Effects of Moisture Contents on Shale Gas Recovery and CO₂ Sequestration

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ABSTRACT: Enhanced recovery of shale gas with CO₂ injection has attracted extensive attention as it combines the advantages of improved efficiency of shale gas recovery and reduced greenhouse gas emissions via CO₂ geological sequestration. On the other hand, the microscopic mechanism of enhanced shale gas recovery with CO₂ injection and the influence of the subsurface water confined in the shale nanopores remain ambiguous. Here, we use grand canonical Monte Carlo (GCMC) simulations to investigate the effect of moisture on the shale gas recovery and CO₂ sequestration by calculating the adsorption of CH₄ and CO₂ in dry and moist kerogen slit pores. Simulation results indicate that water accumulates in the form of clusters in the middle of the kerogen slit pore. Formation of water clusters in kerogen slit pores reduces pore filling by methane molecules, resulting in a decrease in the methane sorption capacity. For the sorption of CH₄/CO₂ binary mixtures in kerogen slit pores, the CH₄ sorption capacity decreases as the moisture content increases, whereas the effect of moisture on CO₂ sorption capacity is related to its mole fraction in the CH₄/CO₂ binary mixture. Furthermore, we propose a reference route for shale gas recovery and find that the pressure drawdown and CO₂ injection exhibit different mechanisms for gas recovery. When the water content increases, the recovery ratio of the pressure drawdown declines, while that of CO₂ injection increases, especially in the first stage of CO₂ injection. The CO₂ sequestration efficiency is higher under higher water content. These findings provide the theoretical foundation for optimization of the shale gas recovery process, as well as effective CO₂ sequestration in depleted gas reservoirs.

1. INTRODUCTION

Shale gas, which predominantly consists of methane, has become an increasingly important energy source owing to its low emissions, high energy efficiency, and abundant reserves in the world.¹,² In contrast to the conventional reservoirs, shale rocks have the characteristics of extremely low permeability in the nanodarcy range and low porosity.³ The development of horizontal and hydraulic fracturing methods has greatly advanced shale gas exploitation in the United States.⁴,⁵ Unfortunately, the widely used depressurization method becomes inefficient and significant amounts remain unrecoverable.⁶ Recently, enhanced gas recovery (EGR) with CO₂ injection is considered to be a promising alternative that can not only enhance shale gas productivity but also mitigate the climate change via geological CO₂ sequestration,⁷ in which CO₂ captured from power plants is injected into the shale gas reservoirs and sequestered in a safe and permanent manner. The idea of swapping CO₂ for CH₄ can also be applied to other replacement reactions, such as the recovery of CH₄ from hydrate reservoirs.⁸

Kerogen makes up the major organic part of the shale rocks⁹ and pores, mainly at the nanoscale, where a large amount of shale gas can be stored.¹⁰ Therefore, it is crucial to understand the adsorption properties of CH₄ and CO₂ in kerogen in an...
attempt to enhance the efficiency of shale gas recovery and CO₂ sequestration. It is also well known that shale is under moist conditions.⁹–¹² For example, kerogen from the Kuonamka Formation was reported to have moisture contents ranging from 0.6 to 5%.¹³–¹⁴ Plenty of experimental work studied the effects of moisture on pure methane adsorption and suggested that the presence of water occupies the pore volume and thus leads to a sharp decrease in the methane adsorption capacity in shale.¹⁵ On the other hand, relatively few experiments focused on the influence of moisture on the competitive adsorption of CH₄ and CO₂. Gensterblum et al.¹⁸ investigated the effect of preadsorbed water on the CH₄ and CO₂ adsorption in coals and observed that the CO₂/CH₄ adsorption ratios at low surface coverage are generally higher in moist coals than in dry conditions, and with the presence of water, the mobility of CO₂ and CH₄ is reduced. Few laboratory studies have been reported on the competitive adsorption of CO₂ and CH₄ in the moist kerogen. Isolation of the kerogen from shale samples with the morphology of the kerogen intact remains challenging for experiments.⁹ Moreover, shale rocks contain a large amount of nanoscaled pores, further increasing the difficulties of experimental approaches in probing the adsorption behaviors in shales.

