Molecular Simulation of Displacement of Shale Gas by Carbon Dioxide at Different Geological Depths

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ABSTRACT

The rising worldwide energy demand has greatly stimulated the exploitation of shale gas. Meantime, global warming mainly caused by CO₂ emission is a significant concern. As a new scenario, injecting CO₂ to displace shale gas is proposed to improve the exploitation efficiency of shale gas and reduce the amount of CO₂ emission. In this work, we use a grand canonical Monte Carlo simulation to investigate the displacement of shale gas by CO₂ and the sequestration of CO₂ simultaneously in a modeled shale matrix at different geological depths from 1 to 4 km, where the shale is modeled by inorganic clay mineral and organic matter. We find that both the displacement amount of CH₄ and the sequestration amount of CO₂ increase with the pore size of the shale at a fixed CO₂ injection pressure, which suggests that the hydro-fracturing technology would be very beneficial for displacement exploitation of shale gas. Moreover, we also find that the optimum operating condition for CO₂ displacing shale gas is at the depth of 1 km, which provides a guidance and reference for displacement exploitation of shale gas by CO₂.

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1. INTRODUCTION

Recently, the exploration and development of shale gas have received extensive attention worldwide because of its numerous advantages such as low pollution, wide distribution, and abundant resource (Howarth et al., 2011). Shale gas, as an unconventional gas source, refers to a kind of natural gas that exists in shale reservoirs (Shaikh and Ji, 2016; Youinou, 2016), and is now increasingly deemed as a low carbon and an environmentally friendly energy option. The United States of America (USA) is the earliest country to apply the horizontal drilling and hydro-fracturing into the exploration and development of shale gas (Arora and Cai, 2014; Connor et al., 2015). The output of shale gas has reached 13.78 billion cubic meters per year in USA, with an average annual growth rate of 47.7% (Zhai et al., 2014), while, the natural gas from shale formations is about 23% in 2010. And, it is anticipated to contribute 49% of gas production by 2035 (Ashmoore et al., 2016). In order to reduce pollution and meet a surge in energy demand, China aims to produce 30 billion cubic meters of shale gas per year by 2020, from the current level of 1.3 billion cubic meters (Wang et al., 2016). Therefore, considerable efforts are undertaken by Chinese enterprises through the development of research programs in industry to make this resource successfully and economically available (Gasparik et al., 2012).

Currently, the ultralow porosity of shale and ultralow permeability of gas reservoirs are still a great challenge in the exploration of shale gas (Clarkson et al., 2016). Hydro-fracturing is a commonly used method to enhance matrix permeability of unconventional reservoirs and enable the economic production of shale gas from the shale reservoirs (Chen and Carter, 2016; Clark et al., 2012; Clarkson et al., 2016). However, the

hydro-fracturing would cause severe environment impacts, e.g. huge water consumption, potential contamination of water and so on (Clark et al., 2012; Connor et al., 2015; Krogulec and Sawicka, 2015; Krupnick and Gordon, 2015). Alternatively, the new scenario, the injection of CO₂ gas to displace the adsorbed CH₄, has been proposed by some researchers (Kowalczyk et al., 2012; Shi and Durucan, 2003; Wang et al., 2015b; Wu et al., 2015; Yu et al., 2008). It arouses extensive interests from scientists, because it can improve the shale gas recovery and sequestrate CO₂ simultaneously.

Most studies on the displacement of CH₄ adsorbed in shale matrix by CO₂ have been carried out by the experiment and computation at present. Wu (Wu et al., 2015) studied the displacement of CH₄ in carbon nanochannels by molecular dynamics (MD) simulations. And they drew a conclusion that CO₂ can displace the adsorbed CH₄ directly. Yuan (Yuan et al., 2015) also explored the displacement of CH₄ by injecting CO₂ on graphene, and found that CO₂ can be adsorbed on graphene more easily than CH₄, which may be a good candidate for displacement of CH₄. Pathak (Pathak et al., 2015) performed MD simulations on the kerogen-methane-carbon dioxide system to understand the absorption-adsorption-desorption phenomena of the super critical CO₂ fluid, and found that CO₂ can sweep the absorbed CH₄ from the kerogen matrix in the shales. Kowalczyk (Kowalczyk et al., 2012) investigated displacement of CH₄ by Monte Carlo simulations, and proposed two-stage mechanism for the displacement of CH₄ from carbon nanospaces by coadsorbed CO₂. Wang (Wang et al., 2015a) conducted experiments to study the coal-bed CH₄ displacement by CO₂ injection, and found that the adsorption capacity of CO₂ is stronger than that of CH₄ under the same condition in the process of displacement.

