



Research paper

Molecular modeling on transportation of CO₂ in montmorillonite: Diffusion and permeation

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ABSTRACT

CO₂ storage in underground saline aquifers is helpful to reduce CO₂ emission in the atmosphere, where gas/fluid diffusion and permeation in clay mineral plays a key role in CO₂ leakage and underground migration. CO₂ Permeability and different fluid diffusivities in clay mineral (montmorillonite, Mt) interlayers are investigated by molecular dynamics (MD). Both CO₂ and H₂O self-diffusivities increase with water concentration and temperature but show a maximum at the CO₂ concentration of 2 molecule/unit-cell unconventionally. The fractional free volume of Mt increases with CO₂ concentration but begins to decrease if CO₂ concentration exceeds 2, thus giving the reason for the above unusual CO₂ self-diffusivity variation. Displacement distribution of CO₂ molecules is found to be characterized by logarithmic normal distribution. The mean value of such distribution further supports the self-diffusivity dependence on CO₂ concentration. M-S and Fick diffusivities of CO₂ are positively related to CO₂, H₂O concentration and temperature. CO₂ permeability is calculated by MD for the first time, which increases with CO₂ pressure and H₂O concentration but exhibits a turning point at temperature 360 K due to low CO₂ solubility at high temperature.

1. Introduction

CO₂ storage in underground saline aquifers provides long-term and large-scale storage of CO₂, which is a promising way to reduce CO₂ emission in the atmosphere. In this process, clay minerals, such as illite, chlorite, kaolinite, and montmorillonite (Mt) (Josh et al., 2012), are the main components of caprocks. Owing to their porous (layered) structure, the clay minerals have remarkable capacity of adsorbing CO₂ (Fu et al., 1990; Khosrokhavar et al., 2014). On the other hand, clay mineral has a low permeability and therefore the clay-enriched caprocks show excellent sealing ability to retain injected CO₂ (Abdou and Ahmaed, 2010; Gaus, 2010; Gernot et al., 2013). Gas leakage and environmental impacts are the most concerned problems for risk assessments of CO₂ storage, which are closely related to fluid (gas) transportation (diffusion and permeation) in clay mineral.

The interactions of CO₂ and clay mineral have been reported by many authors. For example, Giesting et al. investigated impact of CO₂ absorption on Ca-exchanged Mt expansion under different CO₂ pressure (Giesting et al., 2012). CO₂ can migrate the interlayer region of montmorillonite based on the in situ X-ray diffraction (XRD), magic angle spinning nuclear magnetic resonance spectroscopy (NMR) and attenuated total reflection infrared spectroscopy (ATR) (Loring et al., 2014; Loring et al., 2012). In addition, quasi-elastic neutron scattering

experiments (QENS) experiments on hydrated clays have shown that hydrated cation diffusion mobility is probably a complex dynamic process and the diffusion coefficients of the exchangeable cations were estimated (Sobolev et al., 2009). Kozaki et al. determined the apparent diffusion coefficients of Cs⁺ as functions of the temperature (Kozaki et al., 1999). Sánchez et al. discussed that the self-diffusion of water depended on temperature and ionic strength in different kinds of clays (Sánchez et al., 2008). However, there are a few experiments on diffusivity of CO₂ in clay although permeation processes in sediments and clay-rich rocks have been investigated experimentally by many authors (Javadpour et al., 2007). For instance, permeability of CO₂ declined during shearing while increasing sliding velocity reduced the decline rate (Javadpour, 2009). Permeability of simulated granite is highly related to fracture transmissivity (Tanikawa et al., 2014).

Molecular simulation becomes a powerful tool in many fields and has been used for understanding the molecular-scale structural (Lee et al., 2014; Teich-Mcgoldrick et al., 2015), thermodynamic (Boek et al., 1995), mechanical (Zhang et al., 2015), and dynamic (Botan et al., 2010; Krishnan et al., 2013; Malikova et al., 2004; Yang and Zhang, 2005) properties of clay mineral. Grand canonical Monte Carlo (GCMC) method was applied to simulation the adsorption of CO₂ with H₂O (Botan et al., 2010), CH₄ (Jin and Firoozabadi, 2013; Kadoura et al., 2016; Yang et al., 2015), and organic molecules (Krishnan et al.,

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2013; Yu et al., 2003) in Mt. Molecular dynamics (MD) was employed to study the structure and self-diffusion coefficient of carbon dioxide in uncharged clay-like slit pores (Yang and Zhang, 2005). Cygan et al. developed CLAYFF force field (Cygan et al., 2004) for clay mineral and three-site flexible potential modes of CO₂ (Cygan et al., 2012). Botan et al. demonstrated that CO₂ considerably influenced the diffusion of mobile species in clay minerals (Botan et al., 2010). Myshakin et al. showed that the intercalation of CO₂ in Mt caused the significant changes of the d-spacing and described that the distribution and diffusion of CO₂, H₂O, Na⁺ was affected by the number of layers of clay mineral (Makaremi et al., 2015; Myshakin et al., 2014; Myshakin et al., 2013).

Although fluid self-diffusion coefficients (SDC) in clay mineral has been investigated by MD and macroscopic permeability have been discussed experimentally in some of above works, the other transportation diffusivities and permeability of CO₂ have not been explored microscopically by MD yet. MD study on various diffusion coefficients and permeability of CO₂ in clay mineral, Mt, will be performed in this work. The effects of gas concentration, water concentration, and temperature are considered.