Molecular simulations have been successfully applied to interfacial and colloid science,¹⁶ including adsorption,¹⁷ wetting,¹⁸,¹⁹ and surfactants.²⁰ Much research in recent years has made significant progress in understanding the competitive adsorption of CH₄ and CO₂ in kerogens using grand canonical Monte Carlo (GCMC) simulations.²¹–²⁵ Huang et al.²⁶ investigated the effect of moisture on the CO₂/CH₄ competitive adsorption in kerogen matrix and found that the increased moisture content leads to a decrease in adsorption capacity, and the CO₂/CH₄ adsorption selectivity first decreases and then increases. However, most of the work focused on the adsorption inside the kerogen matrix, in which the pores are isolated and not well connected, and the pore size is only a few angstroms. Recently, Wang et al.²⁷ studied the adsorption of CH₄/CO₂ mixtures in moist kerogen using a 2 nm wide slit-pore model and stated that the effect of moisture content on adsorption selectivity is not obvious for shale kerogen slit nanopores. A more realistic kerogen pore structure is used in their study, but the water molecules are placed inside the kerogen matrix rather than within the slit pores. The interaction between water and the adsorbate gas, which is mainly located in the slit pores, is weakened due to the separation. Therefore, the moisture effects on the adsorption of CH₄ and CO₂ are still not fully understood. In addition, the dependence of adsorption selectivity on pressure and pore size is extensively used in the previous research.²⁸–³⁰ To some extent, it can imply the relative adsorption affinity of CH₄ and CO₂ to the adsorbent but fail to reflect the shale gas recovery process with CO₂ injection, namely, CO₂ huff-n-puff process, consisting of three stages: CO₂ injection, soaking, and production.⁶ CO₂ is first injected into the production well (huff) and then the well is shut in and soaks for a period; finally comes the production (puff).⁵ In this work, we aim to reveal the effects of moisture on the competitive adsorption of CH₄/CO₂ binary mixtures in kerogen using GCMC simulations. Kerogen slit-pore models of different pore widths are constructed to represent the pore structure in shale.³¹–³³ First, we analyze the adsorption of pure methane in kerogen slit pores with and without the presence of moisture under a wide range of pressures from 10 to 60 MPa. Then, we discuss the moisture effects on the adsorption of CH₄/CO₂ binary mixtures in detail. Finally, we simulate the enhanced shale gas recovery by CO₂ huff-and-puff and compare the mechanisms of the pressure drawdown and CO₂ injection processes on shale gas recovery. The effects of moisture on the shale gas recovery and CO₂ sequestration are also revealed.

2. METHODS

2.1. Molecular Models. Kerogen can be classified into four types according to the depositional origin.³⁴,³⁵ Type II kerogen, typically derived from marine sediments, is selected in this work for its abundance in shale deposits, as well as good potential for generating oil/gas.¹⁵–³⁰ The kerogen molecular unit (type II-C) used in the simulations was proposed by Ungere et al. on the basis of experimental data from the Duvernay shale formation.³¹–³³ Besides, type II-D kerogen has also been used to study the shale gas sorption behavior.³² Molecular dynamics (MD) simulations are conducted in the canonical ensemble (NVT) and isobaric–isothermal ensemble (NPT) using the large-scale atomic/molecular massively parallel simulator (LAMMPS) package³⁴ to generate kerogen matrices and slit pores. The Dreiding force field³⁵ is employed to describe the kerogen properties. First, the initial structure of the kerogen macromolecule is relaxed individually. Then, 12 relaxed kerogen units are randomly placed in a simulation box of 100 × 100 × 100 Å³. The final configuration of the kerogen matrix was created through a series of annealing procedures, as reported in Coltell et al.³⁶ The density of the simulated kerogen matrix is 1.22 ± 0.02 g/cm³, which is within the range of the experimental value of mature shales (1.18–1.35 g/cm³).³⁷ The pore size distribution of the kerogen matrix is presented in Figure S1, calculated by the method of sphere insertion proposed by Bhattacharya and Gubbins.³⁸ Finally, we extend the simulation box in the Z-direction to create a kerogen slit nanopore, as shown in Figure 1. Note that we use the slit-shaped pore model as slit pores are very common in shale formations.³³,³⁴ The pore width W is defined as the distance between the rightmost atom in the left slab and the leftmost atom in the right slab in the Z-direction. Two pore widths of 2 and 4 nm are constructed to investigate the pore size effects. Methane molecules are simulated using TraPPE force field, and the united-atom model is applied.³⁵ The carbon dioxide molecule is treated as a rigid and linear structure with TraPPE-EH force field, where the C–O bond length and O–C–O bond angle are fixed at 1.16 Å and 180°, respectively.³⁶ The SPC/E model³⁷ is chosen for water with the O–H bond length of 1 Å and the H–O–H angle of 109.47°. Interaction between two atoms is calculated by the sum of Lennard-Jones (LJ) and electrostatic potential energy

\[
u(r) = 4\varepsilon \left[ \left( \frac{\sigma_1}{r} \right)^{12} - \left( \frac{\sigma_1}{r} \right)^{6} \right] + \frac{q_1 q_2}{r}
\]

Figure 1. Atomistic model of kerogen slit nanopore. The pore width is 2 nm. Carbon atoms are depicted by gray balls, hydrogen by white, oxygen by red, nitrogen by blue, and sulfur by purple.
where \( r_{ij} \) is the distance between atoms \( i \) and \( j \); \( \epsilon_{ij} \) and \( \sigma_{ij} \) represent the LJ potential well depth and the zero-potential distance, respectively; \( q \) is the charge of atoms; and \( k_B = 8.988 \times 10^{-5} \text{N}\cdot\text{m}^2\cdot\text{C}^{-2} \) is the electrostatic constant. The force field parameters are listed in Table 1.

