Calculation Model of Shale Reserves Considering the Adsorption Layer Based on Molecular Simulation

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Cite This: ACS Omega 2020, 5, 24138−24144

ABSTRACT: In this paper, molecular simulation methods are used to construct nanopore models of organic matter, montmorillonite, and quartz. The occurrence state of CH₄ molecules in shale nanopores was simulated, and the distribution characteristics of CH₄ molecules at different temperatures, pressures, and pore widths were obtained. The thickness and density of the adsorption layer of CH₄ molecules at different temperatures and pressures were studied. On the basis of these, a calculation model of shale gas reserves considering adsorption is proposed. The results show that CH₄ molecules in shale nanopores present a nonuniform distribution. Two obvious wave peaks form in the space close to the surfaces of the shale nanopore, and the wave peaks increase with the increase of pressure. As the pressure increases, a second peak appears and gradually becomes larger. The adsorption layer formed on the surface of the medium has a certain thickness and density, which are affected by pressure and temperature. In the calculation example, the difference between the calculation results of the shale gas reserve calculation models considering and not considering the adsorption layer is about 26%. The higher the proportion of adsorbed gas, the greater the calculation error, which is related to pressure and adsorption capacity.

1. INTRODUCTION

With the increasing demand for energy and the declining conventional oil and gas production, shale gas, as an important energy option, is receiving more and more attention all over the world.¹⁻¹² Compared with other fossil fuels, shale gas is an environmentally friendly fuel, which helps reduce a country’s overreliance on high-energy-consumption and high-pollution-emission resources and provides more opportunities for reducing air pollutants and greenhouse gas emissions.³⁻⁵ The reserves of shale gas reservoirs are an important indicator to evaluate whether shale gas reservoirs are feasible for development. They also have an important impact on the economic benefits of development. Therefore, it is necessary to accurately calculate the geological reserves of shale gas reservoirs.⁶⁻⁸

In different exploration and development stages, the mastery of shale gas reservoirs is different. Thus, the methods used should be different.⁹ In the early stage of exploration, there are not many exploratory wells. Thus, the basic information obtained is limited. The evaluation of geological reserves often uses a probability statistical method and a category method. The accuracy of the calculated geological reserves is low, and it is only used to estimate the reserves in general.¹⁰,¹¹ When the number of exploratory wells is enough and the core is effectively analyzed, the volume method can be used to calculate the reserves. At present, this method is widely used. Moreover, it can quickly evaluate and grasp the reserve status of shale gas reservoirs.¹²

The key to calculating reserves using a volumetric method is to determine the effective pore volume. Compared with conventional gas reservoirs, an important feature of shale gas reservoirs is that they contain a large amount of adsorbed gas.¹³,¹⁴ Curtis¹⁵ studied several shale gas basins in the United States, and the results showed that the proportion of adsorbed gas in the shale was 20⁻₈₅%. The gas in the shale, especially the adsorbed gas, needs to undergo the processes of desorption, diffusion, and seepage during the production process. Montgomery et al.¹⁶ showed that shale comprises inorganic and organic materials and the adsorbed gas amounts to more than half of the total gas content. Therefore, when calculating the reserves of shale gas reservoirs, the adsorbed gas must be considered.

The influence of adsorbed gas on the calculation of shale gas reservoir reserves by the volumetric method is mainly manifested in two aspects: (1) the gas adsorbed in the shale pores will make the shale pores smaller, so the space occupied by free gas is the shale pore volume minus the adsorption phase volume; (2) the density of the gas adsorbed on the pore surface

Received: August 7, 2020
Accepted: August 31, 2020
Published: September 8, 2020
is quite different from that of the bulk gas. So, the amount of gas adsorbed in shale should be calculated separately. However, shale reservoirs have their own particularities. The porosity and permeability of shale are much lower than those of conventional reservoirs. The pore structure is complicated. The specific surface area is large, and the gas flow in shale is complicated. In addition, the shale mineral composition is diverse, including clay minerals (montmorillonite, illite, etc.), clastic minerals (quartz, etc.), organic matter, etc. The adsorption capacity of these minerals is different. Moreover, the temperatures and pressures have a big influence on the adsorption capacity of these minerals. Therefore, it is important to have a more comprehensive understanding of shale adsorption. Moreover, further research on the influence of adsorption on reserves and development process is necessary.

In this study, three representative shale nanopore models (organic, montmorillonite, and quartz) were constructed based on a molecular simulation method. The occurrence state of methane molecules in shale nanopores was simulated. The distribution characteristics of methane molecules at different temperatures, pressures, and pore widths were studied. The thickness and density of the methane molecular adsorption layer were calculated. Moreover, the influencing factors and influence laws of methane molecular adsorption layer were analyzed. The adsorption phenomenon of methane molecules in shale nanopores was described from the microscopic view. Based on these, a calculation model of shale reserves considering the adsorption layer was proposed. The details of this study and the results are presented in Sections 2 and 3.