2. Methods

2.1. Theoretic aspects

Self-diffusion means random motions or mixing of particles at the thermodynamic equilibrium. SDC, $D_{i\text{self}}$, of component i is computed by Einstein equation

$$D_{i\text{self}} = \frac{1}{2dn_i} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{l=1}^n (r_{l,i}(t) - r_{l,i}(0))^2 \quad (1)$$

where n_i is the number of the molecules of the component i , d is the dimension of the system, and $r_{l,i}(t)$ is position vector of the molecule l at time t .

Fick diffusion is characterized by the particle motions driven by concentration gradient, leading to the net mass transport. Fick's law of diffusion defines the transport diffusivity or Fick diffusion coefficient (FDC), $D_{i\text{Fick}}$, as the proportionality factor between the flux N and the concentration c gradient:

$$N_i = -D_{i\text{Fick}} \nabla c_i \quad (2)$$

Chemical potential gradient is considered as the fundamental driving force for diffusion (Krishna, 2012; Krishna and Jasper, 2005). For a single component diffusion in porous material the transport equation can be expressed as

$$N_i = -L_i \nabla \mu_i \quad (3)$$

where μ_i is the chemical potential of gas i . L is obtained from the MD simulations using (Theodorou et al., 1996)

$$L_i = \frac{1}{2dVk_B T} \lim_{\Delta t \rightarrow \infty} \frac{1}{\Delta t} \left\langle \left(\sum_{l=1}^{n_i} (r_{l,i}(t + \Delta t) - r_{l,i}(t)) \right)^2 \right\rangle \quad (4)$$

where V is the Mt volume, k_B is the Boltzmann constant and T is the temperature. The content in $\langle \dots \rangle$ means an average on the cross displacement correlation function (CDCF). The notation $\langle \dots \rangle$ represents an average on a number of independent particle ensembles rather than single particles.

Using Maxwell-Stefan (M-S) theory (Maxwell, 1867; Stefan, 1871), the diffusion formula of single component follows

$$N_i = -\rho \Theta_{i,\text{sat}} D_{iM-S} \frac{\Theta_i}{k_B T} \nabla \mu_i \quad (5)$$

where ρ is the Mt density expressed as the number of unit cells per cubic meter, $\Theta_{i,\text{sat}}$ is the saturation loading of the component i , μ_i is the chemical potential expressed in Joules per molecule. N_i is the molar flux of

the component i expressed in molecules per square meter per second, the fractional occupancy θ_i is defined as

$$\theta_i = \frac{\Theta_i}{\Theta_{i,\text{sat}}} \quad (6)$$

where Θ_i is the loading of the component i . Combing the Eq. (3) and Eq. (5), the Maxwell-Stefan diffusion coefficient (MDC), D_{iM-S} , is calculated by

$$D_{iM-S} = \frac{k_B T}{\rho \Theta_i} L_i \quad (7)$$

Under isothermal condition, the molecules are considered to move with average velocity subject to a driving force $\nabla \mu_i$, $\mu = \mu_0 + k_B T \ln f$, where f is the fugacity, then $\nabla \mu = k_B T \nabla \ln f$, so that Eq. (2) is equivalent to Eq. (3).

$$N_i = -D_{i\text{Fick}} \nabla c_i = -\rho D_{i\text{Fick}} \nabla \Theta_i = -\rho D_{i\text{Fick}} \Theta_i \frac{\partial \ln \Theta_i}{\partial \ln f_i} \frac{\nabla \mu_i}{k_B T} \quad (8)$$

The FDC and MDC are related by

$$D_{i\text{Fick}} = D_{iM-S} \Gamma \quad (9)$$

where Γ is the thermodynamic factor

$$\Gamma = \Theta_i \frac{\partial \ln f_i}{\partial \Theta_i} \quad (10)$$

Permeability, P , measures the ability of fluids (gas or liquid) to flow through porous media. Solubility coefficient, S , is an important factor to determine the thermodynamic behavior (adsorption) of the fluid in porous media, which are defined as:

$$S = c/f, P = D_{iM-S} S \quad (11)$$

Following the derivation given by Konstantinos Makrodimitris et al. (Makrodimitris et al., 2001), P can be calculated from:

$$P = -\frac{D_{iM-S}}{\Delta f} \int_{f_1}^{f_2} \frac{c(f)}{f} df \quad (12)$$

where c is the concentration in porous media as a function of fugacity, f_1 and f_2 are downstream and upstream pressure in the permeability determination respectively.

2.2. Molecular dynamics simulation details

The sodium-saturated Wyoming-type Mt is used as the clay mineral crystal model with unit formula Na_{0.5}[Si₈](Al_{3.5}Mg_{0.5})O₂₀(OH)₄ (Skipper et al., 1995), which comprises the 2:1 or tetrahedral – octahedral – tetrahedral (TOT) layers. The substitutions of octahedral Al³⁺ by Mg²⁺ lead to net negative layer charge. The interlayer Na⁺ cations are balanced by these negative charges. Three-dimensional periodic boundary condition is applied to a simulation box composed of 32 (8 × 4 × 1) unit cells. Mt model with different number of CO₂ and H₂O are allowed to freely swell to their equilibrium d-spacing. All simulated systems are listed in Table 1. Cn ($n = 1, 2, \dots$) denote the system in which the number of H₂O is fixed and the number of CO₂ is represented by n. Hn ($n = 1, 3, \dots$) represent systems with different number of H₂O. Tn ($n = 1, 2, \dots$) mean systems with varying temperature.