| atom             | \( \epsilon \) (K) | \( \sigma \) (Å) | \( q \) (e) |
|------------------|---------------------|-----------------|-------------|
| methane          | 148                 | 3.73            | 0           |
| carbon dioxide   |                     |                 |             |
| C                | 27                  | 2.80            | 0.70        |
| O                | 79                  | 3.05            | -0.35       |
| water            |                     |                 |             |
| H                | 0                   | 0               | 0.4238      |
| O                | 78.18               | 3.166           | -0.8476     |

Lorentz–Berthelot mixing rules\(^{51}\) are adopted to calculate interactions between unlike atoms. A cutoff distance of 14 Å is employed for short-range Lennard-Jones interactions, and analytical tail corrections are applied.\(^ {52,53}\) As our system has a finite length along the Z-direction, the conventional three-dimensional Ewald summation technique is not valid for the calculation of the long-range electrostatic interactions. Here, we use the same approach as for the three-dimensional Ewald summation, but an empty space is inserted between periodic replicas to avoid the artificial influence from the periodic images in the Z-direction.\(^ {52,53}\) Tests are carried out to ensure the length of the empty space is long enough that the artificial effects could be eliminated. The entire simulation box including the empty space is shown in Figure S2. During the simulations, the molecules are only allowed to move within the kerogen slit pore, but not into the vacuum.

2.2. Simulation Details. GCMC simulations are carried out in the grand canonical ensemble (\( \muVT \)) to investigate the adsorption of \( \text{CH}_4 \) and \( \text{CO}_2 \) in kerogen slit pores. In the GCMM simulations, gases inside the kerogen slit pores are assumed to be in equilibrium with an external bulk reservoir under the same temperature and chemical potentials. The equilibration process is achieved by performing insertion, deletion, and translation moves for the gas molecules. For \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) molecules, rotational moves are also applied. The chemical potentials are obtained by Widom’s insertion method\(^ {54,55}\) using Monte Carlo simulations in the NVT ensemble, where the fluids are simulated in bulk phase without confinement. The calculated chemical potential values are verified by \( \muVT \) simulations compared to those of NIST database\(^ {36}\) (Figure S3). The bulk densities of \( \text{CO}_2 \) and \( \text{CH}_4 \) mixtures at a given pressure and temperature are calculated from the Peng–Robinson equation of state (PR-EOS).\(^ {37,58}\) Bulk densities calculated by PR-EOS have been verified by comparing \( \muVT \) simulations, as shown in Figure S4.

3. RESULTS AND DISCUSSION

In this section, we first investigate the adsorption of pure \( \text{CH}_4 \) and \( \text{CH}_4/\text{CO}_2 \) binary mixtures in kerogen slit pores, and the moisture effects are analyzed in detail. Then, we discuss the practical implications for the shale gas recovery and \( \text{CO}_2 \) sequestration during the \( \text{CO}_2 \) huff-and-puff process.

3.1. Adsorption of Pure \( \text{CH}_4 \) in Kerogen. 3.1.1. Dry Condition. We present methane density distributions in various nanopores under dry conditions at 338.15 K in Figure 2. For all of the pressures, two strong methane adsorption layers are formed near the kerogen surfaces, and the methane density within the adsorption layer increases with pressure. Under higher pressures (over 10 MPa), the \( \text{CH}_4 \)–\( \text{CH}_4 \) interaction becomes stronger and a weak second adsorption layer can be observed. In the middle of kerogen slit pores, the methane density is higher in the smaller pore (\( W = 2 \) nm) due to the strong fluid–surface interactions. As the pore width increases (\( W = 4 \) nm), the fluid–surface interaction becomes weaker. As a result, the methane density in the middle of the kerogen slit pore reaches bulk.

3.1.2. Moist Condition. To investigate the moisture effects on methane adsorption in kerogen, the methane adsorption under different moisture contents is simulated. The snapshots of \( \text{CH}_4 \) and \( \text{H}_2\text{O} \) molecules in the moist kerogen slit pores (\( \rho_{\text{H}_2\text{O}} = 0.186 \text{g/cm}^3 \)) under different pressures are shown in Figure 3. For all of the pressure conditions ranging from 10 to 60 MPa, water molecules form clusters in the middle of the kerogen slit pore, unlike in clay nanopores.\(^ {60}\) This is because the kerogen is hydrophobic, while the clay is hydrophilic. Similar phenomena were also reported on graphene and montmorillonite.\(^ {61}\)

The effects of water on the methane density distribution in 2 nm kerogen slit pores under different pressures are presented in Figure 4. In general, the \( \text{CH}_4 \) density in the middle of the kerogen slit pore decreases significantly as water molecules are predominantly distributed in the middle of the pore in the form of clusters. The methane density distribution in the...
The presence of water is not symmetric because the water cluster is not located exactly at the center of the slit pore. For methane within the adsorption layer, the density also slightly decreases. From the water density distribution (as shown in Figure S5), some water molecules are distributed near the kerogen surface, occupying the adsorption sites on the surface and resulting in the decrease of methane in the adsorption layer.