A large proportion of pores within the gas shale matrix are nanosized, and most of these pores are associated with the constituents of the shale matrix and the contents of each components (Cui et al., 2009). In addition, the shale matrix often contains some free gases in relatively large pores and adsorbed gas on the organic matter and inorganic minerals (Zhang et al., 2012). To deal with the complex situation, it is necessary to simplify the complicated structure of shale matrix to gain some basic insights into its adsorption behavior. There are two ways to address this topic in the literatures. One is to assume the clay-rich shale as the crystal structure of montmorillonite with the basal spacing and number of ions changing (Zhai et al., 2014). The disadvantage of this method does not include the organic matter. In fact, the organic matter is an indispensable factor on the CH_4 adsorption in shale matrix. The other method is to model the complex natural matrixes as a collection of independent, on-interconnected slit pores with perfect graphitic walls without consideration of inorganic minerals (Hu et al., 2011). As a result, it is important to construct an all-atom shale model including inorganic minerals and organic matter to investigate the adsorption and displacement of CH_4 in gas shale matrix.

In this work, we proposed a modified and generalized shale matrix model including inorganic minerals and organic matter. Then, the mechanism of the displacement of CH_4 by CO_2 in shale matrix model was investigated through molecular simulations. Finally, some discussion was also addressed.

2. Computational details

2.1 Models and potentials

Since CH_4 is the major component of shale gas, we use it to represent the shale gas. The

components of gas shale matrix include organic matter, inorganic clay minerals, quartz, carbonate, calcite, pyrite, and the others (Tan et al., 2014). The main ingredients in the gas shale matrix from different places are nearly the same, but their contents of the components are different. Here, we mainly consider the case of CH₄ in shale matrix, which contains organic matter and inorganic clay minerals. To construct the shale matrix model containing inorganic clay mineral and organic matter, we used two perfect montmorillonite sheets to represent the inorganic clay mineral. Montmorillonite is a typical 2:1 inorganic clay mineral, and the unit cell consists of an Al–O octahedral sheet and two Si–O tetrahedral sheets, while the Al–O sheet is sandwiched between Si–O sheets. Generally, it is believed that the polycyclic aromatic hydrocarbon is a major organic component of shale matrix, especially for shale gas reservoirs. Therefore, we used methylnaphthalene to represent the organic matter in the shale matrix here.

We constructed a simulation box (31.1×35.9×c Å) that contains two inorganic layers and two organic layers (see Figure 1). As mentioned above, the perfect montmorillonite sheets were used to represent the inorganic layers. The structure of the montmorillonite sheets was obtained from the Cambridge Crystallographic Data Centre (CCDC) database. First, two perfect montmorillonite sheets were stacked each other in such a way as shown in Figure 1. Then, a set of methylnaphthalene molecules were absorbed into the interlayer space, where the pore size of our model was adjustable through the basal spacing. The methylnaphthalene molecules absorbed into the interlayer space were fixed, as the organic matter in shale matrix. During our simulations, the shale matrix model containing organic and inorganic matter was treated as a rigid material with atoms frozen.

