



# Influences of adsorption/desorption of shale gas on the apparent properties of matrix pores



WANG Jing<sup>1,\*</sup>, LUO Haishan<sup>2</sup>, LIU Huiqing<sup>1</sup>, LIN Jie<sup>3</sup>, LI Liwen<sup>3</sup>, LIN Wenxin<sup>4</sup>

1. MOE Key Laboratory of Petroleum Engineering in China University of Petroleum, Beijing 102249, China;

2. Department of Petroleum & Geosystems Engineering, The University of Texas at Austin, Austin 78712, USA;

3. PetroChina Huabei Oilfield Company, Langfang 065000, China;

4. School of Geosciences and Technology, Southwest Petroleum University, Chengdu 610500, China

**Abstract:** The adsorption/desorption effects impact the petro-physical properties of matrix pores during gas depressurizing production, such as effective pore radius, effective porosity, apparent permeability, which will further impact the gas flow regime. In this paper, the dynamic models of effective pore radius and apparent permeability under the action of gas adsorption/desorption are derived. The mathematical model of shale gas flow is established considering the effects of adsorbed gas on apparent properties and gas flow regime. After that, the model is solved and validated using a finite volume method and experimental and field data. Finally, the variations of apparent parameters of matrix pores and gas flow regimes during gas production, and the influences of adsorption on gas production are demonstrated. The results show that the effective pore radius, porosity and apparent permeability increase during gas production; the gas flow regime in stimulated reservoir volume (SRV) changes from slip flow to transition flow; if the impacts of adsorbed gas on gas production is overlooked, both original gas in place (OGIP) and gas production will be significantly overestimated. The cumulative gas production changes slightly as the adsorption layer thickness increases, but the gas recovery factor decreases.

**Key words:** shale gas; adsorption; desorption; matrix pore; apparent properties; flow regime; flow model

## Introduction

Large scale development of shale gas is affecting the supply of natural gas in the world. It is estimated that the global production of shale gas will reach  $4\ 000 \times 10^8\ \text{m}^3$  by 2020<sup>[1]</sup>. However, the shale gas development is very difficult because shale gas reservoirs have extremely low permeability of generally  $10^{-9}$  to  $10^{-6}\ \mu\text{m}^2$ , and low porosity of less than 10%<sup>[2]</sup>. The pore size of shale reservoir is also very small. According to statistics, pores less than 10 nm in radius occupy about 42% of the total pore volume, and part of pores and flow channels are even less than 2 nm. Only a small portion of pores are larger than 50 nm in radius<sup>[3–4]</sup>. Shale gas reservoirs are typical self-generation and self-storage gas reservoirs, in which gas exists in the form of free gas and absorbed gas, and the absorbed gas up accounting for 20%–80% must firstly desorb before production<sup>[5–6]</sup>. Because the size of shale pores is in nano-scale, a large amount of gas is adsorbed on the pore surface, and gas flow and gas desorption occur simultaneously, the flow regime of shale gas in matrix pores is complicated,

and influenced by a number of factors, including the pore size and pore pressure, as well as the process of gas adsorption and desorption, and finally impacts the production of shale gas. Nowadays, a large number of studies overlook the impact of adsorbed gas on the pore size, which, on one hand, leads to the overestimation of geological reserves<sup>[7–8]</sup>; on the other hand, makes it impossible to consider the effect of gas adsorption/desorption on the apparent properties of shale and gas flow regime during the shale gas production.

In this paper, the dynamic models of effective pore radius and apparent permeability under the action of gas adsorption/desorption are derived. On this basis, a mathematical model of shale gas flow considering the impact of adsorbed gas on apparent properties and gas flow regime is established. Then, the model is solved using a finite volume method. Finally, the variations of apparent parameters of matrix pores and gas flow regimes due to gas adsorption/desorption, and its influences on gas production are investigated using this model.

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\* **Corresponding author.** E-mail: wangjing8510@163.com

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## 1. Distribution and flow regimes of shale gas in nano-pores

Gas in matrix pores mainly includes free gas and adsorbed gas, as shown in Fig. 1. A lot of research indicates<sup>[9–10]</sup> that the adsorption rule of shale gas obeys the Langmuir model which is usually used to describe the monolayer adsorption, therefore, the effective pore radius,  $R_e$ , is the difference between the absolute pore radius,  $R_0$ , and the molecular diameter of methane,  $d_{CH_4}$ , under the saturated adsorption state. With the gas production, adsorbed gas on the pore surface desorbs and then flows out as the pore pressure reduces. During this process, the adsorption layer gets thinner, and the effective pore radius becomes larger. Because the size of shale pores is extremely small, the impact of the variation of effective pore radius caused by gas adsorption/desorption on apparent properties cannot be overlooked.