The average density of methane stored in the kerogen slit pore can be given as

$$\rho_{\text{ave}} = \frac{\langle N \rangle}{V N_A}$$

(2)

where $\langle N \rangle$ is the ensemble averaged number of methane molecules in kerogen slit pores, $V$ denotes the volume of the slit pore, and $N_A$ is the Avogadro constant. We only consider the methane molecules in slit pores, excluding those inside the kerogen matrix. Figure S5 shows the total uptake of CH$_4$ at 338.15 K in kerogen slit pores of different pore widths with and without moisture. Statistical uncertainties on the sorption isotherms are examined, and the errors bars are less than the symbols. For both pore widths, the amount of adsorbed methane decreases monotonically with increasing water content. As shown in Figure S5, the water molecules are distributed in the middle of the slit pore in the form of clusters and occupy a fraction of the pore volume. Thus, they impede the pore filling of methane molecules in the middle of the pore.

By comparing the CH$_4$ total uptakes in different pores (Figure S5), the reduction in the average density of methane is similar for 2 and 4 nm kerogen slit pores, when they have the same water volumetric density ($\rho_{\text{H}_2\text{O}}$ ave = 0.186 g/cm$^3$) rather than the same surface density. It demonstrates that the volumetric density of water may be more appropriate to define the water content in kerogen to quantify the effect of moisture on gas adsorption. CH$_4$ excess sorption isotherms in 2 and 4 nm dry kerogen slit pores are also calculated using effective pore volume from helium adsorption, and the results are shown in Figure S6. It first reaches a maximum at around 15 MPa and then decreases with increasing pressure. Excess sorption in 2 nm kerogen slit pores is larger than that in 4 nm kerogen slit pores due to the stronger fluid–wall interaction.

### 3.2. Adsorption of CH$_4$/CO$_2$ Mixtures in Kerogen

#### 3.2.1. Dry Condition

The density distributions of CH$_4$ and CO$_2$ in the equimolar mixtures at 10 MPa and 338.15 K in kerogen slit pores of different pore widths are presented in Figure 6. The density distributions of both CO$_2$ and CH$_4$ have two peaks near the kerogen walls, but the density of CO$_2$ is much higher than that of CH$_4$, as CO$_2$ has a stronger affinity to kerogen than CH$_4$.

In the middle of 2 nm kerogen pores, both the densities of CO$_2$ and CH$_4$ are higher than the bulk density due to the strong fluid–surface interactions. When $W = 4$ nm, the fluid–surface interaction becomes weaker. Therefore, the densities in the middle of pores approach the
bulk density. The density distributions of pure methane in kerogen slit pores under the same pressure are also shown in Figure 6 for comparison. With the competitive adsorption of CO$_2$, the density of methane decreases significantly, especially on the adsorption layer.

Figure 7 displays the total uptake of CH$_4$–CO$_2$ binary mixtures of different compositions in the dry kerogen slit pores of different pore widths at 338.15 K and over a wide range of pressures from 10 to 60 MPa. Similar trends can be observed for CH$_4$ in the kerogen slit pores of different pore widths that the average density increases quickly with pressure at the beginning and gradually reaches a plateau. The average density of CH$_4$ in kerogen slit pores increases as its mole fraction in the mixtures increases. For CO$_2$ molecules, sorption increases gradually with the increasing pressure. Similar to CH$_4$, as the mole fraction of CO$_2$ in the binary mixtures increases, an increase in the corresponding CO$_2$ adsorption can be observed. In the equimolar mixtures, the CO$_2$ average density in kerogen slit pores is much higher than that of CH$_4$.

3.2.2. Moist Condition. Sorption of CH$_4$/CO$_2$ binary mixtures in the moist kerogen slit pores is also investigated using GCMC simulations. As shown in Figure 8, water clusters are formed in the kerogen slit pores with the sorption of CH$_4$/CO$_2$ binary mixtures under pressures ranging from 10 to 60 MPa as pure CH$_4$ sorption with moisture. When there is only

![Figure 6. Density distributions of CH$_4$ and CO$_2$ molecules at 10 MPa and 338.15 K, respectively, in kerogen slit pores of widths (a) 2 nm and (b) 4 nm. The blue dashed lines represent the CH$_4$ density distribution in single-component adsorption and the solid lines represent the CH$_4$ and CO$_2$ density distributions in a binary mixture with a mole fraction of 0.5. The black dashed lines represent the bulk density of CH$_4$/CO$_2$.](image1)

![Figure 7. Average density of CH$_4$ (left) and CO$_2$ (right) in mixtures of different compositions confined in kerogen slit pores with pore widths of 2 nm (top) and 4 nm (bottom) under different pressures at 338.15 K.](image2)

![Figure 8. Snapshots of CH$_4$/H$_2$O mixtures (top) and CH$_4$/CO$_2$/H$_2$O mixtures (bottom) in 2 nm kerogen slit nanopores at 338.15 K under different bulk pressures: 10, 30, and 60 MPa from left to right with an average water density of 0.186 g/cm$^3$. The mole fraction of CH$_4$ in the CH$_4$/CO$_2$ binary mixtures is 0.5.](image3)
methane sorption in the moist kerogen slit pore, the pore surface is occupied by methane molecules. With the CO₂ cosorption, the adsorption sites on the kerogen surface are mainly covered by CO₂ molecules. Besides, the solubility of methane in water is much lower than that of CO₂. As a result, CH₄ sorption in the moist condition is significantly reduced due to the cosorption of CO₂.

