



Original Paper

Adsorption behavior of CO₂/H₂S mixtures in calcite slit nanopores for CO₂ storage: An insight from molecular perspective



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ARTICLE INFO

Article history:

Received 5 September 2023

Received in revised form

18 March 2024

Accepted 20 March 2024

Available online 22 March 2024

Edited by Yan-Hua Sun

Keywords:

Adsorption behavior

CO₂/H₂S binary mixtures

Molecular perspective

Calcite slit nanopores

CO₂ sequestration

ABSTRACT

It is acknowledged that injecting CO₂ into oil reservoirs and saline aquifers for storage is a practical and affordable method for CO₂ sequestration. Most CO₂ produced from industrial exhaust contains impurity gases such as H₂S that might impact CO₂ sequestration due to competitive adsorption. This study makes a commendable effort to explore the adsorption behavior of CO₂/H₂S mixtures in calcite slit nanopores. Grand Canonical Monte Carlo (GCMC) simulation is employed to reveal the adsorption of CO₂, H₂S as well as their binary mixtures in calcite nanopores. Results show that the increase in pressure and temperature can promote and inhibit the adsorption capacity of CO₂ and H₂S in calcite nanopores, respectively. CO₂ exhibits stronger adsorption on calcite surface than H₂S. Electrostatic energy plays the dominating role in the adsorption behavior. Electrostatic energy accounts for 97.11% of the CO₂-calcite interaction energy and 56.33% of the H₂S-calcite interaction energy at 10 MPa and 323.15 K. The presence of H₂S inhibits the CO₂ adsorption in calcite nanopores due to competitive adsorption, and a higher mole fraction of H₂S leads to less CO₂ adsorption. The quantity of CO₂ adsorbed is lessened by approximately 33% when the mole fraction of H₂S reaches 0.25. CO₂ molecules preferentially occupy the regions near the pore wall and H₂S molecules tend to reside at the center of nanopore even when the molar ratio of CO₂ is low, indicating that CO₂ has an adsorption priority on the calcite surface over H₂S. In addition, moisture can weaken the adsorption of both CO₂ and H₂S, while CO₂ is more affected. More interestingly, we find that pure CO₂ is more suitable to be sequestered in the shallower formations, i.e., 500–1500 m, whereas CO₂ with H₂S impurity should be settled in the deeper reservoirs.

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1. Introduction

Excessive consumption of fossil fuels has caused a surge in carbon dioxide (CO₂) emissions (Metz et al., 2005; O'Neill, 2020). In 2021, the CO₂ emissions from energy increased to 36.3 Gt to reach their highest ever annual level (International Energy Agency, 2022; Liu and Rui, 2022). Meanwhile, the environmental problems caused by excessive CO₂ emissions have also attracted increasing attention all over the world. The fifth assessment report of the United Nations

Intergovernmental Panel on Climate Change (IPCC) proposed that the 450 ppm CO₂ equivalent concentration would be achieved by 2100 (the temperature rise should be controlled within 1.5 °C) (Liu and Rui, 2022). CO₂ capture, utilization, and storage (CCUS) technology will be an essential technique to control carbon dioxide emissions and mitigate climate problems (Bui et al., 2018; Cui et al., 2018; Tyne et al., 2021). Some CCUS techniques have been proposed for carbon neutrality such as CO₂-enhanced gas recovery (CO₂-EGR), CO₂-enhanced coal bed methane recovery (CO₂-ECBM), CO₂-enhanced geothermal systems (CO₂-EGS), gas hydrate based CO₂ storage (Hu et al., 2022; Shi et al., 2018; Sun et al., 2023). One of the most effective CCUS techniques includes storing CO₂ in deep salt-water aquifers and drained oil and gas reserves (Iglauer, 2017;

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Villarrasa and Carrera, 2015). Injecting CO₂ into oil and gas reservoirs combines CO₂ sequestration and CO₂ enhanced oil recovery (CO₂-EOR) to bring economic benefits to oil companies (Clark and Santiso, 2018; Li H. et al., 2021; Liu S. et al., 2022; Liu Y. et al., 2022).

Apart from the location of CO₂ storage, another major barrier that hinders the widespread application of CCUS should be the significant expense of CO₂ separation from CO₂-rich industrial waste gas (Cui et al., 2021a; Kolle et al., 2021; Lu et al., 2016). The process of removing CO₂ from industrial waste gas and purifying it would consume a significant amount of energy (Keith et al., 2018; Wei et al., 2015). The reduction of the requirement for CO₂ purity would be a feasible way to minimize costs in all capture processes (Wang et al., 2015). Hence, lowering the standard of impurity gas in CO₂ injected into the formation can significantly reduce the expenditure of the whole CO₂ geo-storage project (Wang et al., 2016; Yu et al., 2021). As one of the primary CO₂ sources, industrial exhaust, when captured and separated, can be injected into geological formations to achieve carbon sequestration and emission reduction. However, the impurity gases present in the separated CO₂-rich industrial exhaust, such as SO₂, H₂S, CH₄, CO, continue to exert an influence on carbon sequestration. Among these, hydrogen sulfide (H₂S) is a typical gas found in industrial waste gas and depleted reservoirs (Cholewinski et al., 2016; Hutcheon, 1999; Talman, 2015). On the outskirts of Edmonton, a depleted oil reservoir started to pump gases with compositions ranging from 83% H₂S + 14 % CO₂ to 2% H₂S + 95% CO₂ (Zhang et al., 2011). In the Western Canada Sedimentary Basin, the concentration of dissolved CO₂ at the forefront of the fluid flow might exceed 50% (Ghaderi et al., 2011). H₂S contained in the stored CO₂ and originally in the depleted oil and gas reservoirs should not be ignored because it makes the CCUS projects much more complicated and expensive. The toxicity of H₂S is another factor concerning public safety, and that requires a different set of regulations. Therefore, the influence of hydrogen sulfide on the adsorption characteristics of CO₂ in formation is worthy of being investigated. The study of the impact of impurities like H₂S on CO₂ sequestration is very limited, while most of the literature pays heavy attention to mineral dissolutions, multiphase fluid transport, phase behavior, and gas solubility in the formation water (Bolourinejad and Herber, 2014; Ji and Zhu, 2013; Li D. et al., 2021; Li and Jiang, 2020). Li and his coworkers (Li D. et al., 2021; Li and Jiang, 2020) studied the combined effect of native H₂S and other impurity gases existing in CO₂ gas flow on CO₂ storage in saline aquifer. They found that H₂S dissolution caused a reduction in the concentration of injected gas at the two-phase interface and weakened the convection process. The presence of H₂S in CO₂ flows could result in two-phase flow, and the bubble and dew pressures drop with increasing H₂S concentration in H₂S/CO₂ mixes (Ji and Zhu, 2013). Bolourinejad and Herber (2014) experimentally examined the impacts of H₂S on salt precipitation and mineral dissolution in the process of CO₂ flooding and found that the presence of H₂S damages the permeability due to the aggravation of salt and mineral precipitation.

Subsurface aquifers and depleted oil and gas reserves are regarded as the two main CO₂ storage sites. In both brine aquifers and oil reservoirs, calcite is a very prevalent mineral component (Cui et al., 2021b; Jayasekara et al., 2020). When CO₂ is sequestered, it is inevitable to discuss the interaction between CO₂ containing H₂S impurity gases and calcite due to the highly probable existence of H₂S gas in the injected CO₂ or formation. While GCMC simulation is a widely used research approach, we applied GCMC simulation to reveal the adsorption behavior of individual components (CO₂ and H₂S) and their binary combination in this work (Deng et al., 2022; Liu et al., 2019b; Wang et al., 2021). Previous research examined the effect of contaminants in CO₂ gas on its geological storage using molecular modeling. Chen et al. (2018)

found that the presence of H₂S reduces the interfacial tension of CO₂-water and improves the contact angle in the CO₂/water/silica system. The reduction of interfacial tension enhances the CO₂-water interaction and CO₂ dissolution trapping, while the promotion of contact angle weakens the CO₂ adsorption on the silica wall. Kamath and Potoff (2006) adopted the originally optimized Monte Carlo algorithm to predict the phase behavior of CO₂/H₂S/CH₄ mixtures, and the simulation results are in good agreements with experimental data. Fazelabdolabadi and Alizadeh-Mojarad (2016) probed the structural anisotropy of various hydrocarbon fluid/H₂S/CO₂/H₂O combinations and discovered the ordered arrangement of pure H₂O/H₂S/CO₂ within the adsorption molecules on the carbonate wall.

However, limited studies concentrated on the adsorption characteristics of individual CO₂, H₂S, and binary mixtures. This study examines the adsorption performance of CO₂/H₂S mixture in calcite slit nanopores by conducting Monte Carlo simulations. A wide range of temperatures (293.15–383.15 K) and pressures (0–30 MPa) is tested to cover the conditions of conventional reservoirs. The pore size is set at the micropore level (< 2 nm) because micropores contribute significantly to the adsorption of hydrocarbons and other gases in the formation with ultra-low permeability and developed micro-nano pores (Zhang et al., 2020). The influence of pressure, temperature, the mole fraction of gas, and moisture content on the adsorption capacity of CO₂, and H₂S in calcite nanopores were examined, and the competitive adsorption behavior of (CO₂ + H₂S) binary mixtures was also presented. The conclusion of this work is expected to be beneficial to the competitive adsorption of multicomponent gas in nanopores and the effects of impurities on CO₂ sequestration.