2. ESTABLISHMENT OF NANOPORE MODELS

According to the composition of shale, organic nanopore, montmorillonite nanopore, and quartz nanopore models are constructed. In this study, organic matter in shale is represented by graphene. Under natural conditions, the distance between graphene layers is 0.335 nm. To prevent the interference between gas molecules in different pores, three layers of graphene under natural conditions are taken as one layer of organic nanopores. Montmorillonite is a TOT-type clay mineral. There is a layer of aluminum oxide octahedron between the two layers of silicon–oxygen tetrahedron. Its crystal is a monoclinic system with the space group C2/m, where a and b are 0.523 and 0.906 nm, respectively. The value of c is variable and is related to the interlayer water content of mineral crystals. Both α and γ are 90°, and β is 99°. The crystal structure data can be obtained through experiments, and the specific atomic coordinates are shown in Table 1.

The construction of the three types of nanopore models is similar. First, the unit cell was established. Then, the structure of the unit cell was optimized, and the optimized structure was expanded into a supercell. Then, the surface was intercepted. Finally, the cut surface group was used to form nanopore models with different widths. The single-sided pore surface areas of graphene, montmorillonite, and quartz were 17.2165 × 22.2999, 18.9789 × 22.4378, and 14.73 × 25.5131 nm², respectively. The surface areas of the three models are different, which will affect the occurrence of gas. To eliminate the influence of surface area, the simulation results can be converted into the amount of adsorption per unit surface area. In this paper, to compare the existence of the three models, the structure with a surface area of 400 nm² is defined as a unit cell (UC). The distance between the centroids of two corresponding surfaces was defined as the pore width (2 nm). The models are shown in Figure 1.

In this study, molecules of methane were established and optimized to study their movements in shale nanopores. Grand Canonical Monte Carlo (GCMC) was used to simulate the transport of CH₄ in shale nanopores. In the GCMC method, ensemble configurations were created based on random numbers, and the relevant physical quantities of the system were calculated. Then, the ensemble configurations were changed. The relevant physical quantities of the system were calculated again. The changes in the relevant physical quantities were compared to filter the results. At present, this method is widely used for gas sorption in micropores, and it has a good agreement with the actual data.

3. RESULTS AND DISCUSSION

3.1. Microscopic Distribution of CH₄ Molecules in Nanopores

The occurrence of methane in nanopores was simulated, and the distribution characteristics of methane at different temperatures, pressures, and pore widths were studied, as shown in Figures 2 to 4.

| Table 1. Coordinates of Particles in the Unit Cell of Montmorillonite |
|-----------------|--------|--------|--------|
| type     | x      | y      | z      |
| Al       | 0.000  | 3.020  | 12.500 |
| O        | 0.808  | 4.530  | 11.250 |
| Si       | 0.472  | 1.510  | 9.580  |
| O        | 0.772  | 1.510  | 11.200 |
| O        | 0.0000 | 3.020  | 12.500 |
| O        | 0.0000 | 4.530  | 11.250 |
| O        | 0.0000 | 4.530  | 11.250 |
| H        | 0.772  | 4.530  | 10.812 |
| H        | 0.772  | 4.530  | 10.812 |
Figure 2 shows the effect of pressure on gas distribution. Figure 3 shows the effect of temperature on gas distribution, and Figure 4 shows the effect of pore type on gas distribution. As can be seen from the above figures, the lower the pressure and the higher the temperature, the more obvious the uneven distribution caused by gas adsorption. This is due to the presence of organic matter, clay minerals, and nanopores in shale reservoirs, where some methane gas exists in the form of the adsorption state. The adsorption state of the gas has an influence on the distribution of gas in pores, so that the number of gas molecules on the surface of the medium is significantly higher than that in the middle of pores, resulting in the uneven distribution of gas molecules.

Because of the adsorption, the gas distribution in the confined space is not uniform. Compared with the central region far away from the rock surface, within a certain range close to the rock surface, there are more gas occurrences with high density. The gas state of this part is also greatly different from that of the bulk phase gas. To study the nonuniform distribution of gas in the restricted nanospheres, the restricted spaces with parallel slits were stratified, and the number of gas molecules in each layer was counted according to the coordinates of the positions of the gas so as to calculate the density distribution. The specific calculation process is as follows.