Effects of moisture contents on the total uptake of CH₄/CO₂ binary mixtures are illustrated in Figure 9. Similar to the trends in dry conditions, the average densities of both CH₄ and CO₂ in moist kerogen slit pores increase when their mole fraction increases. As the moisture content increases, the methane average density decreases significantly, independent of its mole fraction in the mixtures (Figure 9a). However, the effect of moisture content on CO₂ adsorption is associated with the mole fraction of CO₂ in the binary mixtures. For the case of low CO₂ bulk mole fraction in mixtures (\(y_{\text{CO}_2} = 0.25\)), a slight increase in CO₂ adsorption can be found in the moist condition, while the opposite is true at high CO₂ mole fraction (\(y_{\text{CO}_2} = 0.75\)). As stated in the previous section, the presence of moisture fills up the pore volume in kerogen slit pores, which results in the reduction in CH₄ sorption. With the CO₂ cosorption, the water−CH₄ binary interaction turns into the water−CH₄−CO₂ ternary interaction. Since the water−CO₂ interaction is much stronger than the water−CH₄ interaction, the decrease in accessible pore volumes for CH₄ can partially be occupied by the more favorable CO₂ sorption. Besides, within the region near the kerogen surface, CO₂ exhibits a higher affinity to kerogen compared to CH₄. Therefore, the CO₂ has a competitive advantage over CH₄ both in the middle of the kerogen slit pore and near the surface, which are shown in the snapshots (Figure 8) and density profiles (Figure S7).

When the bulk mole fraction of CH₄ is relatively high, the decrease in methane sorption caused by the presence of water is pronounced. When the mole fraction of CO₂ is higher, both CO₂ and CH₄ need to compete with water for adsorption sites or space. The occupation of water in the kerogen slit pores limits the sorption of CO₂ and CH₄, thereby diminishing their sorption capacities. The sorption selectivity of CO₂ over CH₄ with different moisture contents is presented in Figure S8 to characterize the preferential adsorption. For the moisture contents considered in this work, the CO₂/CH₄ adsorption selectivity increases with increasing moisture content.

3.3. Implications for Shale Gas Recovery and CO₂ Storage. As outlined in the Introduction, this work aims to unravel the CH₄ recovery mechanisms under moist condition during the pressure drawdown process and CO₂ injection to investigate the recovery and sequestration efficiency. The simplified recovery process consists of two pressure drawdowns and two CO₂ injections, as illustrated in Figure 10. The initial pressure of the target shale gas reservoir is assumed to be 30 MPa, which is within the typical pressure range of realistic reservoir conditions. The CH₄ sorption amount in the kerogen slit pores is obtained by GCMC simulations. Then, the shale gas recovery is initiated by the primary pressure drawdown process, and the reservoir pressure is reduced to 20 MPa, while the amount of CH₄ residing in the kerogen slit pores is calculated via μVT simulation. Subsequently, CO₂ is injected into the shale gas reservoirs. During this process, we assume that the pore volume in the fractures (external bulk reservoir) remains the same; therefore, the CH₄ density in the bulk phase of CH₄/CO₂ mixtures is the same as that in pure CH₄. The resulting CH₄/CO₂ mixtures in the kerogen slit pores are determined by the chemical potentials of CH₄/CO₂ mixtures, which are obtained by NVT simulations. After the system has reached equilibrium, a pressure depletion process is applied.
again, while the bulk CH₄/CO₂ composition stays the same. The dynamics and transport processes are not considered. This process achieves one cycle of CO₂ huff-n-puff in enhanced gas recovery. Consequently, a second CO₂ huff-n-puff process is operated.

Evolution in the composition of fluids in the kerogen slit pores during the shale gas recovery process is shown in Figure 11. During the pressure drawdown, the average CH₄ density in the kerogen slit pores decreases continuously, and with the injection of CO₂, the CH₄ molecules are further released. The CO₂ molecules are sequestered in the kerogen slit pores after injection. The effects of moisture content are also shown in Figure 11; as the moisture content increases, the average density of methane at the initial stage is reduced from 13.2 mmol/cm³ in the dry condition to 7.68 mmol/cm³ with an average water density of 0.372 g/cm³, but the recovery ratio of CH₄ after the whole recovery process is increased from 58.5 to 70.1%.

To compare the efficiency of the shale gas recovery and CO₂ sequestration during every intermediate process and quantify the effects of moisture contents, we introduce two parameters: CH₄ recovery ratio and CO₂ sequestration ratio, taking the initial pressure (30 MPa) of the reservoir as the reference. The CH₄ recovery ratio is defined as the number of CH₄ molecules released during a single process relative to the initial amount in the kerogen slit pore under 30 MPa with/without moist. The CO₂ sequestration ratio is defined as the number of CO₂ molecules sequestered during the CO₂ injection process relative to its adsorption amount in the kerogen slit pore under 30 MPa, namely, the maximum amount of CO₂ sequestration.
while the CO₂ injection recovers CH₄ from the adsorption pressure drawdown releases the free gas in the middle of pores, the adverse effect of moisture on the CO₂ injection method is negligible, as the water–CH₄ interaction is much stronger than the water–CO₂ interaction. Hence, the presence of water could further improve the efficiency of the CO₂ injection method. Generally, in the moist conditions, the CO₂ injection behaves better, while the efficiency of the pressure drawdown is lower.