2. Models and methodology

2.1. Calcite slit nanopore model

The calcite slit nanopore model is composed of two calcite slabs, and each slab has six calcite layers. The single calcite layer with a thickness of 18.21 Å is obtained by cutting the (1 0 1 4) crystallographic face first and the supercell operation following. The X, Y, and Z dimensions of the simulation calcite model are set as 32.38, 34.93, and 49.55 Å, respectively, as shown in Fig. 1, and the width of the pore (Z-direction) is fixed at 13.0 Å. In all directions, periodic boundary conditions are implemented. The calcite and two gas molecules (CO₂ and H₂S) are rigid entities, and the charges of individual atoms and the lengths of the bonds are listed in Table 1.

2.2. Force field

A force field is essential for molecular simulation, and a suitable force field can accurately calculate the interaction and potential energy between different molecular structures. COMPASS II (Condensed-phase optimized molecular potentials for atomistic simulation studies) force field is an optimized version of COMPASS force field and permits the precise and simultaneous estimation of gas-phase and condensed-phase features such as structure, equation of state, and vibration frequency over a wide range of molecules and polymers (Liu et al., 2019a; Luo et al., 2020). The COMPASS force field is the first high-quality force field integrating organic and inorganic material parameters (Sun, 1998). The COMPASS II is adopted to perform the entire simulation using the Materials Studio software package based on the previous literature (Sun and Wang, 2020; Wang et al., 2018). Plenty of research adopted the COMPASS II force field in calcite-gas molecule-water systems and the outcomes are consistent with the experimental data (Li et al., 2022; Zhang et al., 2021). The basic mathematical

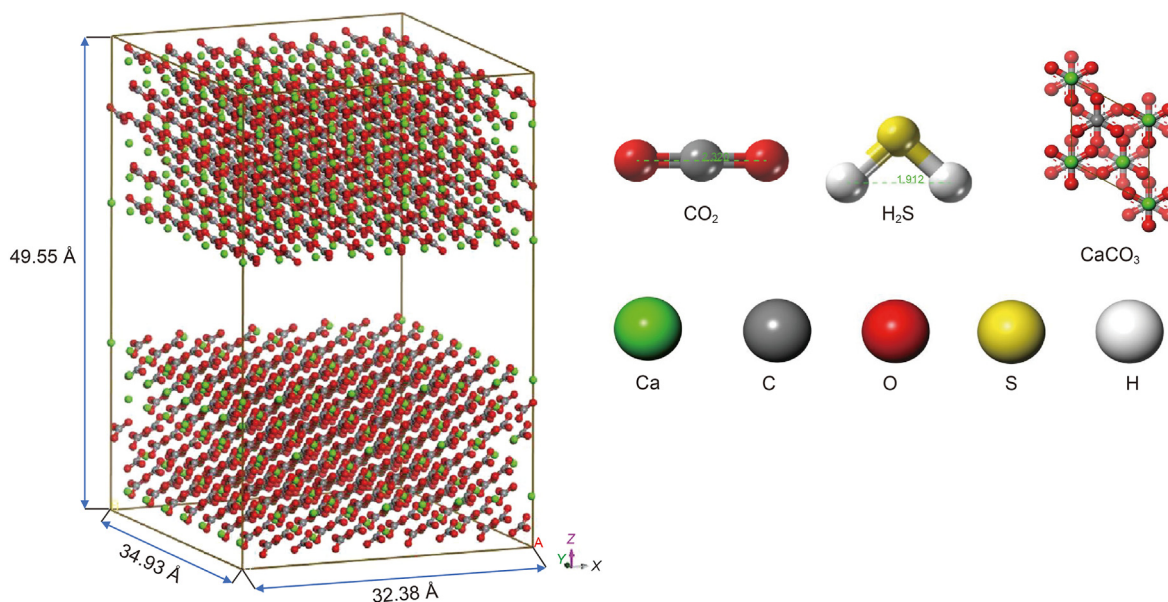


Fig. 1. Model schematic of a calcite nanopore with a pore size of is 13 Å and the individual molecules in the simulation. Color scheme: green-Ca ion; gray-C; red-O; yellow-S; white-H.

Table 1
Molecular structure parameters of CO₂ and H₂S.

Molecule	Atom	Charge, e	Bond length, Å
CO ₂	C	0.80	2.320
	O	−0.40	
H ₂ S	S	−0.338	1.912
	H	0.169	

expression of COMPASS II force field is shown as follows (Sun et al., 2016):

$$E_{\text{total}} = E_b + E_\theta + E_\phi + E_\chi + E_{bb'} + E_{b\theta} + E_{b\phi} + E_{\theta\theta'} + E_{\theta\phi} + E_{\theta\phi'} + E_{\phi\phi'} + E_{\text{vdW}} + E_{\text{ele}} \quad (1)$$

The sum of valence terms, including diagonal and off-diagonal cross-couplings and nonbonded interaction terms, represents the entire potential energy in the COMPASS II force field. E_b , E_θ , E_ϕ , and E_χ are the valence terms for the bond, angle, torsion, and out-of-plane angle coordinates, respectively. $E_{bb'}$, $E_{b\theta}$, $E_{b\phi}$, $E_{\theta\theta'}$, $E_{\theta\phi}$, and $E_{\theta\phi'}$ are the valence terms for cross-coupling terms between internal coordinates (Sun et al., 1998). Coulombic potentials, which describe the electrostatic interaction, and Lennard-Jones 9-6, which describes the van der Waals interaction, serve to define the non-bonded potential. The non-bonded potential is on behalf of intermolecular interaction. The electrostatic interaction and van der Waals interaction are expressed as follows (McQuaid et al., 2004):

$$E_{\text{vdW}} = \sum_{ij} E_{ij} \left[2 \times \left(\frac{r_{ij}^0}{r_{ij}} \right)^9 - 3 \times \left(\frac{r_{ij}^0}{r_{ij}} \right)^6 \right] \quad (2)$$

$$E_{\text{ele}} = \sum_{ij} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (3)$$

2.3. GCMC simulation

The adsorption behavior is investigated through the GCMC algorithm, and each GCMC simulation is carried out under the Fix pressure mode with a total calculation step of 2×10^7 . The first ten million steps are set for the equilibration of the calcite-gas molecule system and the subsequent ten million steps are developed to compute the adsorption process's thermodynamic characteristics. The electrostatic interaction and the van der Waals interaction are characterized by the Ewald & Group algorithm and the Atom-based algorithm with a cutoff radius of 1.55 nm, respectively. The simulation utilizes fugacity instead of pressure to perform CO₂ and H₂S adsorption, and the fugacity of CO₂ and H₂S is determined using the Peng–Robinson equation.

3. Results and discussion

3.1. The isotherms of CO₂ and H₂S adsorption

3.1.1. Adsorption isotherms

The adsorption isotherms of pure CO₂ and H₂S in calcite nanopores at various pressures and temperatures are indicated in Fig. 2. Pure CO₂ can adsorb more readily in calcite nanopores at higher pressures but is less effective at higher temperatures. In calcite nanopores, the effects of pressure and temperature on H₂S adsorption are similar to those of CO₂. The adsorption isotherms of H₂S rise dramatically compared to CO₂. The ability of the calcite nanopores to adsorb gas is improved as the pressure rises. The high temperature improves the thermal motion of the CO₂ and H₂S, increasing the molecule's kinetic energy as a consequence. Therefore, gas molecules are less inclined to adsorb on the nanopores, decreasing the adsorption amounts. Additionally, under identical circumstances, the maximum adsorption amount of H₂S is larger than that of CO₂, and the maximum adsorption capacity of CO₂ is more sensitive to variations in temperature and pressure than that of H₂S.

3.1.2. Density distributions

Fig. 3 illustrates the density profiles of CO₂ and H₂S at 323.15 K in

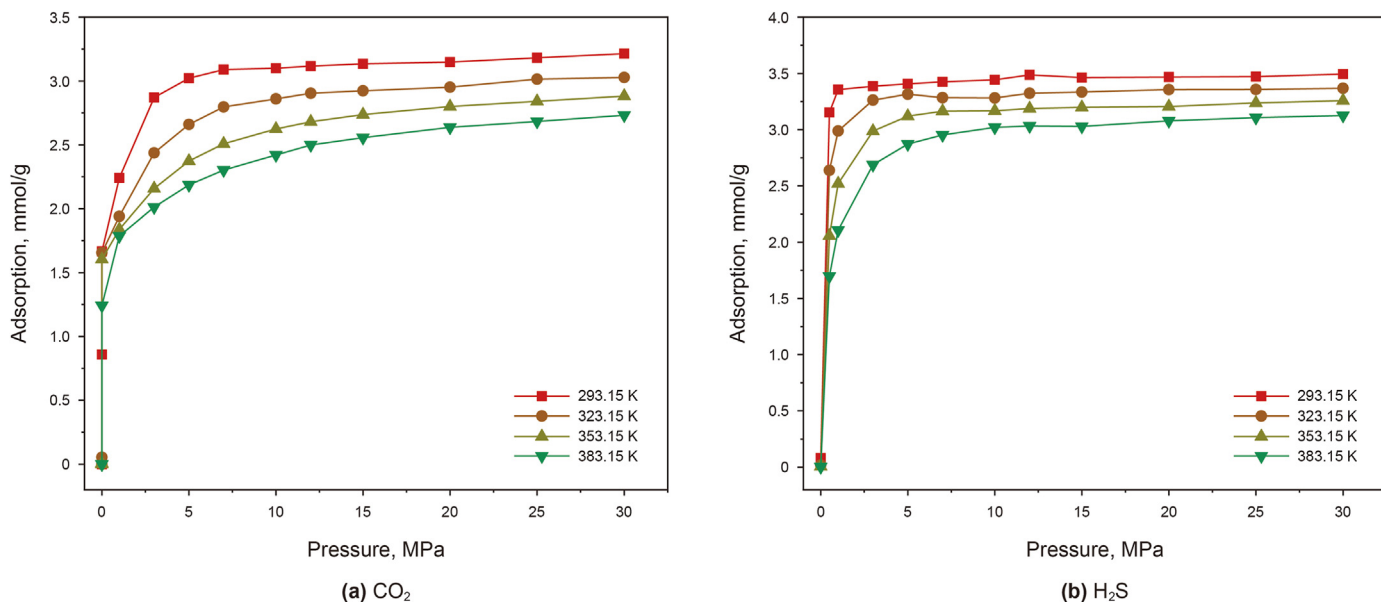


Fig. 2. Adsorption isotherms of CO₂ and H₂S within calcite nanopores.