The number of gas molecules located in the $i$ layer is first counted, marked as $N_i$, and the statistical range is $[Z_i - h, Z_i + h]$. $Z_i$ represents the coordinates of the $i$ layer, and $h$ represents half of the statistical width. The area of each small layer is assumed to be $S$, and the size of the area is related to the size of the model constructed. Then, the gas density of the $i$ layer is written as

$$\rho_i = \frac{0.001MN_i}{N_A \times S \times 2h} \quad (1)$$

where $\rho_i$ is the gas density, kg/m$^3$; $M$ is the molar mass of the gas, for methane gas, 16.04276 g/mol; and $S$ and $h$ are the area and height of the layer, m$^2$ and m, respectively.
For the analysis of the slit model constructed in this paper, $h = 0.15$ nm was used to carry out statistics within the width range of 0.3 nm before and after the sitting punctuation, and the average density obtained within this range is the density value of the coordinate point.

When temperature is 283 K, the density distribution diagrams of the gas in the organic matter pores at 1, 8, 19, and 25 MPa are shown in Figure 5.

Figure 5 shows that two distinct peaks appear in the space near the two surfaces of the organic matter pores, and the peaks increase with the increase of pressure. When the pressure is 1 MPa, the peak of the wave is less than 400 kg/m$^3$. When the pressure is 25 MPa, the peak of the wave increases to almost 600 kg/m$^3$. As the pressure increases, a second peak gradually appears after the first peak, and the second peak is very weak when the pressure is 1 MPa. When the pressure increases to 8 MPa, the second peak value appears obviously. With the further increase of the pressure, the second peak value gradually increases. As the pressure increases, the density in the middle of the pore also increases correspondingly.

3.2. Adsorption Layer Thickness and Density. From the above analysis, it can be seen that an adsorption layer will form on the surface of organic matter. For the study of the adsorption layer, the two more important aspects are the thickness and density of the adsorption layer. The density distribution of gas in the pore shows that the density of the adsorption layer is much higher than that of other positions in the pore. Based on this, the thickness of the adsorption layer can be calculated at different temperatures and pressures. The variation of the thickness of the adsorption layer on the surface of organic matter is shown in Figure 6. A functional relation of the change of adsorption layer thickness with pressure was obtained by fitting the relevant data.

At low pressure, the adsorbed gas is very close to the surface and can be considered as monolayer adsorption. Therefore, the thickness difference of the adsorption layer corresponding to 283, 303, and 333 K is small at low pressure. With the increase of pressure, more and more gas is adsorbed, which changes from a single adsorption layer to multiple adsorption layers. However, the binding of the surface to the gas is weakened. The higher the temperature, the more difficult the adsorption of the gas behind the first adsorption layer, and the smaller the adsorption layer formed. The influence of temperature on the thickness of the adsorption layer increases with an increase in temperature.

According to the thickness of the adsorption layer on the surface of organic matter at different temperatures and pressures, the gas mass within the thickness range was calculated. The density value of the adsorption layer was calculated based on the mass and the volume of the adsorption. The density values of the adsorption layer at different temperatures and pressures are shown in Figure 7.

Figure 7 shows that the density of the adsorption layer varies with different temperatures and pressures. The adsorption layer density increases when the temperature decreases and the pressure increases. However, the density of the adsorption layer is more sensitive to pressure, and with the change of pressure, the density value of the adsorption layer changes more. When the temperature is 333 K and the pressure rises from 1 to 40
MPa, the adsorption layer density changes from 180 to 337 kg/m³.

In the same way, the thickness and density of the adsorbed layer of methane in the montmorillonite and quartz holes were calculated, and the calculated value was also affected by temperature and pressure; moreover, the influence law was similar to that of the organic matter holes.

3.3. Establishment of Reserve Model Considering the Adsorption Layer. The gas in shale gas reservoirs includes free gas, adsorbed gas, and dissolved gas in water. Generally, the dissolved gas content is relatively small, which is often ignored in the calculation. Therefore, the calculation formula of shale gas reserves can be expressed as follows

\[
G_t = G_f + G_a
\]

(2)

where \(G_t\) is the total shale gas reserves, m³/t; \(G_f\) is the free gas quantity, m³/t; and \(G_a\) is the adsorbed gas quantity, m³/t.

In conventional gas reservoirs, both the porosity and pore diameter are large. The gas is basically not adsorbed or the amount of adsorbed gas is very small, so the measured pore volume is the occurrence space of free gas. However, the porosity and pore diameter are ultrasmall, and large amounts of adsorbed gas exist on the surface of pores. The adsorption of gas on the pore surface further reduces the pore diameter, and the influence of adsorbed gas on pore volume cannot be ignored. Therefore, it is necessary to modify the pore volume of free gas, that is, the calculation model of shale gas reserves should consider the adsorbed gas. The physical model with the volume occupied by adsorbed gas and the volume not taken into account is shown in Figure 8.