**4. CONCLUSIONS**

In this work, the effects of moisture on the adsorption of pure CH₄ and CH₄/CO₂ binary mixtures in kerogen slit pores are investigated using GCMC simulations. The shale gas recovery mechanisms of the pressure drawdown and CO₂ injection are studied, and the moisture effects on the shale gas recovery and CO₂ sequestration efficiency are further explored.

Our simulation results show that for the sorption of pure CH₄ in the moist conditions, water clusters are formed in the middle of a kerogen slit pore and the clusters occupy the volume in the slit pore, thereby impeding the pore filling of CH₄. Regarding the sorption of CH₄/CO₂ binary mixture, the CH₄ sorption capacity in the mixture decreases with increasing moisture content, while the effect of moisture on CO₂ adsorption capacity depends on the mole fraction of CO₂ in the mixture due to the ternary interactions among CH₄, CO₂, and H₂O. During the shale gas recovery process, the pressure drawdown and CO₂ injection present different mechanisms. The pressure drawdown releases CH₄ molecules in the middle of kerogen slit pores, while CO₂ injection can release CH₄ molecules in the adsorption layer. As the water content increases, the recovery ratio of the pressure drawdown declines, while that of CO₂ injection increases, especially in the first stage of CO₂ injection. Finally, the CO₂ sequestration efficiency is higher under moist conditions.

This work provides important insights into the effects of moisture content on gas adsorption in kerogen. As the subsurface water in the shale formations is saline, further work is planned to examine the effects of saline water on the recovery process. Besides, the recovery process introduced in this work can be extended to the optimization of the shale gas recovery process. For example, adjusting the CO₂ injection pressure and depletion pressure may lead to optimal shale gas recovery efficiency or CO₂ sequestration efficiency. The recovery process can also be applied to other displacement processes in confined systems.

**ASSOCIATED CONTENT**

* Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.9b00862.

Chemical potentials of pure methane and mixtures (Table S1); additional details of bulk fluids (Table S2); pore size distribution of the kerogen matrix (Figure S1); entire simulation box (Figure S2); densities of bulk CH₄ (Figure S3); validation of the PR-EOS (Figure S4); water density distributions (Figure S5); CH₄ excess adsorption isotherms (Figure S6); density distributions.
(Figure S7); CO$_2$/CH$_4$ adsorption selectivity (Figure S8); total shale gas recovery ratio (Figure S9); and CO$_2$ density distributions (Figure S10).

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**Notes**

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**REFERENCES**

(1) Vidic, R. D.; Brantley, S. L.; Vandenbossche, J. M.; Yootheimer, D.; Abd, J. D. Impact of Shale Gas Development on Regional Water Quality. *Science* 2013, 340, No. 1235009.

(2) Melikoglou, M. Shale Gas: Analysis of Its Role in the Global Energy Market. *Renevable Sustainable Energy Rev.* 2014, 37, 460–468.

(3) Arogundade, O.; Sohraph, M. A Review of Recent Developments and Challenges in Shale Gas Recovery, *SPE Saudi Arabia Section Technical Symposium and Exhibition*, 8–11 April 2012, Al-Khobar, Saudi Arabia, 2012.

(4) Middleton, R.; Viswanathan, H.; Currier, R.; Gupta, R. CO$_2$ as a Fracturing Fluid: Potential for Commercial-Scale Shale Gas Production and CO2 Sequestration. *Energy Procedia* 2014, 63, 7780–7784.

(5) Yang, R.; Goktekin, E.; Gleason, K. K. Zwitterionic Antifouling Coatings for the Purification of High-Salinity Shale Gas Produced Water. *Langmuir* 2015, 31, 11895–11903.

(6) Yu, W.; Lashgari, H.; Sephehroo, K. Simulation Study of CO2 Huff-n-Puff Process in Bakken Tight Oil Reservoirs, *SPE Western North American and Rocky Mountain Joint Meeting*, Society of Petroleum Engineers, 17–18 April, Denver, Colorado, 2014.

(7) Loring, J. S.; Iltan, E. S.; Thompson, C. J.; Martin, P. F.; Rosso, K. M.; Felmly, A. R.; Schaef, H. T.; et al. In Situ Study of CO2 and H2O Partitioning between Na–Montmorillonite and Variety Wet Supercritical Carbon Dioxide. *Langmuir* 2014, 30, 6120–6128.

(8) Wang, X. H.; Sun, Y. F.; Wang, Y. F.; Li, N.; Sun, C. Y.; Chen, G. J.; Liu, B.; Yang, L. Y. Gas Production from Hydrates by CH4-CO2/H2 Replacement. *Appl. Energy* 2017, 188, 305–314.