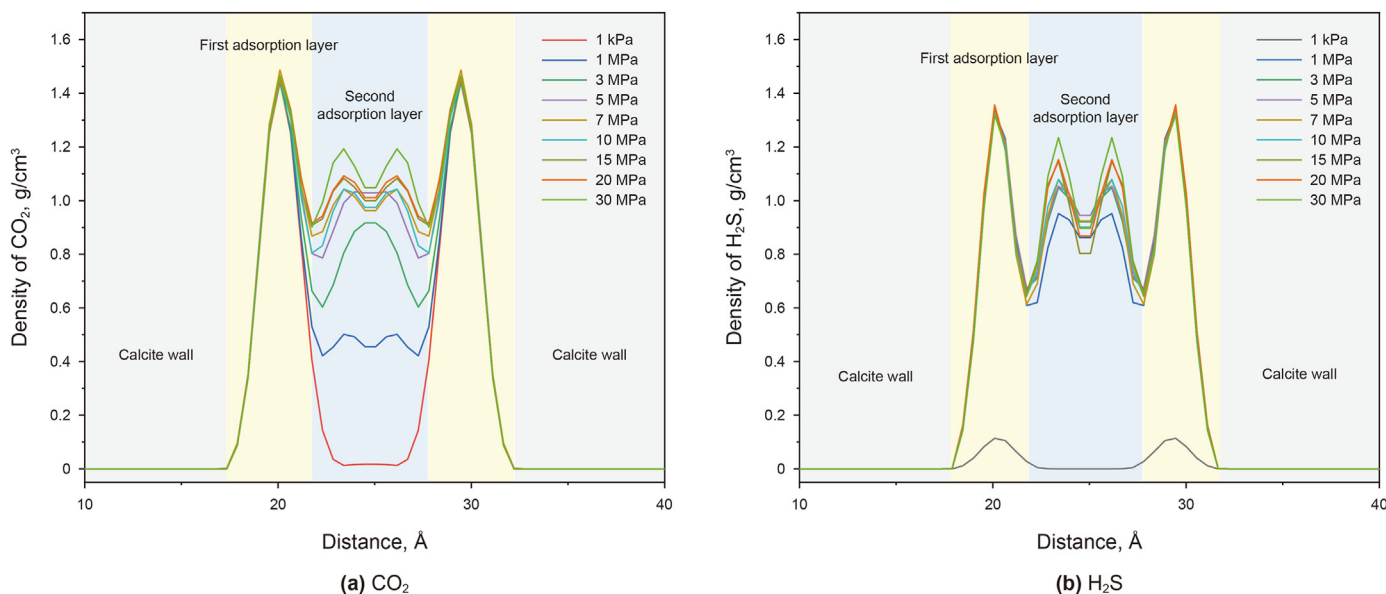


Fig. 3. Density curves of CO₂ and H₂S adsorbed in calcite nanopores at 323.15 K.

calcite nanopores along the Z-axis. In general, the density profile of two pure gases rises when the pressure increases, and gas molecular layers adsorbed on the calcite surface would transform from single to double layers with the increasing pressure. Similar to the first adsorbed layer, the density of the second adsorbed layer also increases as the pressure ascends. As seen in Fig. 3(a), only one adsorbing layer for CO₂ can be observed when the pressure is lower than 5 MPa, while H₂S forms double-layer adsorption on the calcite surface at 1 MPa (Fig. 3(b)). The influence of pressure is consistent with Section 3.1.1, and the adsorption of H₂S increases more sharply than that of CO₂ as the pressure increases. Compared with H₂S, the initial CO₂ adsorption layer has a greater density than the H₂S layer, suggesting that the adsorption amount of CO₂ in the first adsorption layer is larger than that of H₂S. The adsorbed gas molecules in the closest layer usually present stronger interactions, and CO₂

shows a tighter interaction with calcite.

The CO₂ and H₂S density profiles in calcite nanopores at 5 MPa along the Z-axis are illustrated in Fig. 4. As the temperature increases, the density of pure CO₂ and H₂S tends to decline, while the first and second adsorption layers of two pure gases both decrease correspondingly. In addition, the two adsorption peaks of the second adsorption layer gradually evolved into a single adsorption peak when the temperature increases. The second adsorption layer of CO₂ is more affected by temperature than H₂S based on the density variation. As mentioned in Section 3.1.1, the elevation in temperature amplifies the thermal motion of gas molecules, consequently diminishing their adsorption density within nanopore.

Furthermore, changes in the secondary adsorption layer reflect the effects of temperature more clearly. The rise in temperature

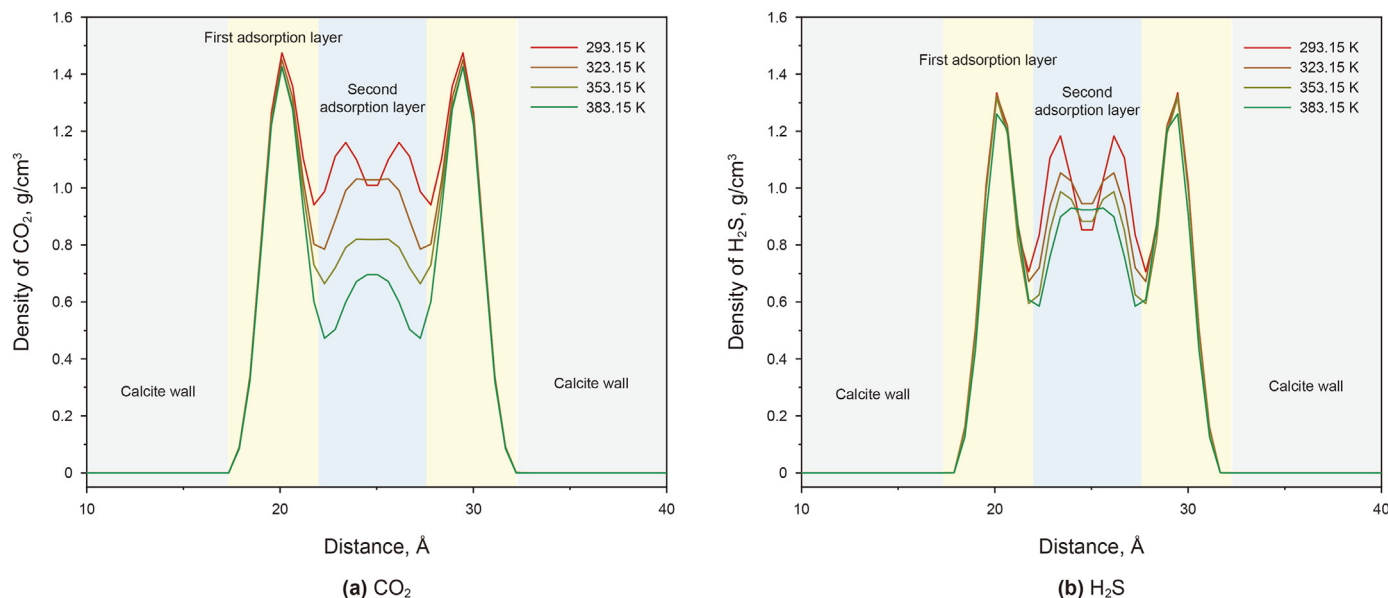


Fig. 4. Density curves of CO₂ and H₂S adsorbed in calcite nanopores at 5 MPa.

diminishes the density of the second adsorption layer, transforming the double adsorption peak into a single adsorption peak. This is primarily attributable to the reduction in density leading to a decrease in the number of molecules, insufficient to sustain the formation of a bilayer adsorption. Simultaneously, it is also a consequence of the diminished attraction exerted by the calcite surface on gas molecules within the second adsorption layer. The peak value of the first adsorption layer has little variation in CO₂ and H₂S density curves. It is because of the strong attraction between the first adsorption layer and the calcite. The calcite surface exhibits pronounced variations in the interactions with molecules in different adsorption layers, and the fundamental cause lies in the distance from the surface; the closer to the surface, the stronger the attraction, with less susceptibility to temperature influence. Conversely, greater distances are subject to more substantial temperature effects. In addition, CO₂ has a greater density in the first adsorption layer than H₂S and H₂S prefers to form double-layer adsorption than CO₂ at high temperatures. As for CO₂ sequestration, the low pressure and high temperature are not conducive to raise storage. The increase in pressure can effectively strengthen the adsorption and CO₂ storage in calcite formation.