In this work, CH₄ was represented by a spherical united-atom model (Cao et al., 2003; Lan et al., 2010), CO₂ was modeled as a three-site rigid linear molecule with three charged Lennard-Jones (LJ) interaction sites (Liu and Wilcox, 2013). The potential parameters were taken from the transferable potentials for phase equilibrium (TraPPE) model (Jorgensen et al., 1996). The realistic CLAYFF force field (Cygan et al., 2004) for inorganic clay minerals in the shale matrix model was used in this work, and the Dreiding force field (Mayo et al., 1990) was adopted for the organic matter in the shale matrix model. The site-site LJ potentials were adopted to calculate the CH₄–CH₄ and CH₄–shale intermolecular interactions. In addition, when calculating the CO₂–CO₂ and CO₂–shale intermolecular interactions, the Coulombic potentials were added. In the MUSIC software, to avoid the conversion of chemical potential into pressure, the normal move acceptance probability was transformed to relate with the component fugacity of gas bulk phase, which was calculated by the Peng–Robinson equation of state (EOS) (Peng et al., 2011). All the Lennard–Jones (LJ) cross-interaction parameters were determined by the Lorentz–Berthelot mixing rules [$\sigma_{ij}=(\sigma_{ii}+\sigma_{jj})/2$ and $\epsilon_{ij}=(\epsilon_{ii} \cdot \epsilon_{jj})^{1/2}$], where corresponding parameters are shown in Table 1.

2.2 Grand canonical Monte Carlo simulations

The grand canonical Monte Carlo (GCMC) simulations were used to investigate the displacement of CH₄ in shale matrix at different geological depths. First, the CH₄ molecules were preadsorbed into the nanochannels of the shale matrix. The partial pressure of CH₄ in the binary CH₄–CO₂ bulk mixture, which is corresponding to the geological pressure condition of shale gas, determines the preadsorption amount of CH₄ in the shale matrix. Then, we injected a small amount of CO₂ molecules into the bulk CH₄ gas and equilibrated

the resulting mixture in the shale reservoirs. After equilibration, the adsorption amounts of CO₂ and CH₄ in shale matrix were calculated by analyzing the compositions of the adsorbed mixture. Finally, we gradually increased the CO₂ partial pressure (i.e. CO₂ injection pressure) in the binary CH₄-CO₂ bulk mixture up to 90 MPa, which makes it possible to study the microscopic mechanism of the displacement of CH₄ from the shale matrix. In each case, 2×10^7 configurations were generated. The first half is for the system to reach the equilibrium, whereas the second half is for sampling.

In the displacement process of CH₄ by CO₂, the displacement amount of CH₄ is defined as

$$N_{displacement} = N_{initial} - N_{P_{CO_2}} \quad (1)$$

The percentage of displacement is defined as

$$\eta_{displacement} = \frac{N_{initial} - N_{P_{CO_2}}}{N_{initial}} \quad (2)$$

Where $N_{initial}$ and $N_{P_{CO_2}}$ denote absolute amount of CH₄ adsorbed in the nanochannel of shale matrix when the partial pressure of CO₂ in bulk mixture is equal to zero (i.e. pure CH₄) and P_{CO_2} , respectively.

The pore volume of the adsorbent accessible to the gas molecule is calculated by the method of Myers from the ideal gas law (Talu and Myers, 2001)

$$V_{pore} = \frac{RN_m T}{pm_m} \quad (3)$$

where R is the gas constant, T is the temperature, p is the pressure, and N_m is the number of adsorbed probe molecules per molar mass of the adsorbents, which is obtained from the GCMC simulations of non-adsorbed helium ($\epsilon_{He}/K_b = 10.22$ K; $\sigma_{He} = 2.85$ Å) gas in shales at low pressure and ambient temperature.

The temperatures and pressures corresponding to the specific geological depths were introduced in the simulations to reproduce the T/P conditions encountered in a typical sedimentary basin, mainly based on the fact that the compacting stress gradient is 15 MPa/km and the geothermal gradient is 30 K/km(Cygan et al., 2004; Titiloye and Skipper, 2005). The T/P conditions were listed in Table 2. All the GCMC simulations were performed by using the computational packages MUSIC(Gupta et al., 2003).