(9) Vandenbroucke, M.; Largeau, C. Kerogen Origin, Evolution and Structure. *Org. Geochem.* 2007, 38, 719–833.

(10) Ortiz Cancino, O. P.; Peredo Mancilla, D.; Pozo, M.; Pérez, E.; Bessières, D. Effect of Organic Matter and Thermal Maturity on Methane Adsorption Capacity on Shales from the Middle Magdalena Valley Basin in Colombia. *Energy Fuels* 2017, 31, 11698–11709.

(11) Parfenova, T. M.; Kontorovich, A. E.; Borisova, L. S.; Melenesvkii, V. N. Kerogen from the Cambrian Deposits of the Kuonamka Formation (Northeastern Siberian Platform). *Russ. Geol. Geophys.* 2010, 51, 277–285.

(12) Chalmers, G. R.; Bustin, M. R. The Effects and Distribution of Moisture in Gas Shale Reservoirs Systems, *AAPG Annual Convention and Exhibition*, New Orleans, Louisiana, April 11–14, 2010.

(13) Ruppert, L. P.; Sakurovs, R.; Blach, T. P.; He, L.; Melnichenko, Y. B.; Mildner, D. F. R.; Alcantar-Lopes, L. A USANS/SANS Study of the Accessibility of Pores in the Barnett Shale to Methane and Water. *Energy Fuels* 2013, 27, 772–779.

(14) Ross, D. J. K.; Bustin, R. M. The Importance of Shale Composition and Pore Structure upon Gas Storage Potential of Shale Gas Reservoirs. *Mar. Pet. Geol.* 2009, 26, 916–927.

(15) Zhang, T.; Ellis, G. S.; Ruppel, S. C.; Mililken, K.; Yang, R. Effect of Organic-Matter Type and Thermal Maturity on Methane Adsorption in Shale-Gas Systems. *Org. Geochem.* 2012, 47, 120–131.

(16) Li, X.; Krooss, B. M. Influence of Grain Size and Moisture Content on the High-Pressure Methane Sorption Capacity of Kimmridge Clay. *Energy Fuels* 2017, 31, 11548–11557.

(17) Gasparik, M.; Bertier, P.; Gensterblum, Y.; Ghanizadeh, A.; Krooss, B. M.; Littke, R. Geological Controls on the Methane Storage Capacity in Organic-Rich Shales. *Int. J. Coal Geol.* 2014, 123, 34–51.

(18) Gensterblum, Y.; Busch, A.; Krooss, B. M. Molecular Concept and Experimental Evidence of Competitive Adsorption of H2O, CO2 and CH4 on Organic Material. *Fuel* 2014, 115, 581–588.

(19) Razavi, S.; Koplik, J.; Kretzschmar, I. Molecular Dynamics Simulations: Insight into Molecular Phenomena at Interfaces. *Langmuir* 2014, 30, 11272–11283.

(20) Rezlerová, E.; Zakal, A.; Čejka, J.; Siperstein, F. R.; Brennan, J. K.; Lisal, M. Adsorption and Diffusion of C1 to C4 Alkanes in Dual-Porosity Zeolites by Molecular Simulations. *Langmuir* 2017, 33, 11126–11137.

(21) Billemont, P.; Coasne, B.; Weireld, G. De Adsorption of Carbon Dioxide, Methane, and Their Mixtures in Porous Carbons: Effect of Surface Chemistry, Water Content, and Pore Disorder. *Langmuir* 2013, 29, 3328–3338.

(22) Brochard, L.; Vandamme, M.; Pellenq, R. J.; Fen-chong, T. Adsorption-Induced Deformation of Microporous Materials: Coal Swelling Induced by CO2–CH4 Competitive Adsorption. *Langmuir* 2012, 28, 2659–2670.

(23) Savoy, E. S.; Escobedo, F. A. Molecular Simulations of Wetting of a Rough Surface by an Oily Fluid: Effect of Topology, Chemistry, and Droplet Size on Wetting Transition Rates. *Langmuir* 2012, 28, 3412–3419.

(24) Wei, N.; Lv, C.; Xu, Z. Wetting of Graphene Oxide: A Molecular Dynamics Study. *Langmuir* 2014, 30, 3572–3578.

(25) Storm, S.; Jakobtorweihen, S.; Sminova, I.; Panagiotopoulos, A. Z. Molecular Dynamics Simulation of SDS and CTAB Micellization and Prediction of Partition Equilibria with COSMOmic. *Langmuir* 2013, 29, 11582–11592.

(26) Sui, H.; Yao, J. Effect of Surface Chemistry for CH4/CO2 Adsorption in Kerogen: A Molecular Simulation Study. *J. Nat. Gas Sci. Eng.* 2016, 31, 738–746.

(27) Wang, T.; Tan, S.; Li, G.; Sheng, M. Selective Adsorption of Supercritical Carbon Dioxide and Methane Binary Mixture in Shale Kerogen Nanopores. *J. Nat. Gas Sci. Eng.* 2018, 50, 181–188.