Fig. 2 shows the gas flow regimes classified by the Knudsen number,  $Kn$ . Knudsen number is defined as the ratio of mean free path of gas molecule to the pore diameter<sup>[11–12]</sup>.

$$Kn = \frac{\lambda}{D} \quad (1)$$

When  $Kn \leq 10^{-3}$ , gas flow belongs to Darcy flow; when  $10^{-3} < Kn \leq 10^{-1}$ , gas flow belongs to slippage flow; when  $10^{-1} < Kn \leq 10$ , gas flow belongs to transition flow; when  $Kn > 10$ , gas flow belongs to molecular-free flow. According to the above analysis, the effective pore radius is smaller than real radius due to the adsorbed layer. As the adsorbed gas desorbs, the effective radius gradually increases and then influences the gas flow regime. Therefore, the actual  $Kn$  is the ratio of the mean free path of gas molecule to the average pore effective diameter  $D_e$ :

$$Kn = \frac{\lambda}{D_e} \quad (2)$$

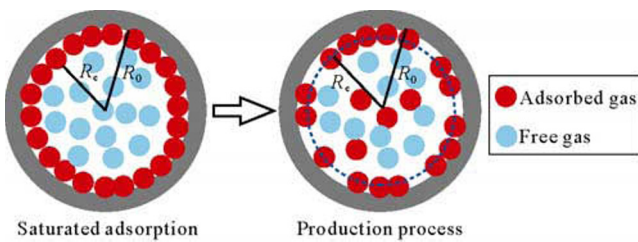


Fig. 1. Distribution of shale gas in a matrix pore.

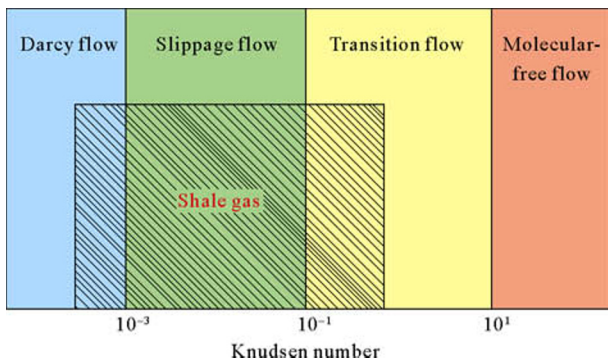


Fig. 2. Division of gas flow regimes.

## 2. Mathematical model of shale gas flow

### 2.1. Mass conservation equation

In order to establish the mathematical model of shale gas flow, several assumptions are proposed as follows: (1) shale matrix pores are spherical; (2) shale gas reservoirs do not contain water, or the bound water does not affect adsorbed gas; (3) adsorption of shale gas obeys the Langmuir isotherm; (4) gas reservoir is an isothermal system without consideration of energy exchange; (5) the equilibrium of adsorption/desorption is reached immediately. Therefore, the mass conservation equation of shale gas flow in nano-pores can be expressed as

$$\nabla \cdot \left( \frac{K_a \rho_g}{\mu_g} \nabla \Phi_g \right) + \rho_g q_g = \frac{\partial}{\partial t} (\rho_g \phi_e) + \frac{\partial \dot{m}}{\partial t} \quad (3)$$

### 2.2. Modeling of apparent permeability of shale gas flow

Gas flow regimes in nano-pores include Darcy flow, slippage flow, transition flow, and molecular-free flow. Shi et al.<sup>[13]</sup> deduced an apparent permeability model covering these flow regimes:

$$K_a = K_0 \left[ \frac{410(1+5Kn)}{410+Kn^4} + \frac{128\tau_m \mu_g \delta^2}{3\kappa_B \phi_e} \sqrt{\frac{1000\pi R}{MT}} \frac{Kn^5}{410+Kn^4} \right] \quad (4)$$

However, since gas molecules are adsorbed on the pore surface, causing decrease of the absolute permeability of matrix, the absolute permeability is a function of adsorption, and then Eq. (4) is transformed into

$$K_a = K_{0c} \left[ \frac{410(1+5Kn)}{410+Kn^4} + \frac{128\tau_m \mu_g \delta^2}{3\kappa_B \phi_e} \sqrt{\frac{1000\pi R}{MT}} \frac{Kn^5}{410+Kn^4} \right] \quad (5)$$

Moreover, the effective pore radius continuously changes and then impacts the Knudsen number during the process of desorption. Previous studies about the microscopic pore structure of shale indicate that the organic pore is nearly spherical or ellipsoidal<sup>[14–15]</sup>, hence, the matrix pore is approximately considered spherical. Then, the volume of a single pore without adsorbed gas is

$$V_0 = \frac{4}{3} \pi R_0^3 \quad (6)$$

The effective volume of a single pore under saturated adsorption condition is

$$V_{sa} = \frac{4}{3} \pi R_{sa}^3 \quad (7)$$

From Eq. (6) and Eq. (7), we can get

$$V_0 - V_{sa} = \frac{4}{3} \pi (R_0^3 - R_{sa}^3) = mV_L \quad (8)$$

Shale gas in matrix pore obeys the Langmuir isotherm, so

$$V_0 - V_e = \frac{4}{3} \pi (R_0^3 - R_e^3) = mV_L \frac{p_g}{p_g + p_L} \quad (9)$$

Combining Eq. (8) and Eq. (9) gives

$$\frac{R_0^3 - R_{sa}^3}{R_0^3 - R_e^3} = \frac{p_g + p_L}{p_g} \quad (10)$$

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