All simulations are performed with the Accelrys Material Studio software (<http://accelrys.com/>). The CLAYFF force field is used (Cygan, 2004 #42). The Ewald summation method is applied to the electrostatic interaction. The atom-based summation method is used in the van der Waals interactions. Gas diffusions are simulated as follows: gases are first inserted into the above equilibrium configuration by grand canonical Monte Carlo (GCMC) method to get a new clay-gas cell. The cell is minimized and equilibrated by NPT and NVT runs. Then the cell runs in an NVT ensemble (0.5 ns) followed by a long-time (5 ns) NVE run. The trajectories in the NVE run are saved for diffusion coefficient

Table 1

Details of simulated systems. Number in bracket indicates the corresponding CO₂ or H₂O concentration in molecules/cell.

Number of CO ₂	Number of H ₂ O	Temperature	d-spacing	Short-name
10 (0.331)	160 (5)	313.15	12.50	C1
16 (0.5)	160 (5)	313.15	12.70	C2
32 (1)	160 (5)	313.15	13.50	C3
48 (1.5)	160 (5)	313.15	14.00	C4
64 (2)	160 (5)	313.15	14.50	C5
80 (2.5)	160 (5)	313.15	14.75	C6
64 (2)	32 (1)	313.15	11.90	H1
64 (2)	96 (3)	313.15	13.00	H3
64 (2)	160 (5)	313.15	14.50	H5
64 (2)	224 (7)	313.15	15.50	H7
64 (2)	288 (9)	313.15	17.25	H9
32 (1)	128 (4)	273.15	12.50	T1
32 (1)	128 (4)	313.15	12.50	T2
32 (1)	128 (4)	353.15	12.50	T3
32 (1)	128 (4)	393.15	12.50	T4
32 (1)	128 (4)	433.15	12.50	T5

computation. Integration time step is set to 1 fs. Gas concentration, water component and temperature are varied to investigate their impacts on gas diffusions.

3. Results and discussion

3.1. SDC

Molecular dynamics (MD) simulation can be used to obtain not only gas diffusion coefficients but also the microscopic details of the diffusion process, which is helpful to understand underlying diffusion mechanism in a confined space. Diffusion coefficients are calculated based on statistically averaging the motion of large amounts of particles, and their accuracy relies on the sample size. Each system is run ten times independently to get reliable results. The resulting MSDs are averaged to calculate SDC. Note that Unless stated otherwise, the diffusion coefficients in this paper refer to that of diffusion in the x-y plane. MSD_{xy} of the C4 system varies with time is taken as an example (Fig. 1). MSD_{xy} displays a good linear correlation with time. The SDC can then be determined using eq.(1). The resulting SDC is $7.584 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for CO₂ in the C4 system, which is close to the result of Myshakin et al. (2013). The SDC of CO₂ in Mt is lower than that of CO₂ in pure water, $2.93 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Tamimi et al., 1994), which is due to the confinement effect of Mt interlayer surface. Diffusion coefficients are related to many factors including type and concentration of the gas, pore size, temperature and so on. Injection pressure of CO₂, moisture content and underground temperature are key factors in the geological storage of CO₂.

The influence of CO₂ concentration on its SDC is considered first.

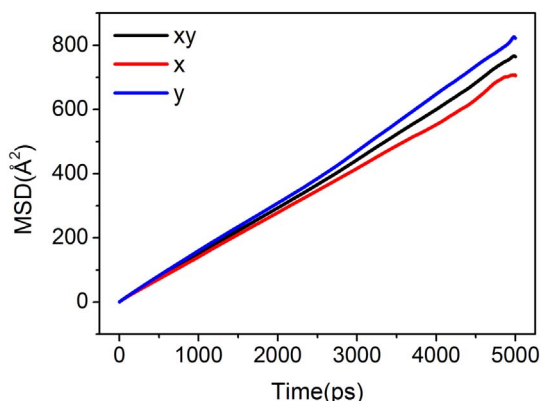


Fig. 1. The average MSD vs time in C4 system.

The number of water molecules is set to 5 molecules per unit cell and the temperature to 313.15 K (approximately the temperature of 1000 m underground). The Monte Carlo method is used to insert varying amounts of CO₂ molecules into the system. The system is then relaxed to equilibrium through NPT and NVT run, with resulting interlayer distances (d-spacing) shown in Table 1. The equilibrated system is then subject to dynamic run in NVE ensemble to compute SDC, as shown in Fig. 2(a). With the increase of CO₂ concentration, the SDCs of CO₂ and H₂O first increase and then decrease. At the CO₂ loading value of 64 (C6 system), the SDCs of both reach maximum values. The SDC of H₂O remains higher than that of CO₂, which originates from the smaller thermodynamic diameter of H₂O (2.65 Å) compared with that of CO₂ (3.3 Å).

However, many studies have shown the SDCs of gases in porous media to decrease with the increase of their concentrations (Krishna and Paschek, 2002; Skoulidas and Sholl, 2005; Skoulidas et al., 2003), which is different from the aforementioned result in Fig. 2(a). In order to explore the reason for the variation of SDC, the effect of CO₂ on the Mt structure is further analyzed. As shown in Table 1, the d-spacing of Mt continues to increase with CO₂ concentration, which could provide fluids with larger space for diffusion, resulting in larger diffusion coefficient. It may be expected that SDC should increase with CO₂ concentration monotonously. However, our simulations reveal a lower SDC in high-concentration system C6 compared to the low-concentration system C5. In order to explore the reason for this unusual SDC variation further, fractional free volume (FFV) of the system which is defined as the ratio of interlayer space unoccupied by fluids to the total volume of Mt:

