Three mechanisms model of shale gas in real state transport through a single nanopore

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Abstract. At present, the apparent permeability models of shale gas consider only the viscous flow and Knudsen diffusion of free gas, but do not take into account the influence of surface diffusion. Moreover, it is assumed that shale gas is in ideal state. In this paper, shale gas is assumed in real state, a new apparent permeability model for shale gas transport through a single nanopore is developed that captures many important migration mechanisms, such as viscous flow and Knudsen diffusion of free gas, surface diffusion of adsorbed gas. According to experimental data, the accuracy of apparent permeability model was verified. What's more, the effects of pressure and pore radius on apparent permeability, and the effects on the permeability fraction of viscous flow, Knudsen diffusion and surface diffusion were analysed, separately. Finally, the results indicate that the error of the developed model in this paper was 3.02%, which is less than the existing models. Pressure and pore radius seriously affect the apparent permeability of shale gas. When the pore radius is small or pressure is low, the surface diffusion cannot be ignored. When the pressure and the pore radius is big, the viscous flow occupies the main position.

1. Introduction

There are many types of nanopores in shale gas reservoirs. The flow regimes of shale gas in nanopores are slip flow or transition flow [1]. At present, the apparent permeability models of shale gas are mainly Beskok-Karmiadakis model [2], Javadpour model [3] and Klinkenberg model [4]. The Jones-Owens [5], Florence [6], Ertekin [7], Michel [8], Sakhaee-Bryant [9] and Civan [10] models are based on the Klinkenberg model, and the main difference of these models is that the computing methods of slippage factor are different. These models assume that shale gas is in ideal state, without considering the intermolecular force and molecular size of shale gas. In addition, these models only take the viscous flow and the Knudsen diffusion of free gas into account, but not consider the surface diffusion of adsorbed gas.

In this paper, shale gas is assumed in real state, and a new apparent permeability model for shale gas transport through a single nanopore is developed that captures many important migration mechanisms, such as viscous flow and Knudsen diffusion of free gas, surface diffusion of adsorbed gas. Then, according to experimental data, the accuracy of apparent permeability model was verified. Finally, according to the new model, the effect of surface diffusion to apparent permeability is discussed.
2. Theory

2.1. Viscous flow of free gas

It is assumed that the cross section of the pore is round, the inner walls are smooth. According to Hagen–Poiseuille equation [6], the mass flux of shale gas flowing in a single nanopore is given below:

\[ J_{vs} = -\rho \frac{r^2}{8 \mu} \frac{dp}{dz} \]  \hspace{1cm} (1)

where \( J_{vs} \) denotes mass flux of shale gas of viscous flow in kg/(m\(^2\) s), \( \rho \) is density of shale gas in kg/m\(^3\), \( r \) is pore radius in m, \( \mu \) is viscosity of shale gas in Pa·s, \( p \) is pressure in Pa, and \( z \) is shale gas transport distance in m.

Based on state equation of real gas, the density of shale gas is given by

\[ \rho = \frac{M}{RT} \frac{p}{Z} \]  \hspace{1cm} (2)

where \( M \) is molecular mass in kg/mol, \( R = 8.314 \) J/(mol·K) is universal gas constant, \( T \) is absolute temperature in K, and \( Z \) denotes compressibility factor of shale gas.

Then we substitute Eq. (2) to Eq. (1), Eq. (1) becomes:

\[ J_{vs} = -\frac{r^2}{8 \mu RT} \frac{dp}{dz} \]  \hspace{1cm} (3)

Eq. (3) is the viscous flow equation of shale gas in real state transport through a single nanopore.

2.2. Knudsen diffusion of free gas

The Knudsen diffusion equation of shale gas is given below [11):

\[ J_K = -MD_K \frac{dC}{dz} \]  \hspace{1cm} (4)

where \( J_K \) is mass flux of shale gas of Knudsen diffusion in kg/(m\(^2\) s), \( C \) is molar density of shale gas in mol/m\(^3\), and \( D_K \) is Knudsen diffusion coefficient of shale gas in m\(^2\)/s given by

\[ D_K = \frac{2r}{3} \sqrt{\frac{8ZRT}{\pi M}} \]  \hspace{1cm} (5)

According to state equation of real gas, the molar density of shale gas is given below:

\[ C = \frac{n}{V} = \frac{p}{ZRT} \]  \hspace{1cm} (6)

where \( n \) is gas moles in mol, and \( V \) is gas volume in m\(^3\).

Then we substitute Eq. (6) to Eq. (4), Eq. (4) becomes:

\[ J_K = -\frac{MD_K}{RT} \frac{d}{dz} \left( \frac{p}{Z} \right) \]  \hspace{1cm} (7)

However, compressibility factor is the function of temperature and pressure. We assume that the temperature is constant, then the below equation is derived:

\[ \frac{d}{dz} \left( \frac{p}{Z} \right) = \frac{dp}{dz} Z - \frac{dZ}{dz} \frac{dp}{Z} = \frac{p}{Z} \left( 1 - \frac{1}{Z} \frac{dZ}{dp} \right) \frac{dp}{dz} \]  \hspace{1cm} (8)

The isothermal compressibility of shale gas in real state is given below [12]:

\[ C_g = \frac{1}{p} = \frac{1}{Z} \frac{dZ}{dp} \]  \hspace{1cm} (9)
where \( C_g \) is isothermal compressibility of shale gas in \( 1/\text{Pa} \).