3.1.3. Radial distribution function

The radial distribution function (RDF) refers to the distribution frequency of other particles in the space around a given particle (how far away from the given particle). RDF reflects the intensity of calcite and gas molecule interactions. Meanwhile, RDF has a consistent trend over a range of temperature and pressure settings. The RDFs of CO₂ and CaCO₃ at 323.15 K and 1 MPa are displayed in Fig. 5. The first chart indicates the RDF of CO₂ and the Ca²⁺ of CaCO₃ and the latter chart is the RDF of CO₂ and the CO₃²⁻ of CaCO₃. The maximum of CO₂-Ca²⁺(CaCO₃) is higher than those of CO₂-CO₃²⁻(CaCO₃), which shows that CO₂ favors the adsorption with the Ca²⁺ of calcite. The peak value of Ca²⁺(CaCO₃)-O(CO₂) emerges at 2.26 Å, and that of Ca²⁺(CaCO₃)-C(CO₂) emerges at 3.30 Å, suggesting that the distance between the oxygen atom of carbon dioxide and Ca²⁺ is less than that of the carbon atom and Ca²⁺. Therefore, the strongest interaction within the CO₂-calcite system belongs to the intermolecular forces between the oxygen atom of carbon dioxide and the calcium ion in calcite, which is in accord

with the previous study (Jayasekara et al., 2020).

Fig. 6 displays the RDF curves of CO₂ and CaCO₃ (calcite). Fig. 6(a) and (b) indicate the RDF of CO₂ and the Ca²⁺ of CaCO₃ and that of CO₂ and the CO₃²⁻, respectively. In Fig. 6(a), the highest values of RDFs of three kinds of atom in CaCO₃ and S(H₂S) are apparently higher than the peak value of the three kinds of the atom and the hydrogen atom. It can be inferred that the surfer atom with negative charge is more prone to attach to a calcite surface than the hydrogen atom with positive charge. Taking the ranges between the S of H₂S and three kinds of atoms in CaCO₃ into consideration, the smaller the distance means the stronger the interaction between the two atoms, and the gap space between the surfer atom and calcium ion reaches a minimum value. In a word, the interaction between the surfer atom and calcium ion is strongest in the H₂S-calcite system.

The RDF curves of Ca²⁺(CaCO₃)-CO₂ and Ca²⁺(CaCO₃)-H₂S are plotted in Fig. 7. The maximum values of the two RDF curves are 4.59 and 2.25 and the distances between the calcium ion and two gas molecules are 2.26 and 3.62 Å, correspondingly. It is obvious that the affinity between CO₂ and Ca²⁺ is better than that of H₂S and Ca²⁺, indicating a more readily interaction of CO₂ molecules with CaCO₃.

3.1.4. Interaction energy

The intermolecular interaction energy between calcite and gas molecules is considered as the interaction energy (E_{int}) and the interaction energy consists of the van der Waals energy (E_{vdw}) and electrostatic energy (E_{elec}). The interaction energy values between calcite and pure CO₂/H₂S and the percentage denoting the proportion of E_{elec} and E_{vdw} in the E_{int} are presented in Table 2. The absolute values of the interaction energy reveal the intensity of the attraction between gas molecules and calcite, which is indicated by its negative value. The interaction energy of calcite-CO₂ dominantly comes from the electrostatic energy that accounts for 97.11% of E_{int} . As for the calcite-H₂S system, the strengths of E_{vdw} and E_{elec} are similar and have a proportion of 43.67% and 56.33%, respectively. The E_{int} of calcite-CO₂ is higher than that of calcite-H₂S, showing a more intense attraction in the calcite-CO₂ system, which explained the more readily interaction of CO₂ molecules with the CaCO₃.

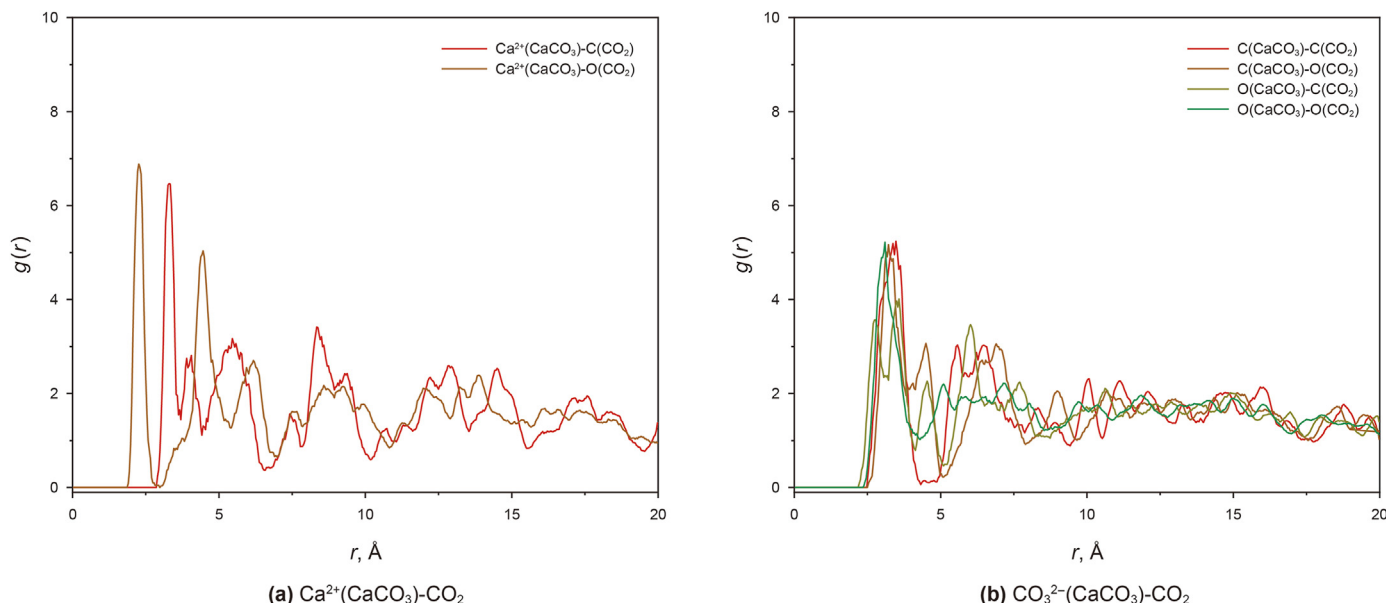


Fig. 5. The radial distribution function between the atom of CO_2 and the atoms of CaCO_3 at 323.15 K and 1 MPa.

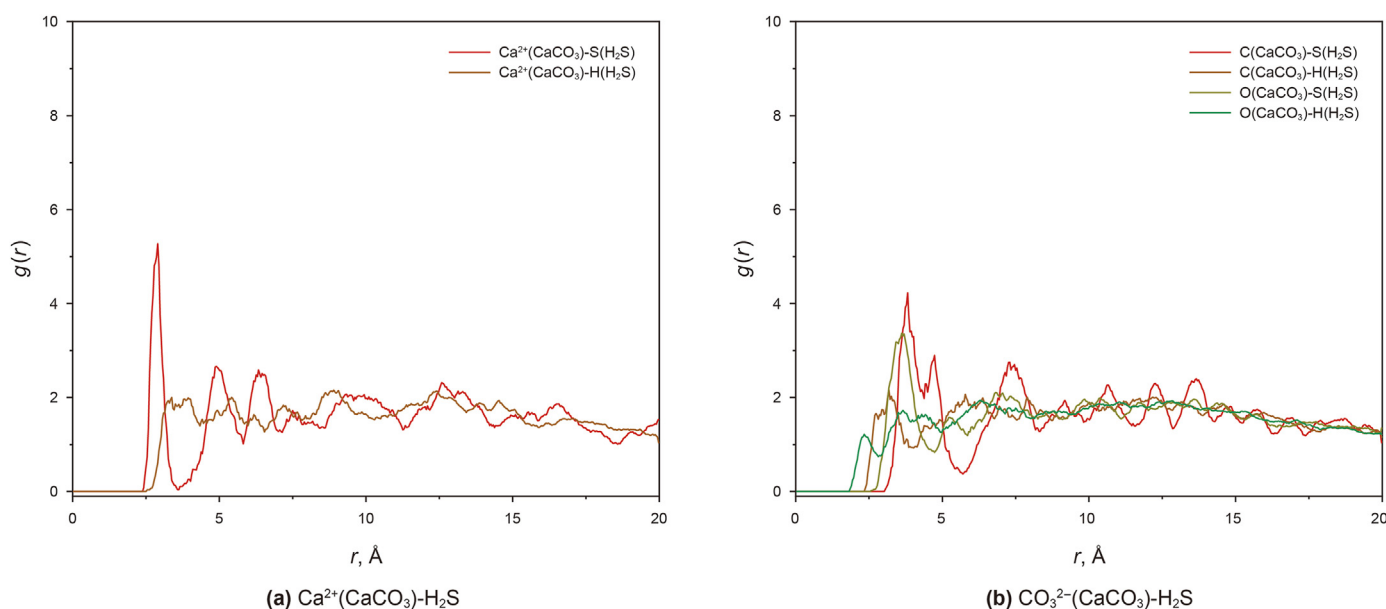


Fig. 6. The radial distribution function between the atom of H_2S and the atoms of CaCO_3 at 323.15 K and 1 MPa.