$$\text{FFV} = \frac{V_{\text{free}}}{V_{\text{total}}} \quad (13)$$

where V_{free} is the free (unoccupied) volume in the Mt interlayers, and V_{total} is the total volume of the simulated Mt cell. The FFV can be determined by molecular probes (Connolly, 1983; Ronova et al., 2003). FFV increases with the CO₂ concentration first and peaks at 64 CO₂ molecules also, which is in accordance with the position of the maximum of CO₂ SDC (Fig. 3(a)). This indicates two counter-interactions: first, the increase of CO₂ concentration could cause the expansion of d-spacing in the system and provide fluids with more space for diffusion; on the other hand, the increase of CO₂ molecules occupies more space, resulting in a decrease of free volumes. The fluid molecules become more crowded and diffuse more slowly. Therefore, fluid SDC depends on the free space in the interlayer. At the initial stage of CO₂ injection, the rapid expansion of d-spacing raises the free volume in the interlayer, which is beneficial for fluid diffusion, and causes CO₂ SDC to increase; the free volume reaches a maximum at 64 CO₂ molecules; the free volume decreases despite the continued expansion of d-spacing, which hinders gas diffusion and causes descending SDCs of CO₂ and H₂O (Fig. 3(a)).

Water is the most important geological fluid and water content varies with the location and the depth of storage aquifer. A Mt system with 2CO₂ molecules per unit cell is used to investigate quantitatively the impact of water concentration on the diffusion. Temperature is fixed at 313 K. SDCs of both CO₂ and H₂O increase with H₂O concentration (Fig. 2(b)). Similarly, the FFVs under different moisture contents can be calculated. FFV increases with moisture content (Fig. 3(b)), showing the same trend as the SDCs. This indicates the increase of water molecules raises the free volume in the interlayer space and contributes to the fluid diffusion.

At last, temperature is considered. As shown in Fig. 2(c), the increase of temperature can accelerate the thermal motion of molecules and then increase their kinetic energy, causing the fluid SDC to increase gradually. It is revealed that the relationship between SDC and temperature follows the classical Arrhenius formula:

$$D = D_0 e^{-\frac{E_a}{RT}} \quad (14)$$

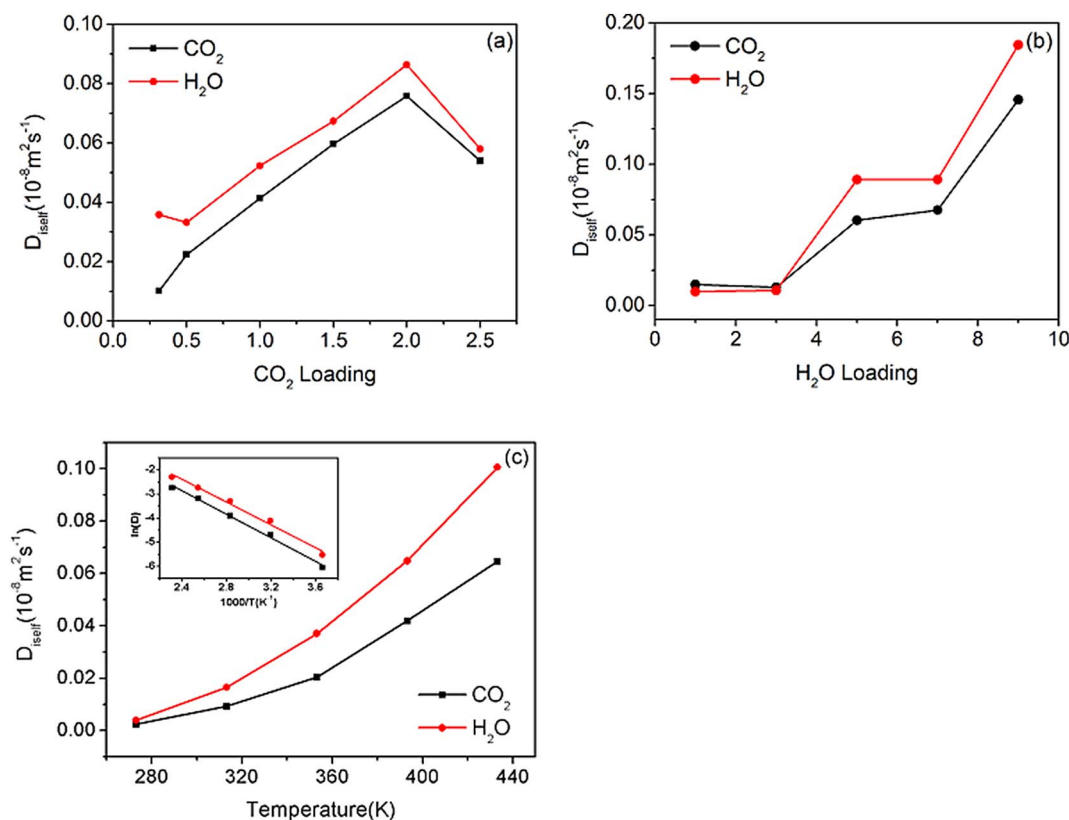


Fig. 2. The self-diffusion coefficient D_{self} of CO_2 and H_2O in Mt variation with: (a) CO_2 loading, (b) H_2O loading and (c) temperature. Inset of (c) shows Arrhenius plot of SDC versus temperature.

where D_0 is a constant, and E_a is the activation energy of diffusion. According to the equation, the activation energy for CO_2 diffusion in Mt is 20.26 kJ/mol (see Fig. 2(c)), which is greater than its activation energy of diffusion in pure water 17.8904 kJ/mol (Tamimi et al., 1994). This implies the Mt layers impose restriction on CO_2 diffusion, leading to a higher activation energy in Mt.