Then we substitute Eq. (8) and (9) to Eq. (7), Eq. (7) becomes:

\[
J_K = -\frac{MD_K}{RT} \frac{p \, dp}{Z \, dz}
\]  

(10)

Eq. (10) is Knudsen diffusion equation of shale gas transport through a single nanopore.

2.3. Surface diffusion of absorbed gas

The shale gas is adsorbed on the pore wall because of the organic matter and clay minerals in the shale, and the nanometer scale of the pores. The adsorbed gas on the pore wall is not stationary, but moves along the adsorption layer. This phenomenon is called surface diffusion. The surface diffusion mass flux of shale gas can be calculated by the Fick diffusion law [13, 14]:

\[
J_S = -MD_S \frac{dC_S}{dz}
\]  

(11)

where \( J_S \) is the surface diffusion mass flux of shale gas in \( \text{kg/(m}^2\cdot\text{s)} \), \( D_S \) is surface diffusion coefficient in \( \text{m}^2/\text{s} \). \( C_S \) denotes the concentration of adsorbed shale gas in \( \text{mol/m}^3 \), it means moles of adsorbed gas per unit volume in shale. The calculation method of \( C_S \) is related to the adsorption type of shale gas. Lots of literatures show that the adsorption of shale gas is monolayer adsorption, so \( C_S \) is expressed by Langmuir isotherm [15]:

\[
C_S = \frac{C_L p}{p_L + p}
\]  

(12)

Substituting Eq. (12) to Eq. (11), the surface diffusion equation of shale gas is given below:

\[
J_S = -MD_S C_L \frac{p_L}{(p_L + p)^2} \frac{dp}{dz}
\]  

(13)

where \( C_L \) is Langmuir maximum adsorption capacity in \( \text{mol/m}^3 \), \( p_L \) is Langmuir pressure in \( \text{Pa} \), and it represents the pressure when the amount of adsorption is half of the maximum amount of adsorption.

The surface diffusion coefficient is given below [16]:

\[
\frac{D_S}{D_{S0}} = \frac{1 - \theta + \frac{\gamma}{2} \theta (2 - \theta) + H (1 - \gamma) \frac{\gamma}{2} \theta^2}{(1 - \theta + \frac{\gamma}{2} \theta)^2}
\]  

(14)

\[
H = \begin{cases} 
0 & \gamma \geq 1 \\
1 & 0 \leq \gamma < 1
\end{cases}
\]

\[
\gamma = \frac{k_b}{k_m}
\]

where \( \theta \) is the gas surface coverage on nanopore wall at an equilibrium state, dimensionless. It is given by

\[
\theta = \frac{p}{p_L + p}
\]  

(15)

\( D_{S0} \) is surface diffusion coefficient when surface coverage is 0 in \( \text{m}^2/\text{s} \). \( \gamma \) is blockage parameter, dimensionless. \( k_b \) is blocking velocity coefficient of surface gas molecule in \( \text{m/s} \), and \( k_m \) is forward velocity coefficient of surface gas molecule in \( \text{m/s} \). \( H \) is a parameter related to \( \gamma \).

\( D_{S0} \) is expressed by [17]

\[
D_{S0} = 8.29 \times 10^{-7} T^{0.5} \exp \left( -\frac{\Delta H^{0.8}}{RT} \right)
\]  

(16)

where \( \Delta H \) is isosteric heat of adsorption in \( \text{J/mol} \).
2.4. Apparent permeability model of shale gas in real state

The total flux through a porous medium of shale gas due to a pressure gradient can be described as the sum of the fluxes due to viscous flow and Knudsen flow, without considering surface diffusion [18]. If the surface diffusion is considered, the total flux is the sum of the bulk flow flux of free gas flux and the surface diffusion flux of the adsorption gas [19]. So, the total flux through a porous medium of shale gas is the sum of viscous flux, Knudsen diffusion flux and surface diffusion flux, and it is given below:

\[
J = J_{vs} + J_K + J_S = -\left(\frac{r^2M}{8\mu RT} + \frac{2r}{3} \sqrt{\frac{8ZM}{\pi RT}} C_g \frac{p}{Z} + \frac{MD_S C_L p_L}{(p_L + p)^2}\right) \frac{dp}{dz}
\]

(17)

According to Eq. (8) and Eq. (17), the volume flux of shale is given by

\[
q = \frac{JA}{\rho} = -\pi r^2 \left[\frac{r^2}{8\mu} + \frac{2r}{3} \sqrt{\frac{8ZRT}{\pi M}} C_g \frac{ZRT D_S C_L p_L}{p(p_L + p)^2}\right] \frac{dp}{dz}
\]

(18)

The Darcy’s law is expressed by

\[
q = -\pi r^2 \frac{k_{app}}{\mu} \frac{dp}{dz}
\]

(19)

So, according to Eq. (18) and (19), the apparent permeability model of shale gas in real state through a single nanopore is derived. It is given below:

\[
k_{app} = \frac{r^2}{8} + \frac{2\mu r}{3} \sqrt{\frac{8ZRT}{\pi M}} C_g + \frac{\mu ZRT D_S C_L p_L}{p(p_L + p)^2}
\]

(20)

where \(k_{app}\) is apparent permeability of shale gas in m².