3. RESULTS AND DISCUSSION

3.1 Modeling.

The total organic content and basal spacing of the shale matrix model were determined by fitting the experimental and simulation data. To validate the simulated data and the model, we made a series of comparisons with available experimental data from the literature. An experimental adsorption isotherm of CH₄ in the shale with the total organic content of 5.08%, was measured at 363 K by Zeng et al(Zeng et al., 2014). In agreement of the total organic content of shale matrix with the experimental sample, fourteen methylnaphthalene molecules were absorbed into the slit pore formed by two perfect montmorillonite sheets. Then, a series of adsorption isotherms of CH₄ in the shale model with different basal spacing were simulated at 363 K. By comparing the GCMC simulated isotherms and experimental one (see Figure 2), we could determine the basal spacing about 7Å for the shale model. The simulated pore volume of our shale model is 0.0173 cm³/g, which is consistent with the experimental result of 0.0162–0.0448 cm³/g(Clarkson et al., 2013). So, we believe that the shale model proposed here is rational, and further use the model to investigate the displacement of CH₄ by CO₂ in the shale matrix.

3.2 The Displacement of Shale Gas by Carbon Dioxide at Different Basal Spacings

First, we used GCMC simulations to investigate the displacement of CH₄ by CO₂ in the shale at geological depth of 1 km, in which the partial pressure of CH₄ and the temperature are 15 MPa and 310 K, respectively, corresponding to the condition of the shale gas at the geological depth of 1 km (i.e. Case 1 in Table 2). Then, we injected CO₂ into the shale, and the CO₂ injection pressure is increased from 0 to 90 MPa. After equalization, the composition of the adsorbed mixture is further recorded and analyzed.

To explore the effect of pore size on the displacement of CH₄ by CO₂ in shale, we explored a series of modeled shales with different basal spacings. Figure 3a and 3b show the loading amount of CH₄ and the sequestration amount of CO₂ in the nanochannels of the shale at different CO₂ injection pressures. With the increase of CO₂ injection pressure, the loading amount of CH₄ in the shale decreases monotonically except for the case of 100Å, and the sequestration amount of CO₂ goes up steadily, which means the CH₄ adsorbed in the shale nanochannel is displaced by CO₂ and it is sequestered simultaneously in the shale nanochannels. The reason for this phenomenon is that the shale nanochannel has stronger affinity to CO₂ than to CH₄, and shows selective adsorption for CO₂. As a result, the CH₄ molecules adsorbed in the nanochannel surfaces of shales are displaced by CO₂ molecules, and the CH₄ molecules are pushed back to the bulk phase finally.

A peak is observed in the case of the basal spacing 100 Å in Figure 3a. At low CO₂ injection pressure, the adsorbed CO₂ molecules induced the enhancement of CH₄ adsorption compared with the pure CH₄ adsorption; while at high CO₂ injection pressure, the displacement of CH₄ by CO₂ is pronounced. This phenomenon was also observed in the

work of Kowalczyk et al (Kowalczyk et al., 2012). At low CO_2 injection pressure, some additional CH_4 molecules are pumped from the bulk mixture gas into the shale. The adsorbed CO_2 molecules can be acted as a part of the external field that overall enhances the solid-fluid interactions with bulk CH_4 molecules (Kowalczyk et al., 2012), which leads to the slight increase of adsorption amount of CH_4 .

It is noted that the basal spacing of the shale model, i.e. the pore size, is crucial to the displacement amount of CH_4 and the sequestration of CO_2 in shales. For further explanation, Figure 3c and 3d show the displacement amount of CH_4 and the sequestration amount of CO_2 at the CO_2 injection pressure of 80 MPa. The shale gas reservoirs often contain the free gas in relatively large pores and the adsorbed gas associated with organic matters and inorganic minerals. Both free and adsorbed gases are important for application of exploitation of shale gas. Hence, the absolute amount is more significant than the excess amount for estimating the storage of shale gas reservoirs. With the increase in the basal spacing of the shale model, the displacement amount of CH_4 and the sequestration amount of CO_2 are increased sharply (see Figure 3c and 3d). In fact, the increase of the basal spacing in the shale model will result in the enhancement of the pore volume. As a result, the absolute amount of CH_4 and CO_2 adsorbed in relatively large pores will be increased significantly. When CH_4 is displaced by CO_2 at the CO_2 injection pressure of 80 MPa, the displacement amount of CH_4 and the sequestration amount of CO_2 in relatively large pores exceed that in relatively small pores obviously (see Figure 3c and 3d).