MD can provide more details such as the paths and displacements of molecules to study the microscopic mechanism of gas diffusion. Since layered Mt provides anisotropic confined space without interconnected micropores, diffusion of gas in such structure is different from random movements of gas in unlimited environment. The displacement distribution of CO_2 molecules is further analyzed. All the distributions have single peak and no peak is shown at large displacements (Fig. 4). The displacements generally fall within the 0.6–1.0 Å. As CO_2 concentration increases, the displacement peak (i.e. the prevailing displacement) moves toward the right and becomes wider, reaching the maximum width in the C5 system (Fig. 4(a)). This indicates increases of both the prevailing displacement and the number of fast-speed molecules. Therefore, with the increase of CO_2 concentration, SDC of CO_2

increases and reaches a maximum at C5 system. Similarly, the increase of moisture and temperature lead to both increase of prevailing displacement and peak width, causing the SDC to increase (Fig. 4(b)–(c)). The displacement distributions can be fitted to logarithmic normal distribution function (LNDF):

$$y = \frac{e^{-\frac{(-a + \log(x))^2}{2b^2}}}{d\sqrt{2\pi}x} \quad (15)$$

The curves are well-fitted with the data ($R^2 > 0.98$) (Fig. 5(a)). To quantitatively examine the relationship between the displacement distribution and SDC, the mean value of LNDF: $R_{av} = e^{(a + b^2/2)}$ (unit Å), an important characteristic parameter for log-normal distributions, is calculated (Fig. 5(b)–(d)). Here R_{av} increases with CO_2 concentration firstly, reaches a maximum at C5, and then decreases (Fig. 5(b)), showing the same trend as the SDC of CO_2 . The average displacement of molecules in unit time (1 ps) reflects the relative speed of diffusion and hence larger R_{av} results in faster diffusion rate and a higher SDC. In a word, R_{av} is positively related to the SDCs of CO_2 and H_2O . This is

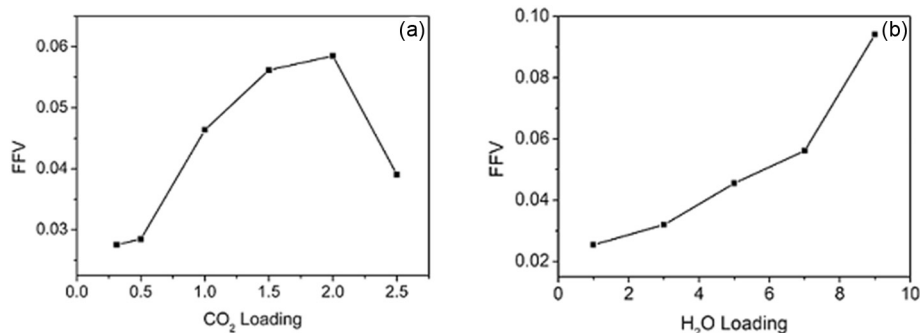


Fig. 3. FFV dependence on: (a) CO_2 loading, (b) H_2O loading.

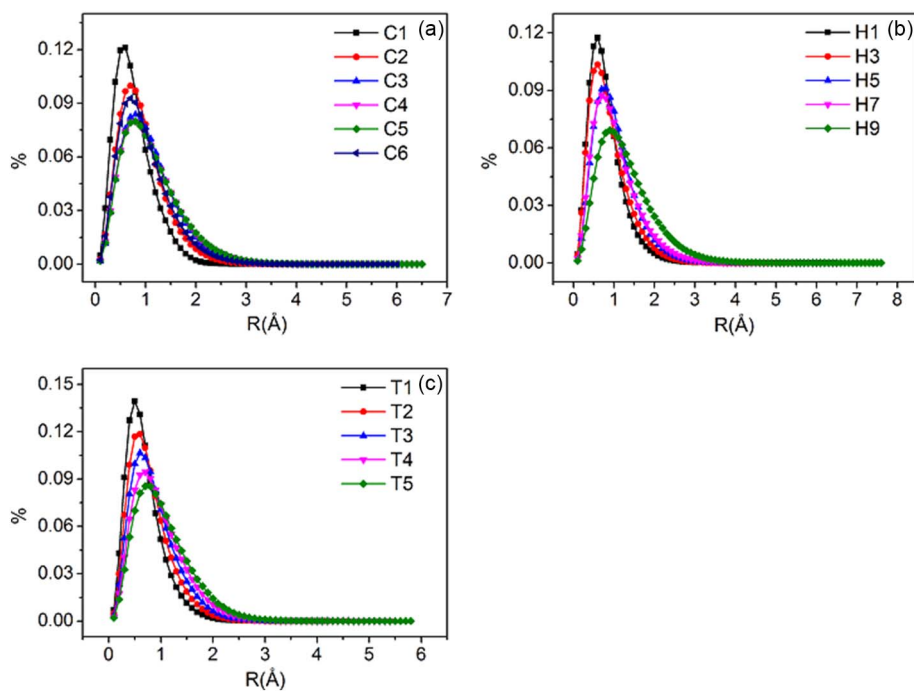


Fig. 4. The distribution of displacement in different systems: (a) CO₂ loading, (b) H₂O loading, (c) temperature.

further validated by systems with varying moisture content and temperatures. As Shown in Fig. 5(c) and (d), R_{av} increases with moisture, and increases linearly with temperature, causing the increase of SDCs of CO₂ and H₂O (Fig. 2).