3.1.5. Adsorption orientation of CO_2 and H_2S

The angle θ marked in Fig. 8(a) formed by the $\text{CO}_2/\text{H}_2\text{S}$ molecules and the calcite contact was calculated to determine the orientations of CO_2 and H_2S . The CO_2 molecules adsorbed on the calcite surface show an angle range of 15° – 45° . The distribution of angles suggests that CO_2 molecules tend to recline on calcite surfaces, as shown in Fig. 8(b). The principal consideration is the strong affinity between the O atom of CO_2 and Ca^{2+} of CaCO_3 . As for the θ of H_2S , the frequency distribution is the highest at 0° and the larger angle is accompanied by the lower frequency distribution, suggesting that the axis of H_2S is inclined to keep a parallel or small angle with the calcite adsorption surface. Explanation for this phenomenon is that the sulfur atoms are always preferentially adsorbed on the calcite surface and two hydrogen atoms with weaker charge have a nearly

equal interaction with the surface force of calcite.

3.2. Adsorption isotherms of $\text{CO}_2/\text{H}_2\text{S}$ mixture

3.2.1. Adsorption isotherms and average isosteric heat

The H_2S content in different sites and injection methods varied dramatically. Generally, the concentration of H_2S in CO_2 injected into oil and gas reservoirs or deep saline aquifers does not exceed 10% (Alpermann et al., 2016; Li et al., 2017). However, in an effort to minimize the emissions of H_2S and CO_2 , Canada has implemented active sour gas injection projects involving the injection of solutions or dense fluids. In such projects, the H_2S component can constitute 2%–83% of the total gas injected (Bachu et al., 2005; Bachu and Bennion, 2009). It should be noted that, in conventional

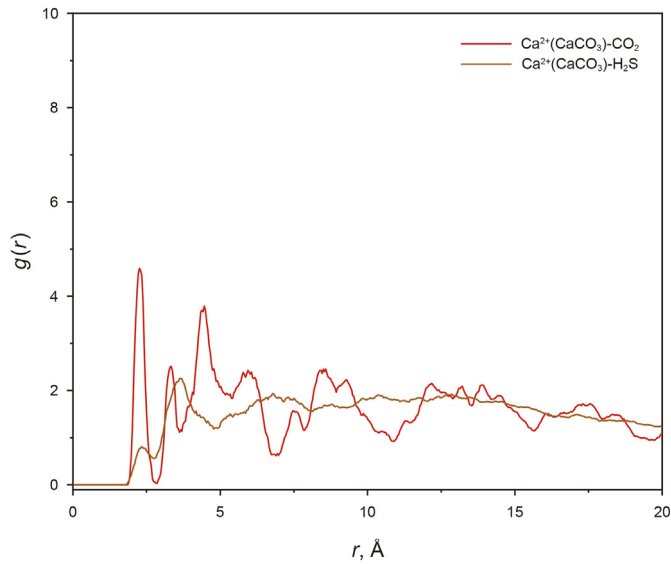
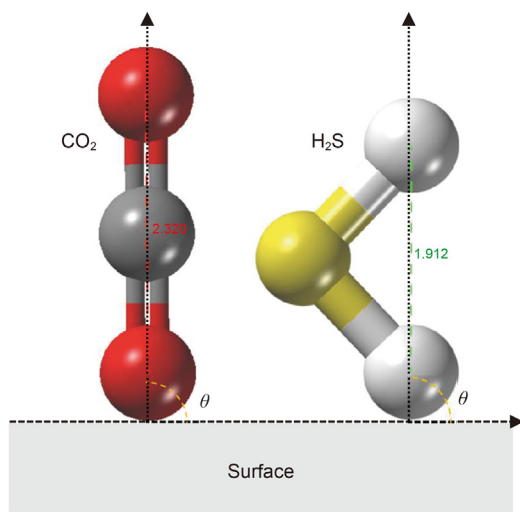


Fig. 7. The RDFs between CO₂/H₂S molecules and calcium ion of CaCO₃ at 323.15 K and 1 MPa.

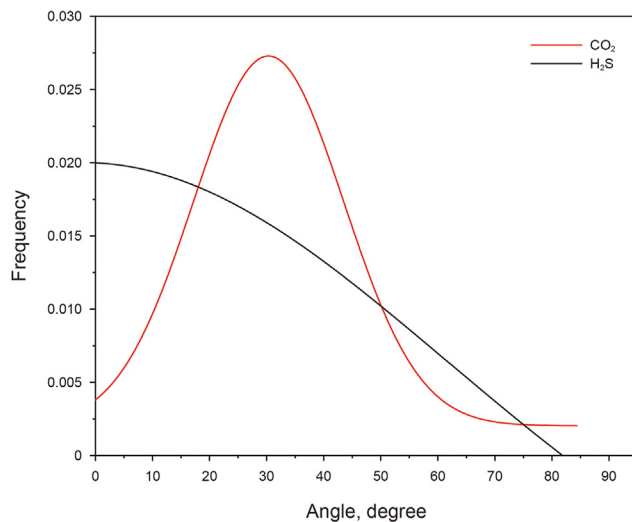
Table 2
Interaction energy between CaCO₃ and CO₂, H₂S systems (10 MPa, 323.15 K).

Pure gas	Interaction energy, kcal/mol			Percentage, %	
	E_{vdw}	E_{elec}	E_{int}	E_{vdw}	E_{elec}
Calcite-CO ₂	-59.92	-2012.22	-2072.14	2.89	97.11
Calcite-H ₂ S	-738.94	-952.98	-1691.92	43.67	56.33

natural gas reservoirs, the content of H₂S typically ranges from 2% to 70% (Bolourinejad and Herber, 2014; Ji and Zhu, 2013; Zhang et al., 2011). Consequently, the actual content of H₂S varies significantly between different locations during field operations. In order to fully characterize the competitive adsorption processes of CO₂ verse H₂S under varied H₂S concentrations, the molar concentrations of CO₂ and H₂S was assigned as 0%, 25%, 50%, 75%, and 100%, respectively.



(a) Inclination of CO₂ and H₂S



(b) Frequency analysis

Fig. 8. Schematic diagram for the inclination of CO₂ and H₂S, and frequency analysis for the angle θ of CO₂ and H₂S at 10 MPa and 323.15 K.

The adsorption isotherms and average isosteric heat of CO₂ and H₂S at the temperature of 323.15 K are plotted in Fig. 9(a) and (b). The adsorption capacity of CO₂ and H₂S in calcite nanopores rises with the ascension of its mole fraction in binary mixes. When the mole fraction of CO₂ is 0.75, the quantity of CO₂ adsorbed is about two-thirds that of pure CO₂. The quantity of CO₂ adsorbed is reduced by approximately 14% when the CO₂ molar ratio falls from 0.5 to 0.25, indicating a faster decline in the adsorption capacity at a relatively high mole fraction of CO₂.

Unlike pure CO₂, CO₂ in binary mixtures reaches its maximum adsorption under lower pressure, while pure H₂S forms maximum adsorption more rapidly than H₂S binary mixtures. Then, CO₂ adsorption isotherms exhibit a modest decrease as the pressure continues to increase with the presence of H₂S. Meanwhile, a mild rise occurs in the adsorption curves of H₂S accordingly. After the system pressure climbs to about 5 MPa, the amount of CO₂ adsorbed starts to increase as H₂S adsorbed begins to decrease progressively. The existence of H₂S does affect the adsorption amount of CO₂ in calcite nanopores due to the competitive adsorption, which would cut down the amount of CO₂ sequestered in calcite rock. A higher mole fraction of H₂S would lead to less CO₂ sequestration.

As shown in Fig. 9, the average isosteric heat of CO₂ adsorption process declines with the increases in pressure and mole proportion of CO₂, while the average isosteric heat of H₂S adsorption increases as the pressure and mole ratio of H₂S ascend gradually. The adsorption potential of both gases is also directly influenced by the pressure and molar ratio. More specifically, when the adsorption amount of two gas molecules increases due to the changes in pressure and molar ratio, the average isosteric heat of CO₂ and H₂S increases and decreases respectively. The differing energy levels of the gas molecules in the multiple adsorption layers account for the contradictory experimental findings and the impact of pressure and gas mole ratio on energy value would be discussed in detail in Section 3.2.3.

3.2.2. Density distributions

The density distribution of CO₂ and H₂S with various mole fractions at 10 MPa and 323.15 K was shown in Fig. 10. The density profile of CO₂ and H₂S in binary mixture generally increases with the increase in gas mole fractions. CO₂ molecules in the binary

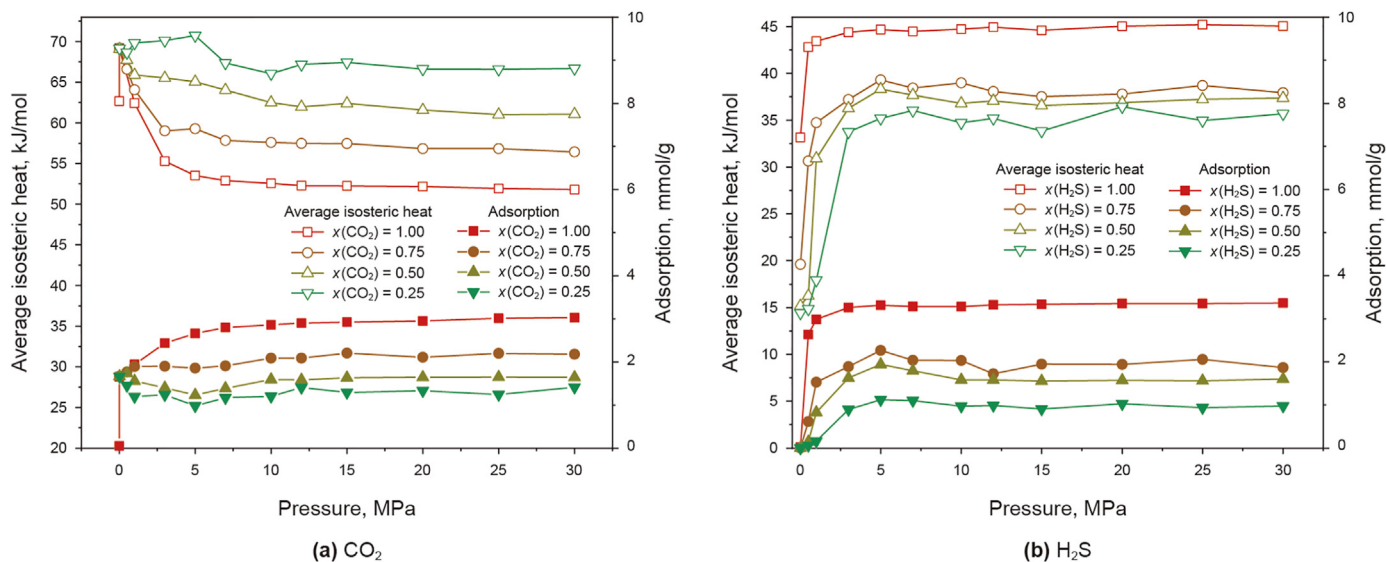


Fig. 9. Adsorption isotherms and average isosteric heat of CO₂ and H₂S at 323.15 K ($x(\text{CO}_2)$ and $x(\text{H}_2\text{S})$ are mole fractions of CO₂ and H₂S in CO₂/H₂S mixture at the initial state).