\(k_{vs}\), \(k_{Kn}\) and \(k_S\) denote the permeability of viscous flow, Knudsen diffusion and surface diffusion, as given below:

\[
k_{vs} = \frac{r^2}{8}, \quad k_{Kn} = \frac{2\mu r}{3} \sqrt{\frac{8ZRT}{\pi M}} C_g, \quad k_S = \frac{\mu ZRT D_S C_L p_L}{p(p_L + p)^2}
\]

(21)

\(\gamma_{vs}\), \(\gamma_{Kn}\) and \(\gamma_S\) denote the ratio of viscous flow permeability, Knudsen diffusion permeability and surface diffusion permeability to the total permeability, as given below:

\[
\gamma_{vs} = \frac{k_{vs}}{k_{app}}, \quad \gamma_{Kn} = \frac{k_{Kn}}{k_{app}}, \quad \gamma_S = \frac{k_S}{k_{app}}
\]

(22)

2.5. Model validation

Roy et al. reported experimental data for homogeneous porous media consisting of relatively cylindrical and straight nanopores in a 60 μm thick membrane (commercial Alumina filters-Anodisc 13). The experimental result and mass flux of other model [5-10] are presented in Figure 1. The new model results and experimental data show a reasonable match with an average error of 3.02%, as shown in Figure 1.
3. Results and discussions

According to Eq. (20) and (22), the apparent permeability and the ratio of viscous flow permeability, Knudsen diffusion permeability and surface diffusion permeability to the total permeability are calculated, separately, as shown in Figure 2. The range of pressure is from 0.1MPa to 100MPa, and the pore radius are 1nm, 5nm, 20nm and 50nm.

**Figure 2.** Effect of pressure and pore radius on apparent permeability and the ratio.

| Pore Radius (nm) | Apparent Permeability $k_{app}$ (mD) | Ratio $\gamma$ |
|------------------|-------------------------------------|---------------|
| 1                | $k_{app}$ vs $k_{Kn}$ vs $k_{S}$     |               |
| 5                | $k_{app}$ vs $k_{Kn}$ vs $k_{S}$     |               |
| 20               | $k_{app}$ vs $k_{Kn}$ vs $k_{S}$     |               |
| 50               | $k_{app}$ vs $k_{Kn}$ vs $k_{S}$     |               |
The apparent permeability of shale gas is sensitive to pressure, even at lower pressure, and it is higher at lower pressure, as shown in Figure 2(a). The position of the apparent permeability curve in the coordinate system is moving up as pore radius increasing. It’s higher in smaller pore.

The ratio of viscous flow permeability to total permeability is increasing as pressure decreasing, and the ratio of surface diffusion permeability to total permeability is decreasing rapidly. At the same time, the Knudsen diffusion mechanism and surface diffusion mechanism of shale gas are becoming more important as pore radius decreasing, and the viscous flow mechanism is less important. Figure 2(a) shows that viscous flow can be ignored at low pressure (<1MPa). Figure 2(d) shows that surface diffusion can be ignored at high pressure (p>10MPa) and in big pore (r>50nm). But there are lots of pores smaller than 50nm in shale rocks, so surface diffusion cannot be ignored under reservoir conditions.

4. Conclusions
In this paper, a new apparent permeability model for shale gas transport through a single nanopore is developed that captures many important migration mechanisms, such as viscous flow and Knudsen diffusion of free gas, surface diffusion of adsorbed gas. According to experimental data, the accuracy of apparent permeability model was verified. The error of this model is 3.02%.

The apparent permeability and the ratio of viscous flow permeability, Knudsen diffusion permeability and surface diffusion permeability to the total permeability are sensitive to pressure and pore radius. The ratio of viscous flow permeability to total permeability is increasing as pressure decreasing, and the ratio of surface diffusion permeability to total permeability is decreasing rapidly. The Knudsen diffusion mechanism and surface diffusion mechanism of shale gas are becoming more important as pore radius decreasing, and the viscous flow mechanism is less important. Surface diffusion cannot be ignored under reservoir conditions.

Acknowledgement
This work was financially supported by National Natural Science Foundation of China (No. 51604293), Shandong Provincial Natural Science Foundation, China (No. ZR2016EEB30), the Fundamental Research Funds for the Central Universities (No. 17CX02009A), Qingdao Applied Basic Research Program (No. 17-1-1-32-jch).

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