It is found from the inset of Figure 3c that the percentage of displacement is inversely proportional to the basal spacing of shale model (i.e. pore size). The reason could be that

the enlargement of basal spacing reduces the selectivity of the shale for CO₂ over CH₄. That is to say, the affinity of the inner surface to CO₂ in relatively small pores is stronger than that in relatively large pores. So, as the basal spacing of shale model increases gradually, the percentage of displacement goes down slightly. However, the displacement amount of CH₄ is more important than the percentage of displacement for the exploitation of shale gas.

To get an insight into the microscopic behavior of CH₄ displaced by CO₂ in shale, Figure 4a-4d show microscopic snapshots of the binary CO₂-CH₄ mixtures adsorbed in the nanochannels of shales at the CO₂ injection pressure of 0, 30, 60, 90 MPa, respectively, in which the CH₄ partial pressure of 15 MPa and T=310 K are fixed, and the basal spacing of the shale model is 25 Å. For comparison, Figure 4e shows the loading amount of CH₄ and the sequestration amount of CO₂ in the shales at different CO₂ injection pressures. At the CO₂ injection pressure of 0 MPa (i.e. the initial state), the nanochannels are fully filled with CH₄ molecules (Figure 4a). As CO₂ is injected into the shale, a certain amount of CO₂ is also adsorbed and a part of CH₄ molecules are driven out from the nanochannels (Figure 4b-4d). The dynamic process is also presented in Supporting Information Video.

3.3 The Displacement of Shale Gas by Carbon Dioxide at Different Geological Depths.

In this section, the influence of the geological depths on the displacement of CH₄ by CO₂ was studied. The T/P conditions corresponding to the specific geological depth were listed in Table 2. Based on the fact that a large proportion of the pores within the gas shale matrix is nanosized, we take into account not only the micropores (17 Å) but also the mesopores (50 Å). The displacement of CH₄ by CO₂ in micropores (17 Å) was investigated first (see Figure 5). Figure 5a shows the relationship between the loading amount of CH₄ in

the shale and the CO₂ injection pressure at different geological depths. It is found that the geological depth plays a key role in the displacement of CH₄ by CO₂. At the CO₂ injection pressure of 0 MPa (i.e. the initial state), the loading amounts of CH₄ in the shales from 1 to 4 km are nearly close with a slight difference. When CO₂ gas is injected into the shale, the loading of CH₄ in the shale goes down gradually. If the CO₂ injection pressure is kept the same, the loading reduction of CH₄ in the shales at the geological depth of 1 km is maximal in the four cases. If we only considered the displacement amount of CH₄, the geological depth of 1 km is the best choice in all the cases studied here. In addition, the sequestration amount of CO₂ is as important as the displacement of CH₄. Figure 5b shows the sequestration amount of CO₂ versus the CO₂ injection pressure at the geological depths from 1 to 4 km. As expected, the sequestration amount of CO₂ increases with the CO₂ injection pressure (see Figure 5b), while it decreases with the increase of geological depth at a fixed CO₂ injection pressure (see Figure 5d). That is to say, the sequestration of CO₂ is maximum at geological depth of 1 km in all the four cases studied (Figure 5d). Actually, the effect of CO₂ injection pressure on the displacement of shale gas is significant. The higher the CO₂ partial pressure, the larger is the displacement amount of CH₄ and the sequestration amount of CO₂. Interestingly, at the geological depth of 1 km, the percentage of displacement at the CO₂ injection pressure of 80 MPa is also the maximum among the four cases studied (see Figure 5c). Consequently, it is concluded that by considering the displacement of CH₄, the sequestration of CO₂ and the percentage of displacement in the shales, we found that it is at the geological depth of 1 km that the displacement efficiency of CH₄ in shales by CO₂ is the highest.

We also studied mesopores by adjusting the basal spacing of shale model from 17 to 50 Å (see Figure 6), and a similar phenomenon with the microporous shales appears. Finally, we propose that the optimum operating condition that the CO₂ gas displaces the CH₄ gas in the shales, is under the geological depth of 1 km no matter what the shales are microporous or mesoporous, which would provide significant information and reference for displacement exploitation of shale gas and sequestration of CO₂.