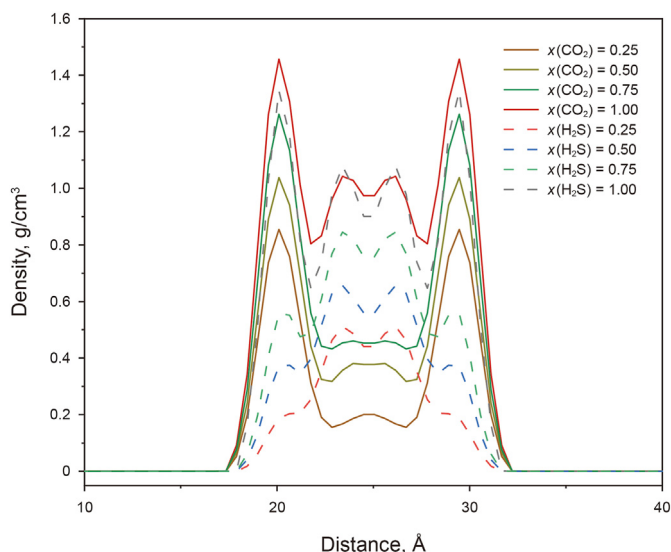


Fig. 10. Density profiles of CO₂ and H₂S in calcite nanopores with different mole fractions (10 MPa, 323.15 K).

mixture always tend to form monolayer adsorption in calcite pore walls and the density profiles of H₂S would transform from monolayer to double layers when comparing the binary mixture with the density distribution of pure gas. For all simulations of CO₂/H₂S mixture in calcite nanopores, as shown in Fig. 11, CO₂ molecules preferentially occupy the regions on both sides of the pores and H₂S molecules prefer to fill up the middle part of the pores according to the density profiles graphics. The density profiles of CO₂/H₂S mixtures imply that CO₂ interacts more favorably with calcite surfaces than H₂S. According to the results of RDF and interaction energy, the attraction between CO₂ and calcite is stronger than that of the calcite-H₂S system. It implies that CO₂ has the propensity to settle on the CaCO₃ surface, and H₂S forms a weaker adsorption layer in areas away from the CaCO₃ surface.

3.2.3. Potential energy distribution

The potential energy distribution profiles of CO₂ and H₂S with

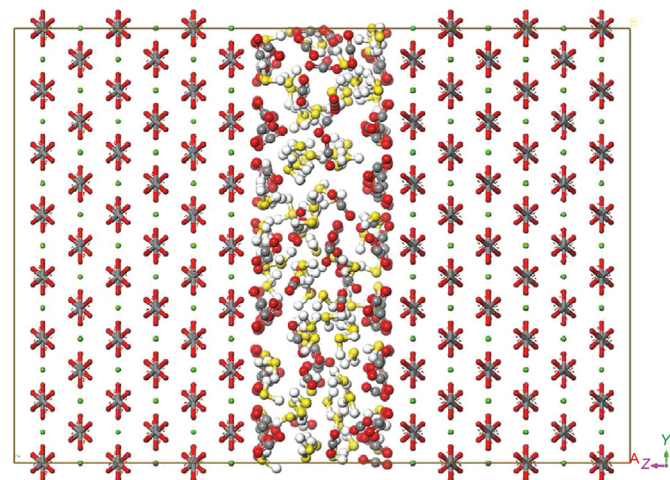


Fig. 11. Schematic diagram for the distribution of CO₂ and H₂S molecules in calcite nanopores at $x(\text{CO}_2) = 0.5$ (10 MPa, 323.15 K).

various mole fractions at 10 MPa and 323.15 K are plotted in Fig. 12. As the mole fractions of the CO₂/H₂S combination in calcite nanopores increases, the distribution of potential energy evolves in the opposite direction. The peaks of CO₂ lines progressively shift to the right as the CO₂ ratio increases, and the peak value of the lower energy site and higher energy site fall and rise, respectively. Changes in energy distribution show that the adsorption of CO₂ in calcite nanopores progressively transforms from lower energy adsorption to higher energy sites as the CO₂ mole fraction rises. While the peak positions of H₂S curves gradually slide to the lower energy sites with the presence of H₂S. The extremum with lower energy increases and the extremum with higher energy declines with the rise of the H₂S proportion. Meanwhile, the distribution probability of CO₂ in low-energy states is always greater than that in high-energy states, and the potential energy distribution of H₂S is opposite to that of CO₂.

The variation in the potential energy distribution of CO₂ and H₂S molecules accounts for the different trends of average isosteric heat in CO₂ and H₂S adsorption. If the initial energy of CO₂ is identical, a higher energy CO₂ molecule in equilibrium means a lower average

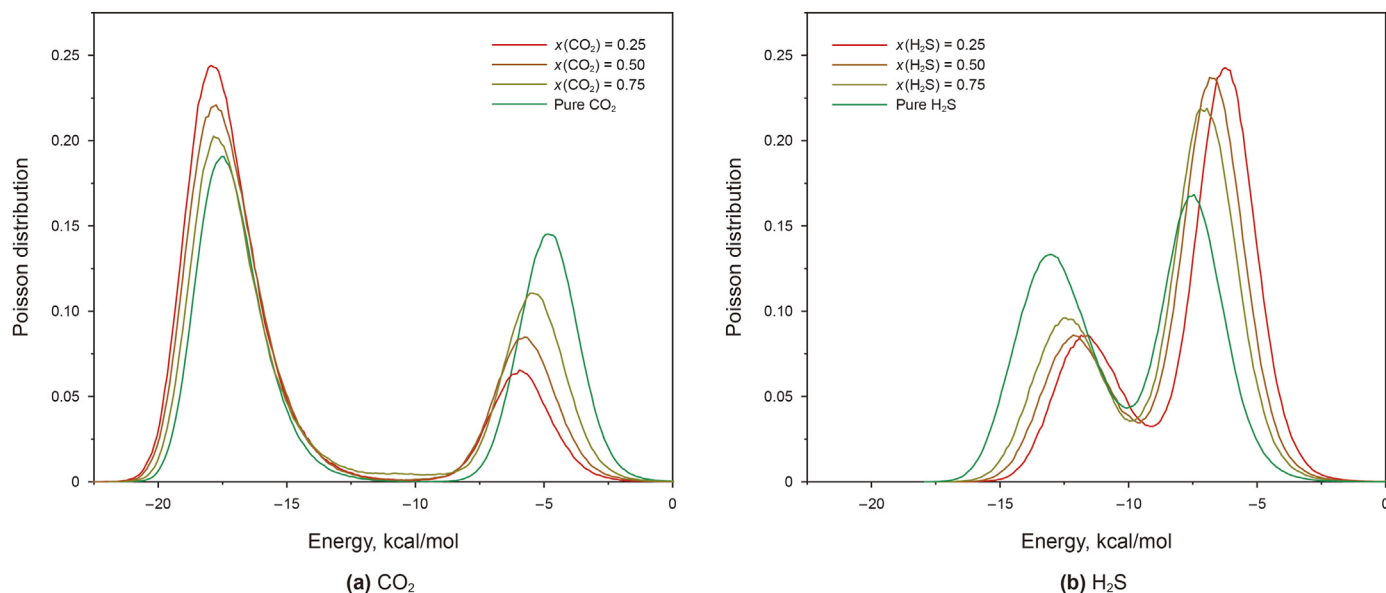


Fig. 12. Potential energy distribution of CO₂ and H₂S in calcite nanopores with different mole fractions (10 MPa, 323.15 K).

isosteric heat. Based on simulation results, the alteration in energy of CO₂ and H₂S in binary mixture matches the trend of the average isosteric heat as the gas mole fraction increases. In general, the energy and average adsorption strength of CO₂ and H₂S molecules in the binary mixture decreases and increases as the gas mole ratio increases separately. The double-layer adsorption of CO₂ and H₂S is the primary cause of this phenomenon. CO₂ adsorbed in the first layer has lower energy and the excess CO₂ in the second adsorption layer exhibits higher energy. Owing to the saturation adsorption of the first layer, as the molar concentration of CO₂ increases, the increased CO₂ molecules will settle more in the second adsorption layer. The increment of CO₂ in the secondary adsorption layer leads to an enhancement of the potential energy of CO₂ molecules and CO₂ molecules as higher energy is less stable. Therefore, CO₂ adsorbing on the calcite surface will be more stably sequestered in the reservoir, and the CO₂ molecules in the second adsorption layer with higher energy are more easily desorbed. For H₂S double-layer adsorption, the first adsorption layer of H₂S similarly has lower energy, while the energy of the second adsorption layer is comparatively higher. In the case of pure H₂S adsorption, the energy distribution is at its lowest state since, at this juncture, the proportion of H₂S molecules in the first adsorption layer is maximized. With an increase in the concentration of H₂S in the mixture, both the density of H₂S molecules in the first and second adsorption layers escalates (as depicted in Fig. 10). However, the additional H₂S molecules tend to be more prominently distributed in the first adsorption layer, thereby resulting in an overall upward trend in the energy of H₂S molecules.