3.2. MDC and FDC

The Onsager coefficient L should be determined using Eq. (4) first to get MDC. Note that, unlike the MSD in Eq. (1) which measures single particle movement, CDCF in Eq. (4) measures the collective motion of all fluid molecules in Mt. Displacement summation of all the particles

within time interval Δt is calculated first. Then the average of the square of the summation plotted against time, whose slope is used to get L according to Eq. (4). This formula not only applies to single fluid diffusion but also suits multi-component fluid diffusion (Hu et al., 2017). There is a good linear correlation between CDCF and time (Fig. 6). L can thus be computed from the slope of the curve, which is used to get MDC from Eq. (7) and FDC using Eq. (9). It is noted that the thermodynamic factor in Eq. (9) requires the adsorption isotherm of CO₂ which can usually be simulated using the GCMC method. The conventional GCMC method assumes a rigid adsorbent (μVT ensemble). However, it is known that Mts wells after adsorbing CO₂. Swollen Mt

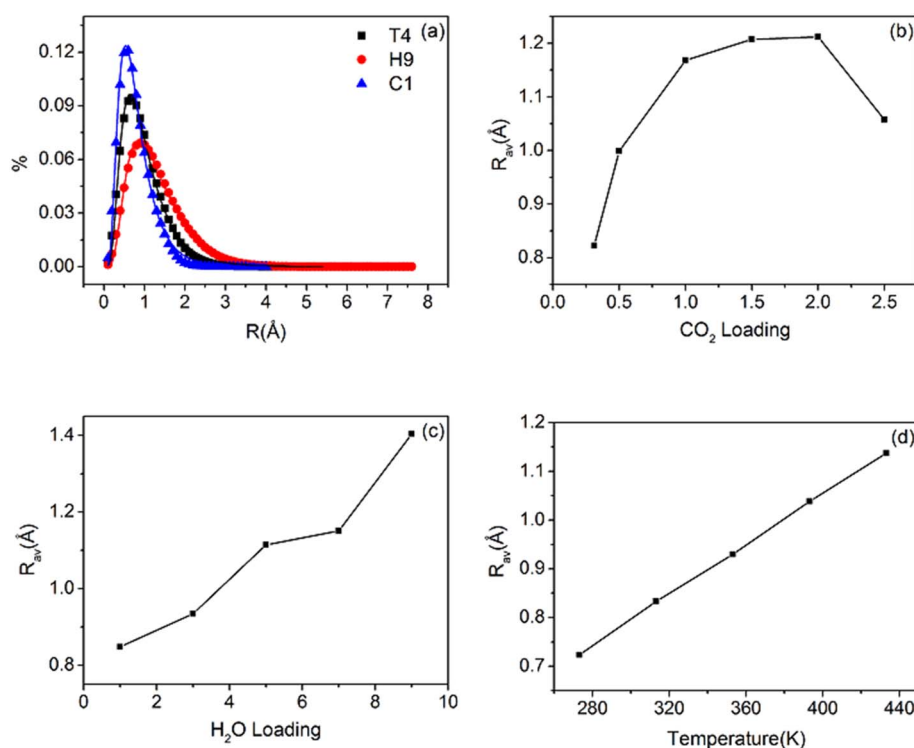


Fig. 5. (a) The distributions of CO₂ displacement, and the lines are fitted by logarithmic normal distribution. The mean value of distribution in different systems: (b) CO₂ loading, (c) H₂O loading, (d) temperature.

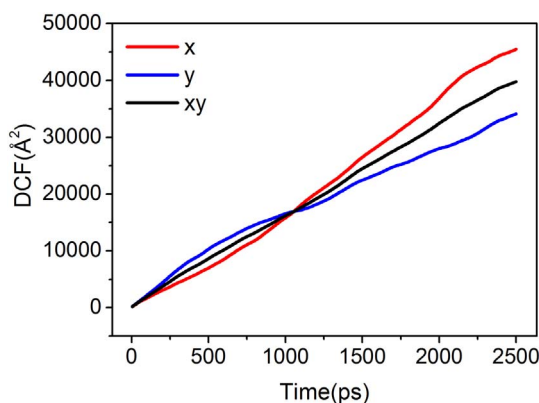


Fig. 6. The average CDCF vs time in C4 system.

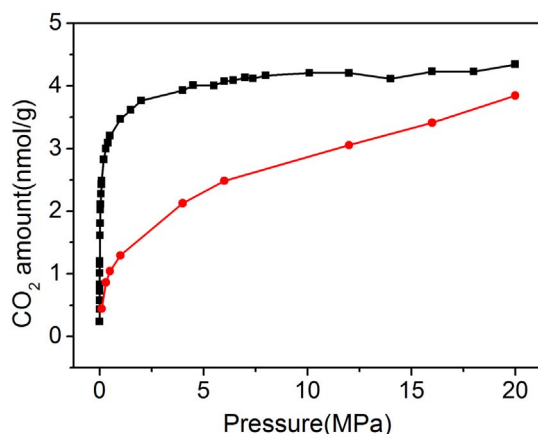


Fig. 7. Adsorption isotherms of CO₂ by conventional GCMC method (black) and flexible adsorption method (red) in C1 system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

can continue to absorb more gas. Therefore, the conventional GCMC is not suitable for calculating adsorption isotherms of CO₂ in Mt. Here a new elastic-adsorption approach is adopted to simulate CO₂ isotherm by taking into account the swelling of Mt. The Mt structure with the initial 224 water molecules is taken as an example for comparison (Fig. 7). Using the conventional GCMC method, one can obtain significantly different adsorption isotherms at different fixed d-spacing values, i.e., the initial d-spacing and swollen d-spacing. In these isotherms, the curves rapidly approach to saturation at low pressure, and the amount of CO₂ adsorption almost keeps constant when the pressure rises above 1 MPa (shown by the black curve in Fig. 7), which is inconsistent with experimental results (Busch et al., 2008). However, the CO₂ adsorption isotherm obtained by the above elastic-adsorption method increases gradually with the CO₂ pressure, which is more qualitatively coincident with the Langmuir formula and the above-