(28) Song, R.; Cui, M. Molecular Simulation on Competitive Adsorption Mechanism of CH4/CO2 on Shale Kerogen. *Arab. J. Geosci.* 2018, 11, No. 403.

(29) Huang, L.; Ning, Z.; Wang, Q.; Zhang, W.; Cheng, Z.; Wu, X.; Qin, H. Effect of Organic Type and Moisture on CO2/CH4 Competitive Adsorption in Kerogen with Implications for CO2 Sequestration and Enhanced CH4 Recovery. *Appl. Energy* 2018, 210, 28–43.

(30) Huang, L.; Ning, Z.; Wang, Q.; Qi, R.; Zeng, Y.; Qin, H.; Ye, H.; Zhang, W. Molecular Simulation of Adsorption Behaviors of Methane, Carbon Dioxide and Their Mixtures on Kerogen: Effect of Kerogen Maturity and Moisture Content. *Fuel* 2018, 211, 159–172.

(31) Wang, T.; Tian, S.; Li, G.; Sheng, M.; Ren, W.; Liu, Q.; Zhang, S. Molecular Simulation of CO2/CH4 Competitive Adsorption on
Shale Kerogen for CO2 Sequestration and Enhanced Gas Recovery. J. Phys. Chem. C 2018, 122, 17009–17018.

32. Sun, H.; Zhao, H.; Qi, N.; Li, Y. Molecular Insights into the Enhanced Shale Gas Recovery by Carbon Dioxide in Kerogen Slit Nanopores. J. Phys. Chem. C 2017, 121, 10233–10241.

33. Chalmers, G. R.; Bustin, R. M.; Power, I. M. Characterization of Gas Shale Pore Systems by Porosimetry, Pycnometry, Surface Area, and Field Emission Scanning Electron Microscopy/Transmission Electron Microscopy Image Analyses: Examples from the Barnett, Woodford, Haynesville, Marcellus, and Doig Uni. AAPG Bull. 2012, 96, 1099–1119.

34. Curtis, M. E.; Cardott, B. J.; Sondergeld, C. H.; Rai, C. S. International Journal of Coal Geology Development of Organic Porosity in the Woodford Shale with Increasing Thermal Maturity. Int. J. Coal Geol. 2012, 103, 26–31.

35. McCarthy, K.; Rojas, K.; Niemann, M.; Palmowski, D.; Peters, K.; Stankiewicz, A. Basic Petroleum Geochemistry for Source Rock Occurrence. Trans., Am. Geophys. Union 1963, 39, 2808.

36. Lemmon, E.; McLinden, M.; Huber, M. NIST Reference Fluid Thermodynamic and Transport Properties—REFPROP, v7. NIST standard reference database.

37. Curri, D.; Robinson, D. B. A New Two-Constant Equation of State. Ind. Eng. Chem. Fundam. 1976, 15, 59–64.

38. Kunz, O.; Klimek, R.; Wagner, W.; Jäschke, M. The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures. GERG Tech. Monogr. 2007.

39. Martin, M. G. MCCCSC Towhee: A Tool for Monte Carlo Molecular Simulation. Molecular Simulation; Taylor & Francis, 2013; PP 1212–1222.

40. Jin, Z.; Firoozabadi, A. Effect of Water on Methane and Carbon Dioxide Sorption in Clay Minerals by Monte Carlo Simulations. Fluid Phase Equilib. 2014, 382, 10–20.

41. Wang, S.; Feng, Q.; Zha, M.; Javadpour, F.; Hu, Q. Supercritical Methane in Clay Nanopores: Effects of Water, Pressure, Mineral Types, and Moisture Content. Energy Fuels 2018, 32, 169–180.

42. Tian, Y.; Yan, C.; Jin, Z. Characterization of Methane Excess and Absolute Adsorption in Various Clay Nanopores from Molecular Simulation. Sci. Rep. 2017, 7, No. 12040.

43. Kang, S. M.; Fathi, E.; Ambrose, R. J.; Akkutlu, I. Y.; Sigal, R. F. Carbon Dioxide Storage Capacity of Organic-Rich Shales. SPE J. 2011, 16, 842.

44. Yamamoto, S.; Alcauskas, J. B.; Crozier, T. E. Solubility of Methane in Distilled Water and Seawater. J. Chem. Eng. Data 1978, 21, 78–80.

45. Bui, K.; Akkutlu, I. Y. Hydrocarbons Recovery From Model-Kerogen Nanopores. SPE J. 2017, 22, 0854–0862.

46. Meng, X.; Meng, Z.; Ma, J.; Wang, T. Performance Evaluation of CO2 Huff-n-Puff Gas Injection in Shale Gas Condensate Reservoirs. Energies 2019, 12, 1–18.

53. Shelley, J. C. Boundary Condition Effects in Simulations of Water Confined between Planar Walls. Mol. Phys. 1996, 88, 385–398.

54. Widom, B. Potential-Distribution Theory and the Statistical Mechanics of Fluids. J. Phys. Chem. 1982, 86, 869–872.

55. Widom, B. Some Topics in the Theory of Fluids. J. Chem. Phys. 1963, 39, 2808.