Unsworth, "Nanoscale gas flow in shale gas sediments," *Journal of Canadian Petroleum Technology*, vol. 46, no. 10, 2007.
- [15] F. Javadpour, "Nanopores and apparent permeability of gas flow in mudrocks (shales and siltstone)," *Journal of Canadian Petroleum Technology*, vol. 48, no. 8, pp. 16–21, 2009.
- [16] H. Darabi, A. Ettehad, F. Javadpour, and K. Sepehrnoori, "Gas flow in ultra-tight shale strata," *Journal of Fluid Mechanics*, vol. 710, pp. 641–658, 2012.
- [17] M. R. Shahri, R. Aguilera, and A. Kantzas, "A new unified diffusion-viscous flow model based on pore level studies of tight gas formations," *SPE Journal*, vol. 18, no. 1, pp. 38–49, 2012.
- [18] J. B. Curtis, "Fractured shale-gas systems," *AAPG Bulletin*, vol. 86, pp. 1921–1938, 2002.
- [19] M. Mavor, *Barnett Shale Gas-in-Place Volume Including Sorbed and Free Gas Volume*, Fort Worth Geological Society, Texas, USA, 2003.
- [20] I. Y. Akkutlu and E. Fathi, "Multiscale gas transport in shales with local kerogen heterogeneities," *SPE Journal*, vol. 17, no. 4, pp. 1002–1011, 2012.
- [21] S. X. Liu, J. H. Zhong, X. G. Liu, L. I. Yong, Z. F. Shao, and L. Xuan, "Gas transport mechanism in tight porous media," *Natural Gas Geoscience*, vol. 25, pp. 1520–1528, 2014.
- [22] X. Cui, A. M. M. Bustin, and R. M. Bustin, "Measurements of gas permeability and diffusivity of tight reservoir rocks: different approaches and their applications," *Geofluids*, vol. 9, no. 3, 223 pages, 2009.
- [23] E. Fathi and I. Y. Akkutlu, "Nonlinear sorption kinetics and surface diffusion effects on gas transport in low-permeability formations," in *SPE Annual Technical Conference and Exhibition*, New Orleans, LA, USA, October 2009.
- [24] R. J. Ambrose, R. C. Hartman, M. D. Campos, I. Y. Akkutlu, and C. Sondergeld, "New pore-scale considerations for shale gas in place calculations," in *SPE Unconventional Gas Conference*, Pittsburgh, PA, USA, February 2010.
- [25] R. T. Yang, J. B. Fenn, and G. L. Haller, "Modification to the Higashi model for surface diffusion," *AIChE Journal*, vol. 19, no. 5, pp. 1052–1053, 1973.
- [26] Y. D. Chen and R. T. Yang, "Concentration dependence of surface diffusion and zeolitic diffusion," *AIChE Journal*, vol. 37, no. 10, pp. 1579–1582, 1991.
- [27] Y. D. Chen and R. T. Yang, "Surface and mesoporous diffusion with multilayer adsorption," *Carbon*, vol. 36, no. 10, pp. 1525–1537, 1998.
- [28] S. T. Hwang and K. Kammermeyer, "Surface diffusion in microporous media," *The Canadian Journal of Chemical Engineering*, vol. 44, no. 2, pp. 82–89, 1966.
- [29] K. Wu, X. Li, C. Wang, W. Yu, and Z. Chen, "Model for surface diffusion of adsorbed gas in nanopores of shale gas reservoirs," *Industrial & Engineering Chemistry Research*, vol. 54, pp. 3225–3236, 2015.
- [30] K. Wua, X. Li, C. Guo, and Z. Chen, "Adsorbed gas surface diffusion and bulk gas transport in nanopores of shale reservoirs with real gas effect-adsorption-mechanical coupling," in *SPE Reservoir Simulation Symposium*, Houston, TX, USA, February 2015.
- [31] K. Wu, X. Li, C. Wang, W. Yu, and Z. Chen, "Apparent permeability for gas flow in shale reservoirs coupling effects of gas diffusion and desorption," in *Proceedings of the 2nd Unconventional Resources Technology Conference*, CO, USA, 2014.

- [32] H. Y. Wang, J. M. Li, and H. L. Liu, "Progress of basic theory and accumulation law and development technology of coal-bed methane," *Petroleum Exploration and Development*, vol. 31, pp. 14–16, 2004.
- [33] Z. Wang, Y. Guo, and M. Wang, "Permeability of high-Kn real gas flow in shale and production prediction by pore-scale modeling," *Journal of Natural Gas Science and Engineering*, vol. 28, pp. 328–337, 2016.
- [34] M. Wang, X. Lan, and Z. Li, "Analyses of gas flows in micro- and nanochannels," *International Journal of Heat and Mass Transfer*, vol. 51, no. 13–14, pp. 3630–3641, 2008.
- [35] Cowling, & George, T., *The Mathematical Theory of Non-uniform Gases*, Cambridge University Press, Cambridge, England, 1970.
- [36] S. A. Mohammad, J. S. Chen Jr., A. M. R. L. Robinson, and K. A. M. Gasem, "Generalized simplified local-density/peng–robinson model for adsorption of pure and mixed gases on coals," *Energy & Fuels*, vol. 23, no. 12, pp. 6259–6271, 2009.
- [37] A. Behrang and A. Kantzas, "A hybrid methodology to predict gas permeability in nanoscale organic materials; a combination of fractal theory, kinetic theory of gases and boltzmann transport equation," *Fuel*, vol. 188, pp. 239–245, 2017.
- [38] M. Zamirian, K. Aminian, E. Fathi, and S. Ameri, "A fast and robust technique for accurate measurement of the organic-rich shales characteristics under steady-state conditions," in *SPE Eastern Regional Meeting*, Charleston, WV, USA, October 2014.
- [39] A. L. Lee, M. H. Gonzalez, and B. E. Eakin, "The viscosity of natural gases," *Journal of Petroleum Technology*, vol. 18, no. 8, pp. 997–1000, 1966.
- [40] P. M. Dranchuk and H. Abou-Kassem, "Calculation of Z factors for natural gases using equations of state," *Journal of Canadian Petroleum Technology*, vol. 14, no. 3, 1975.
- [41] A. Sakhaee-Pour and S. Bryant, "Gas permeability of shale," *SPE Reservoir Evaluation & Engineering*, vol. 15, no. 4, pp. 401–409, 2012.
- [42] A. L. Myers, "Thermodynamics of adsorption in porous materials," *AIChE Journal*, vol. 48, no. 1, pp. 145–160, 2002.
- [43] D. Yang, W. Wang, W. Chen, S. Wang, and X. Wang, "Experimental investigation on the coupled effect of effective stress and gas slippage on the permeability of shale," *Scientific Reports*, vol. 7, article 44696, 2017.
- [44] F. Yang, Z. Ning, Q. Wang, R. Zhang, and B. M. Krooss, "Pore structure characteristics of lower silurian shales in the southern Sichuan basin, China: insights to pore development and gas storage mechanism," *International Journal of Coal Geology*, vol. 156, pp. 12–24, 2016.