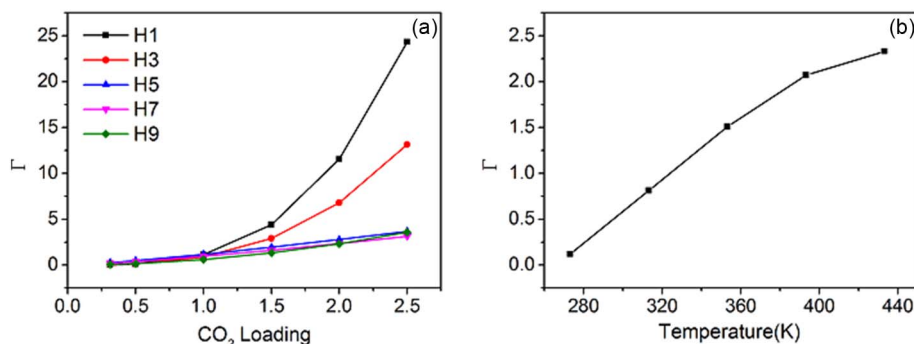


Fig. 8. The thermodynamic factor dependence on CO₂ loading (a) and temperature (b) in the system with 128 H₂O molecules and 32 CO₂ molecules.

mentioned experiment results. The maximum adsorption θ_{sat} is obtained by fitting the Langmuir equation, from which the thermodynamic factor can be calculated by Eq. (10). Thermodynamic factor always increases with CO₂ concentration (Fig. 8(a)); for low CO₂ concentrations, thermodynamic factor is not influenced by H₂O apparently, while for higher CO₂ concentrations, the thermodynamic factor gradually decreases with H₂O content. In a system with 128 H₂O molecules and 32 CO₂ molecules, the higher temperature leads to the larger thermodynamic factor (Fig. 8(b)).

The effects of CO₂ concentration, H₂O content and temperature on MDC and FDC are also examined. The red dots in Fig. 9 represent the variation of CO₂ MDC, which increase with CO₂ concentration, H₂O content and temperature. The black dots in Fig. 9 indicate the FDC. Since the thermodynamic factor is generally above unit, the FDC is usually larger than MDC. Similar to MDC, FDC increases with CO₂ concentration, H₂O content and temperature. This means that CO₂ diffuses faster with the increase of storage depth because of higher CO₂ injection pressure and higher temperature. CO₂ pressure and temperature will decrease with CO₂ diffusing toward ground surface, leading to slower diffusion of CO₂.

3.3. Permeability

Based on the above results of MDC and adsorption isotherms, permeability of CO₂ can be computed through Eq. (12). Note that CO₂ permeability under different CO₂ pressure can be computed from a single adsorption isothermal but multiple CO₂ adsorption isotherms are needed for CO₂ permeability at various H₂O content and temperature. Generally, the permeability of CO₂ in Mt interlayer is very small (Fig. 10), on the order of 10⁻¹²–10⁻¹³ Mol/(m·s·Pa). Permeability depends on gas fugacity. In civil engineering, gas permeability is usually correlated to pressure. Here the CO₂ concentration is converted into CO₂ pressure based on adsorption isotherms. As shown in Fig. 10(a), CO₂ permeability first increases sharply at relatively low CO₂ pressure (pressure < 7 MPa) and tends to reach saturation at high pressure. This originates from the Langmuir type of CO₂ adsorption isothermal which goes up quickly with CO₂ pressure at low pressure and saturates at high pressure. Meanwhile, permeability increases with H₂O content exponentially (Fig. 10(b)): namely P increase gradually at low H₂O content but goes up more sharply at higher H₂O content. However, dependence of permeability on temperature shows different behavior (Fig. 10(c)). CO₂ permeability rises with temperature initially, reaching maximum at 360 K, and decreases once temperature is higher than 360 K. From Eq. (11), permeability is related to both MDC and solubility. The turning point results from the decrease of solubility at high temperature, although D_{im-s} monotonously increases with temperature. From the above, it can be concluded that CO₂ permeability is mainly determined the behavior of solubility parameter because MDC just varies in a limited range. As the increase of storage site depth, CO₂ should be injected with higher pressure and underground temperature increases. It is expected that CO₂ permeates faster with depth increasing