As can be seen from Figure 8, due to the existence of adsorbed gas, the occurrence space of free gas in shale pores decreases, which is equal to the connected pore volume minus the adsorbed gas volume. The calculation model of shale gas reserves considering the adsorbed gas is as follows

The free gas quantity

\[
G_f = \left[ V \times \varphi \times (1 - S_b - S_w) - \frac{G_a}{\rho_a} \right] \frac{P_{Tc}}{ZTP_c}
\]

(3)

The adsorbed gas quantity

\[
G_a = G_{as} \frac{p}{p + p_l}
\]

(4)

In shale reservoirs, the adsorption of gas will form an adsorption layer on the pore surface. The adsorption layer has a certain thickness and density, and its density is much higher than that of the free phase gas under the same temperature and pressure, so the adsorption layer has a certain influence on the calculation of shale gas reserves. In the calculation model, the density of shale rock is 2.5 g/cm³, and the values of other parameters are shown in Table 2.

When the formation pressure is 15 MPa and the temperature is 333 K, the standard temperature is 293K, the standard pressure is 0.101325 MPa, and the density of the adsorption layer is 259.0 kg/m³. The calculated amount of gas is 2.5271 m³/t if the influence of the adsorption layer is ignored. When the formation pressure is 25 MPa and the temperature is 333 K, the adsorption layer density is 298.7 kg/m³. The calculated amount of gas is 4.0733 m³/t without considering the influence of the adsorption layer. The adsorbed gas content, free gas content, adsorbed gas ratio, and the content without adsorption influence are calculated, respectively, under these two formation pressures. The calculation results are shown in Table 3.

Table 3 shows that when the formation pressure is 15 MPa, with the increase of formation adsorption capacity, the adsorbed gas ratio increases from 37.5 to 68.2% and the relative error increases from 12.8 to 26.1%. The higher the proportion of adsorbed gas, the larger the calculation error. This is because at the same formation pressure, the stronger the adsorption capacity of the formation, the more the adsorption of gas. Thus, the adsorption ratio will increase, which will have an influence on the calculation results. When the formation pressure is 25 MPa, compared with 15 MPa, under the same conditions, the proportion of adsorbed gas reserves decreases, and the relative error also decreases rapidly, basically maintaining at about 1–2%. The principle is that when the formation pressure is low, the difference between the adsorption layer and the free gas is great, and the amount of gas contained in the adsorption layer of the same volume is much larger than that in the free phase. When
the formation pressure is high, the difference between the adsorption layer and the free phase decreases, and the gas content of the two is basically the same at the same volume, so the relative error decreases.

4. CONCLUSIONS

In this study, the occurrence state and distribution characteristics of methane molecules in shale nanopores were simulated. The thickness and density of the methane molecular adsorption layer were calculated. Moreover, the influencing factors and influence laws of the methane molecular adsorption layer were analyzed. Based on these, a calculation model of shale reserves considering the adsorption layer was proposed. The conclusions are as follows.

(1) Due to the presence of adsorption, the gas distribution in the restricted space is uneven.
(2) The density of the gas in the space close to the two surfaces of the nanopores will form two distinct peaks, which will increase with the increase of pressure.
(3) With the increase of pressure, the single adsorption layer is transformed into multiple adsorption layers, but the binding of the surface to the gas is weakened. Moreover, temperature has a significant influence on the thickness of the adsorption layer under that condition.
(4) Both temperature and pressure have a great influence on the density of the adsorption layer. However, the density of the adsorption layer is more sensitive to pressure.
(5) A calculation model of shale reserves considering an adsorption layer is proposed. The error between the model considering the adsorption layer and the model without considering the adsorption layer is about 26%. The value of the calculation error is related to the ratio of adsorption gas, adsorption capacity, and pressure.

Table 2. Parameters of Reserve Calculation

| parameter | value |
|---|---|
| $v_t$ (m$^3$/t) | 0.4 0.4 0.4 0.4 0.4 0.4 0.4 0.4 |
| $\Phi$ (%) | 5 5 5 5 5 5 5 5 |
| $S_o/S_w$ (%) | 0/30 0/30 0/30 0/30 0/30 0/30 0/30 0/30 |
| $G_aL$ (m$^3$/t) | 1.4 1.5 1.7 1.8 2.0 2.5 3.0 3.3 |
| $P_t$ (MPa) | 5.7 6.0 6.4 6.7 7.1 8.0 9.0 9.6 |

Table 3. Influence of Adsorption on Reserve Calculations

| formation pressure (MPa) | $G_o$ (m$^3$/t) | $G_f$ (m$^3$/t) | $G_t$ (m$^3$/t) | adsorbed gas ratio | relative error |
|---|---|---|---|---|---|
| 15 | 2.018182 | 4.106153 | 0.308375 | 0.111368 |
| 25 | 2.349398 | 4.115888 | 0.3988 | 0.013765 |

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Notes
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ACKNOWLEDGMENTS
The authors acknowledge financial support of the National Major Science and Technology Projects of China (2016ZX05025004-003), the National Natural Science Foundation of China (No. 51234007), and the Innovation Funding Program of China University of Petroleum (East China) (YCX2019019).
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