Conclusion

We have used GCMC simulation to investigate the displacement of shale gas by CO₂ and the sequestration of CO₂ simultaneously in a modeled shale matrix at different geological depths up to 4 km. the shale model was constructed by organic-inorganic composites, and the rationality of the shale model was evaluated by fitting the experiment data. The results indicate that the CO₂ molecules can displace the shale gas adsorbed in the shales efficiently and the CO₂ is sequestered into the shales simultaneously. It is found that the pore size, i.e. basal spacing, plays an important role in the displacement of CH₄ by CO₂. Interestingly, both the displacement amount of CH₄ and the sequestration amount of CO₂ increase with the pore size of the shales. However, with the increase of the geological depth, all the displacement amount of CH₄, the percentage of displacement and the sequestration amount of CO₂ decrease obviously. Accordingly, we suggest that the geological depth of 1 km is the optimum operating condition for the displacement of CH₄ by CO₂ in the shales discussed here. It is expected that this work would provide microscopic fundamentals and significant reference for displacement exploitation of shale gas and sequestration of CO₂.

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Table 1. Force field parameters for adsorbates and adsorbents

molecules	atoms	charge[e]	$\sigma[\text{\AA}]$	$\varepsilon/k_B[K]$
Methane	CH ₄	0	3.73	148
	C	0.70	2.80	27
Carbon Dioxide	O	-0.35	3.05	79
	H	0.424		
Shale	O (octahedral)	-1.424	3.55	78.26
	O (tetrahedral)	-0.8	3.55	78.26
	O (apical)	-1.0	3.55	78.26
	Al	3.0	4.79	0.0007
	Si	1.2	3.71	0.0009
	C	-	3.47	47.9
	H	-	2.85	7.7

Table 2. Temperature and Pressure Conditions in Different Geological Depths

case	depth	T	P
Case 1	1 km	310 K	15MPa
Case 2	2 km	340 K	30 MPa
Case 3	3 km	370 K	45 MPa
Case 4	4 km	400 K	60 MPa

Figure 1. The scheme of modeled shale matrix. Color scheme: red, oxygen; yellow, silicon; pink, aluminum; white, hydrogen; and black, carbon.

Figure 2. Adsorption isotherms of CH_4 in the shales from experiment and simulation at $T=363$ K.

Figure 3. (a) The loading amount of CH₄ and (b) the sequestration amount of CO₂ in the modeled shales at different CO₂ injection pressures and T = 310 K, where the partial pressure of CH₄ is fixed at 15 MPa, corresponding to the pressure condition of shale gas at the geological depth of 1 km, and the CO₂ injection pressure is increased gradually from 0 to 90 MPa. (c) the displacement amount of CH₄, and the inset of (c) is the percentage of displacement at the CO₂ injection pressure of 80 MPa and T = 310 K. (d) the sequestration amount of CO₂.

Figure 4. The snapshots of the binary CO_2 - CH_4 mixtures adsorbed in the pore of shales at $T=310$ K and different CO_2 injection pressures, (a) 0, (b) 30 MPa, (c) 60 MPa, (d) 90 MPa. In all presented snapshots, the CH_4 partial pressure of 15 MPa is kept fixed in the bulk mixture. The basal spacing of shale model is set to be 25 Å. Color scheme: red, oxygen; black, carbon; blue, methane; yellow, silicon; pink, aluminum and white, hydrogen. (e) The loading of CH_4 and the sequestration of CO_2 at different CO_2 injection pressures

Figure 5.(a) The loading amount of CH_4 and (b) the sequestration amount of CO_2 in shales at different CO_2 injection pressures and different geological depths. (c) The percentage of displacement and (d) the sequestration amount of CO_2 in shale at the CO_2 injection pressure of 80 MPa. The basal spacing of shale model is $17 \text{ \AA}$ (micropores).

Figure 6.(a) The loading amount of CH₄ and (b) the sequestration amount of CO₂ in shales at different CO₂ injection pressures and different geological depths. (c) The percentage of displacement and (d) the sequestration amount of CO₂ in shale at the CO₂ injection pressure of 80 MPa. The basal spacing of shale model is 50 Å (mesopores).

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Molecular Simulation of Displacement of Shale Gas by Carbon Dioxide at Different Geological Depths
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Graphical Abstract