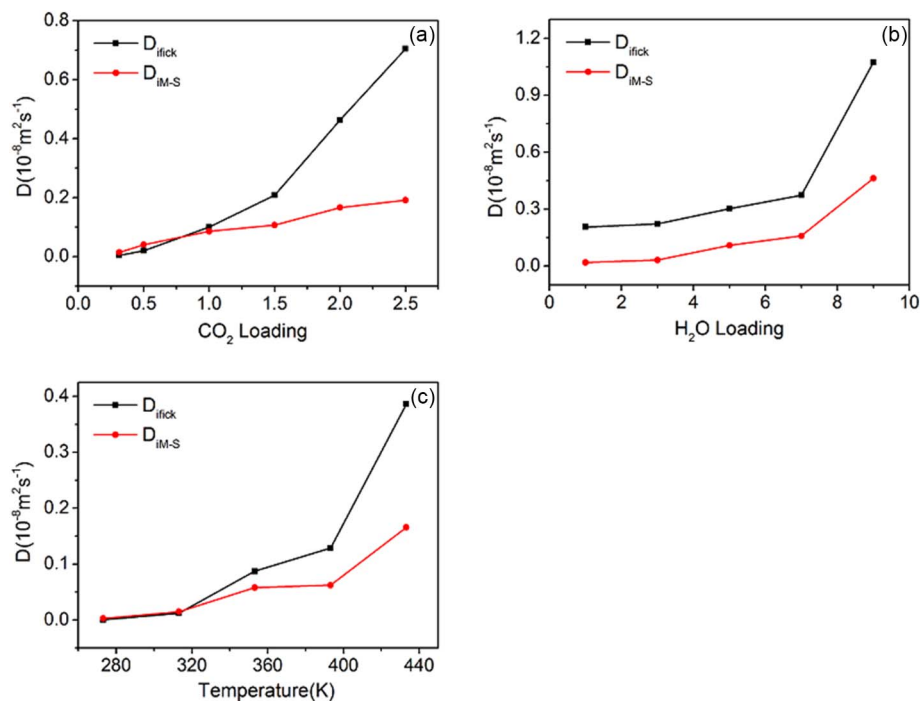


Fig. 9. The $D_{\text{im-s}}$, D_{flick} of CO₂ variation with: (a) CO₂ loading, (b) H₂O loading, (c) temperature.

if storage depth is < 3000 m (around 360 K), but CO₂ permeability could decrease once the depth exceeds 3000 m because CO₂ permeability almost keeps stable for high CO₂ concentration while CO₂ permeability goes down at high temperature. Note that compared with temperature and CO₂ concentration, water content is relatively steady with the depth increase in a specific geologic condition. As to CO₂ storage engineering, it is recommended that less-humidity storage site should be preferred and the storage depth should be < 3000 m to reduce CO₂ leakage.

4. Conclusions

CO₂ diffusion and permeation in Mt under varying conditions is investigated by MD. The results show that while both water content and temperature are positively correlated to the SDC, the SDCs of CO₂ and H₂O display a peak with the increase of CO₂ concentration. To explain the unusual findings of the SDC further, FFV within Mt and the displacement distribution of CO₂ is analyzed. It is found that FFV has an important effect on the diffusion of gas molecules in Mt. The increase of CO₂ concentration causes the Mt to expand, increasing the internal FFV of Mt and providing gas molecules with more space for diffusion. This explains the initial increase of the fluid SDC in Mt. FFV begins to

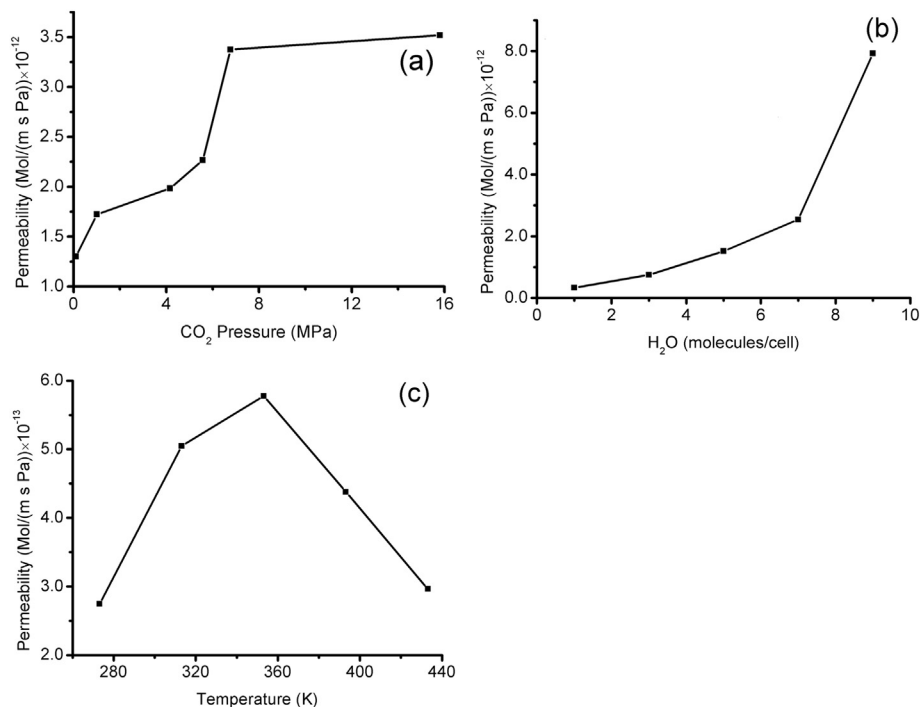


Fig. 10. Dependence of CO₂ permeability on CO₂ pressure (a), water content (b) and temperature (c).

decrease when the CO₂ concentration rises above 2 molecules/unit cell, which hinders the gas diffusion and therefore leads to decreasing SDC. Similarly, the increase of water content also causes the Mt to expand and creates more free space for CO₂ diffusion, resulting in increasing CO₂ SDC. It can be drawn that SDC of the fluid in Mt depends on the FFV of Mt. Furthermore, the displacement distribution of CO₂ follows log-normal distribution, and the mean of the distribution shows the same trend as the SDC, which provides a good explanation of the effects of CO₂ concentration, moisture and temperature on SDC from another perspective.

MDC and FDC increase with CO₂ concentration, moisture and temperature. Based on the aforementioned M-S diffusivities, CO₂ permeability under different conditions is calculated by MD for the first time. CO₂ permeability increases with CO₂ pressure and H₂O content but displays a maximum at temperature 360 K due to decreasing CO₂ solubility at high temperature. This work could provide basic transportation parameters to estimate CO₂ leakage and assess environmental risk of CO₂ underground storage in aquifer.

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