3.3. Adsorption selectivity of CO₂ over H₂S

To define the selective adsorption characteristics of CO₂/H₂S combination in calcite nanopores, we introduce the adsorption selectivity of CO₂ over H₂S, which can be expressed as (Liu and Hou, 2020):

$$S_{\text{CO}_2/\text{H}_2\text{S}} = \frac{x_{\text{CO}_2}/x_{\text{H}_2\text{S}}}{y_{\text{CO}_2}/y_{\text{H}_2\text{S}}} \quad (4)$$

where x_{CO_2} and $x_{\text{H}_2\text{S}}$ indicate the mole fractions of CO₂ and H₂S

adsorbed, respectively, in the first layer; y_{CO_2} and $y_{\text{H}_2\text{S}}$ denote the mole fractions of CO₂ and H₂S adsorbed, respectively, in the second layer. If $S_{\text{CO}_2/\text{H}_2\text{S}}$ is greater than 1, it means that CO₂ has the adsorption priority on the calcite surface over H₂S (Huang et al., 2022; Liu et al., 2016).

The adsorption selectivity of CO₂ over H₂S in calcite nanopores is illustrated in Fig. 13. Each of the computed adsorption selectivity values exceeds 1, which demonstrates that CO₂ is adsorbing predominantly on the calcite as the results of the competitive adsorption of CO₂/H₂S mixture. All adsorption selectivity curves exhibit a downward trend when the system pressure is at a low level (around 7 MPa) and then stays at a relatively stable level as pressure increases, showing a better adsorption capacity of CO₂ in calcite nanopores compared to H₂S.

The impact of CO₂ concentration on adsorption preference at 323.15 K is shown in Fig. 13(a). As the mole fraction of carbon dioxide increases, the adsorption selectivity becomes lower, it indicates that the CO₂ adsorption on the contact of calcite is stronger with a low mole fraction. Fig. 13(b) illustrates the adsorption selectivity of CO₂ over H₂S in nanopores at four different temperatures. We observed that the adsorption selectivity improves as temperature increases, which indicates that the proportion of CO₂ molecules in the first adsorption layer consistently exceeds that of H₂S molecules, and the disparity in the ratio of these two molecules within the first adsorption layer widens with rising temperature. As elevated temperatures result in a reduction in the adsorption performance of gas molecules, it is conjectured that the adsorption ability of carbon dioxide on calcite surface degrades more slowly compared to H₂S. Generally, the mole fraction of CO₂ and the pressure enhance the adsorption capacity of CO₂ in the CO₂/H₂S combination, while the high temperature is reversed. While the adsorption selectivity of CO₂ over H₂S and adsorption isotherms of the mixtures demonstrate that CO₂ adsorption dominates when temperatures ≥ 323.15 K and the pressure in the range of 0–7 MPa, suggesting that CO₂ is more suitable for the sequestration in shallower formations.

3.4. Impact of water content

The adsorption performance of CO₂ and H₂S are simulated in

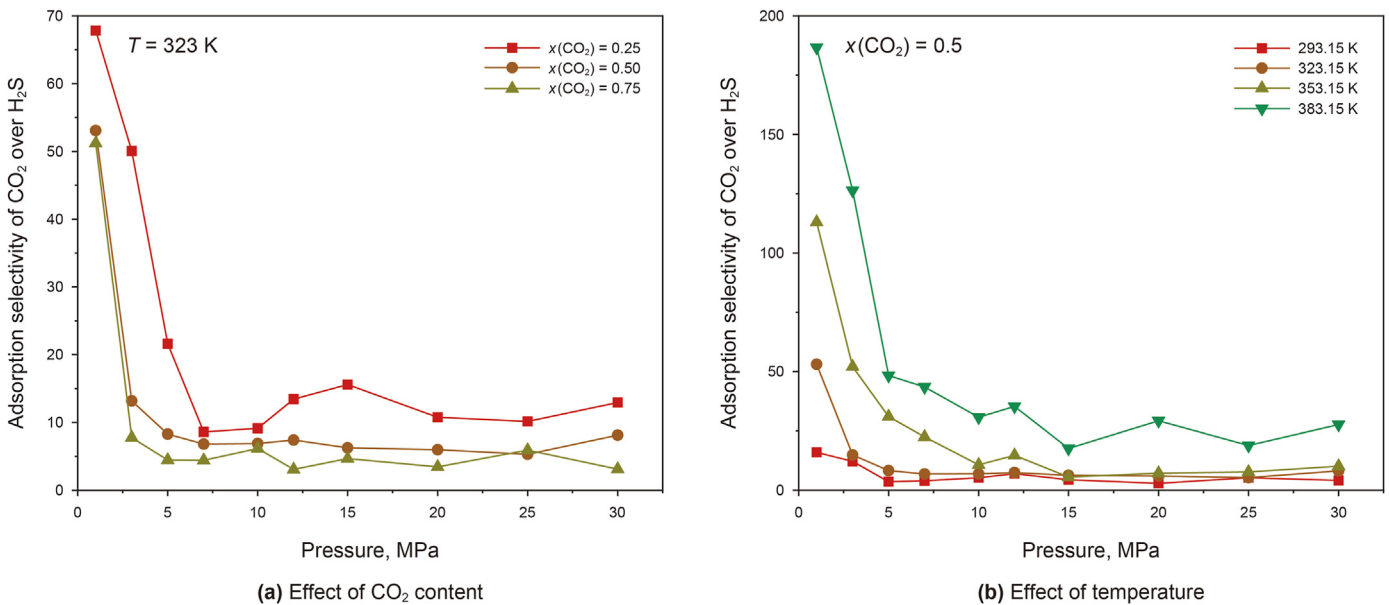


Fig. 13. Adsorption selectivity of CO₂ over H₂S with the different mole fractions of CO₂ and temperatures.

calcite nanopores containing different water content. Noted that the mass fraction of water is calculated from the ratio of the H₂O mass to the total mass of calcite and water. The adsorption capacity of CO₂ and H₂S with various water content at 323.15 K are plotted in Fig. 14. As the increase in water content in calcite nanopores, the CO₂ and H₂S adsorption capability steadily declines. In more detail, the adsorption amount of CO₂ and H₂S with water content of 2.61 wt% is reduced to 71.84% and 71.70%, respectively, compared to that in dry nanopores. According to Table 3, the influence of water content on the capacities of two gases for adsorption is generally coincident. Calcite nanopores were populated by clusters of water molecules and the H₂O molecule shows the highest priority in the adsorption performance in calcite nanopores than CO₂ and H₂S. In other words, the H₂O molecules adsorbed in the calcite nanopores shield the two gas molecules.

Table 3
The ratio of gas adsorption amount with water to that without water (323.15 K, 30 MPa).

Mass fraction of water, wt%	Ratio of gas adsorption amount, %	
	CO ₂	H ₂ S
0	100.00	100.00
0.67	92.33	92.80
1.32	85.13	85.99
1.97	78.49	77.59
2.61	71.84	71.70

As shown in Fig. 15, in CO₂/H₂S mixture, the adsorption of CO₂ in calcite nanopore without water content is slightly higher than that

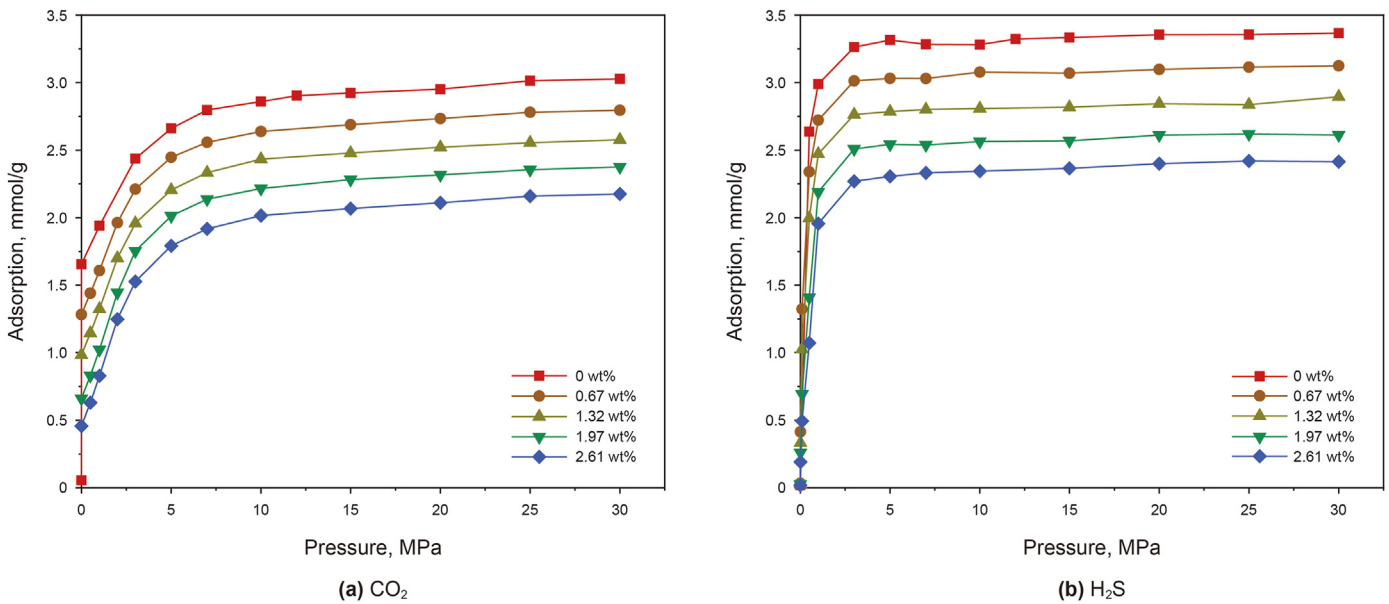


Fig. 14. Adsorption capacity of CO₂ and H₂S with different water content (323.15 K).

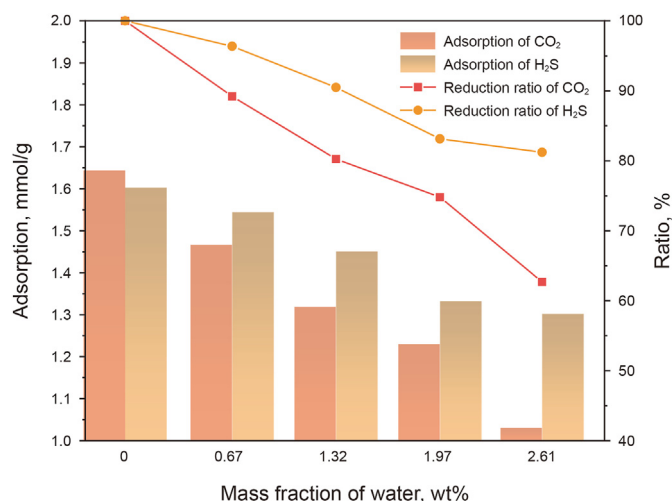


Fig. 15. The adsorption amount of CO₂ and H₂S and the ratio of gas adsorption amount with different water content at $x(\text{CO}_2) = 0.5$ (323.15 K, 30 MPa).

of H₂S. The adsorption of two gases declines as the H₂O content increases; the decline rate of CO₂ adsorption is substantially greater than that of H₂S. When the water content is 2.61 wt%, the amount of CO₂ and H₂S adsorbed drops to 62.70% and 81.22%, which illustrates that the adsorption performance of CO₂ is more impacted by moisture in calcite nanopores compared with H₂S. It is mainly because both H₂O and CO₂ tend to be adsorbed near the pore wall and CO₂ originally adsorbed on the CaCO₃ contact in the binary mixture is replaced by H₂O, which leads to a rapid decline in CO₂ adsorption. Meanwhile, moisture has less impact on H₂S negatively located in the middle region of the nanopore. Hence, the existence of moisture limits CO₂ absorption and sequestration in calcite-rich formations substantially.

3.5. Implications for CO₂ sequestration

The co-injection of impurity gas will influence the total storage of CO₂. Our study indicates that H₂S can indeed reduce the adsorption of CO₂ in calcite pores, suggesting that H₂S in injected CO₂ and native H₂S in the formation will lessen the CO₂ storage in the calcite-rich formation. As has been mentioned, the increases in pressure and temperature have opposite effects on CO₂ adsorption. When CO₂ and impurity gas are stored in the reservoirs, pressure and temperature increase in tandem. Herein, we set up a series of depths with the pressure differences (1.0 MPa/100 m) and the geothermal differences (2.5 °C/100 m, the surface temperature is 20 °C) to optimize the depth for CO₂ sequestration. The adsorption ability of CO₂ at various mole fractions and buried depths are shown in Fig. 16. As for pure CO₂, its adsorption quantity quickly increases to its peak at roughly 2.90 mmol/g and then gradually declines as the depth of formation increases. It can be inferred that the intensifying effect of pressure dominates in shallower formations and then the weakening effect of temperature starts to take over the adsorption behavior when pure CO₂ dives into deeper formations. Hence, pure CO₂ is suggested to be sequestered in the shallower formations, i.e. 500–1500 m.

Moisture has a detrimental effect on the ability of CO₂ to be absorbed, reducing the adsorption amount by about 24%. Moisture significantly weakens CO₂ adsorption and storage. As for CO₂/H₂S mixtures, the adsorption amount of CO₂ increases as the buried depth increases, indicating that the pressure prevails over the competition with temperature. Meanwhile, CO₂ adsorption amount

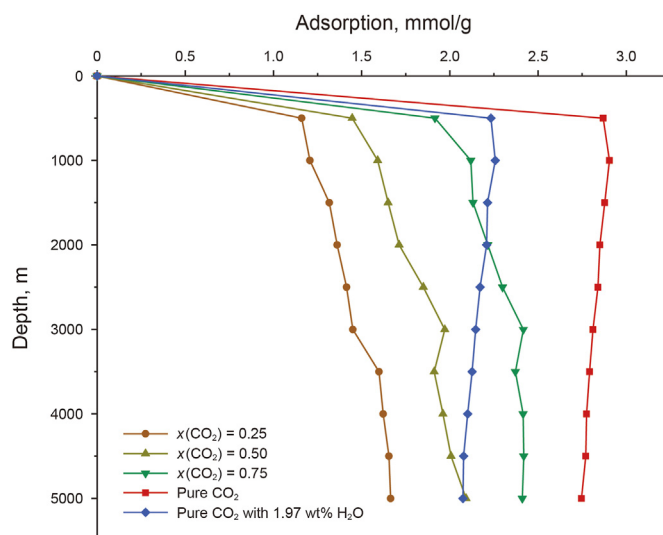


Fig. 16. Adsorption performance of CO₂ under different circumstances at various buried depths.

declines as the increase in H₂S mole fraction, indicating the detrimental effect of H₂S on CO₂ storage capacity. Moreover, as the formation depth grows, the impact of H₂S lessens. It is suggested that CO₂ containing H₂S should be stored in deeper formations.

4. Conclusions

This work investigates the adsorption behavior of CO₂/H₂S mixture in calcite slit nanopores with GCMC simulations. The adsorption performance of CO₂, H₂S, and their binary mixture in CaCO₃ nanopores are simulated to estimate the impact of various factors. The following succinctly states the main conclusions.

- (1) In calcite nanopores, a rise in pressure enhances the adsorption ability of CO₂ and H₂S, whereas the temperature is reversed. CO₂ shows stronger adsorption on the calcite surface and the two gases are both inclined to form double adsorption layers under higher adsorption amounts. Ca²⁺ has a stronger interaction with CO₂ than H₂S and the distance between CO₂ and Ca²⁺ (2.26 Å) is less than that of H₂S (3.62 Å). The interaction energy of calcite-CO₂ and calcite-H₂S is −2072.14 kcal/mol and −1691.92 kcal/mol and electrostatic energy play a major role. The CO₂ adsorbed on the calcite surface shows an angle range of 15°–45° and the axis of H₂S prefers to keep parallel or small angles with the calcite adsorption surface.
- (2) H₂S reduces the adsorption amount of CO₂ in calcite nanopores due to the competitive adsorption of binary mixtures; a higher mole fraction of H₂S causes less CO₂ adsorption. The adsorption amount of CO₂ and H₂S in nanopores promotes as their mole fraction rises. CO₂ molecules preferentially occupy the position close to the nanopore wall and H₂S molecules prefer to fill up the intermediate zone. The potential energy of CO₂ and H₂S rises and falls with the promotion of gas mole proportion, which matches the trend of the average isosteric heat as the gas mole fraction increases.
- (3) The adsorption selectivity values of CO₂ over H₂S exceeds 1, demonstrating the favorably adsorption of CO₂ in the competitive adsorption of the CO₂/H₂S mixture. The moisture in calcite nanopores can lessen the adsorption amount of CO₂ and H₂S; the weakening effect gets stronger as the

water content increases. The weakening effect of water content on CO₂ adsorption is significantly greater than that on H₂S adsorption in the binary mixture. Pure CO₂ is suitable to be buried in the shallower formations i.e. 500–1500 m, whereas CO₂ with H₂S should be settled in the reservoirs as deep as possible.

This work presents insights into the adsorption behavior of the CO₂/H₂S mixture and theoretical assistance for CO₂ storage projects. In future research, a more in-depth investigation should also be performed on the diffusion, mass transfer behavior of CO₂, and its multi-component mixtures to support CO₂ sequestration.

CRediT authorship contribution statement

Cheng Qian: Writing – original draft, Methodology, Investigation, Conceptualization. **Zhen-Hua Rui:** Supervision, Project administration. **Yue-Liang Liu:** Supervision, Data curation. **Kai Du:** Writing – review & editing, Data curation. **Chen Liu:** Visualization, Data curation. **Yang Zhao:** Writing – review & editing, Visualization, Investigation. **Xiao-Min Ma:** Software, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We greatly acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 52004320), the Science Foundation of China University of Petroleum, Beijing (No. 2462021QNXZ012, No. 2462022BJRC001, and No. 2462021YJRC012), and the funding from the State Key Laboratory of Petroleum Resources and Engineering (No. PRP/indep-1-2103).

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