Coupled thermo-hydro-mechanical modelling of carbon dioxide sequestration in saline aquifers considering phase change

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Carbon dioxide (CO$_2$) sequestration in saline aquifers is considered to be one of the most viable measures to control its emissions. During the process of CO$_2$ injection, phase changes of gas, liquid and supercritical CO$_2$ will lead to changes in the density, dynamic viscosity, specific heat capacity and CO$_2$ heat conductivity and solubility in water, which will influence the injection pressure and spatial distribution of CO$_2$. To study the characteristics of injection pressure and spatial distribution of CO$_2$ in saline aquifers, equations of state such as Peng–Robinson equation were used to realize the continuous calculation of the physical property parameters of gas, liquid and supercritical CO$_2$. Based on the continuous physical property parameters, a fully thermo-hydro-mechanical (THM) coupled model was developed and then solved and verified using COMSOL Multiphysics software. It has been shown in this study that: (i) the predicted CO$_2$ injection pressure by the THM coupled model is higher than that obtained from the uncoupled model; (ii) at the top boundary of the reservoir, the spatial distribution of CO$_2$ can be divided into a rapid increase region, a slow decrease region, a rapid decrease region and an initial saturation region along the direction of CO$_2$ migration and (iii) larger the reservoir geothermal gradient, more obvious is the gravity override effect.

Keywords: Carbon dioxide sequestration, phase change, saline aquifers, thermo-hydro-mechanical modelling.

Carbon dioxide (CO$_2$) is considered to be one of the main greenhouse gases (GHGs) that results in global warming of the earth’s atmosphere$^{1-2}$. Methods to effectively dispose of man-made CO$_2$ is important now. CO$_2$ capture and storage (CCS) is one of the most effective methods to reduce massive CO$_2$ emissions into the atmosphere$^{3-4}$. At present, deep saline aquifers, depleted oil, gas and coal reservoirs and salt caverns are considered to be the major geological sequestration media for the next 10–100 years. Deep saline aquifers with large storage capacity and global scope are widely distributed. It is estimated that nearly 600 billion tonnes of CO$_2$, which is equivalent to the total man-made CO$_2$ production in the next 20 years, can be stored in saline aquifers of the Utsira sandstone reservoirs of the Sleipner field in Norway$^{5-6}$.

At present, 15 large commercial CCS projects are being conducted in the Salah of Algeria, the Snøhvit and Sleipner gas fields of Norway, and the Quest project in Canada$^7$. According to the research statistics, seven billion tonnes of CO$_2$ worldwide, needs to be disposed of yearly by geologic sequestration to effectively control man-made CO$_2$ emissions$^5$. A series of physical and chemical changes will occur with massive CO$_2$ injection into saline aquifers, including multiphase fluid flow, change in effective stresses in the saline aquifers, dissolution of CO$_2$ in brine and chemical reactions in brine, reservoir rock minerals and CO$_2$.

CO$_2$ sequestration in deep saline aquifers is a complex, mutually coupled process of seepage fields, stress fields and temperature fields. To describe this complex process, a series of mathematical models have been developed and are gradually being modified. The developed and modification of models has led to the development process from considering a single seepage field to hydro-mechanical coupled fields and then to thermo-hydro-mechanical (THM) coupled fields$^{3-7, 12}$. Numerical simulation is considered as the most suitable method to study the complex relation among different fields during CO$_2$ sequestration. By solving the coupled equations of numerical simulation, the mechanism of CO$_2$ sequestration can be better understood. Moreover, CO$_2$ storage locations can be properly selected by accurate calculation of storage capacity, and the CO$_2$ injection pressure and its spatial distribution in the aquifers can be effectively predicted. CO$_2$ injection pressures can also be controlled to prevent cap rock fracture, which would lead to sequestrated CO$_2$ leaking into the atmosphere$^{1-17}$.

The THM coupled model used in this study consists of the mechanical equilibrium equation, mass continuity equation and equation of energy conservation. The physical parameters of CO$_2$ density, dynamic viscosity, specific...
heat capacity, thermal conductivity coefficient and solubility of CO₂ in water are used in these three equations. The physical parameters of CO₂ will change with changes in environmental temperature and pressure.

Under standard conditions, CO₂ can be considered an ideal gas with a density of 1.872 kg/m³. The pressure and temperature in saline aquifers are usually higher than the critical temperature (304.25 K) and critical pressure (7.39 MPa) of CO₂. Under such conditions, the density of CO₂ is similar to that of a liquid, whereas its dynamic viscosity is close to that of a gas. This CO₂ state is called the supercritical state. During injection of CO₂ from the ground into deep saline aquifers, the CO₂ phase will change from gas to liquid and then to the supercritical state. Therefore, it is impractical to consider CO₂ density as a constant. Moreover, the ideal equation of state (EoS) of a gas can be used to calculate the density of CO₂ in the gaseous state. To calculate density of CO₂ in its different states (gas, liquid and supercritical according to one formula), the Peng–Robinson state equation, and the Span and Wagner state equation have been developed\(^\text{18}\).

Although coupled models of the geologic sequestration process have been continuously improved, currently some disadvantages remain in the models used. Using the Peng–Robinson state equation, and the Span and Wagner state equation, the fully coupled model can be used to calculate the density of CO₂ in different states. However, other physical parameters, such as dynamic viscosity, specific heat capacity, thermal conductivity coefficient and solubility of CO₂ in water cannot be calculated.

To study the effects of changing physical parameters on the CO₂ injection process, we first studied the calculation models for CO₂ density, dynamic viscosity, specific heat capacity, thermal conductivity coefficient and CO₂ solubility in brine. The physical parameters of CO₂ in different states were then calculated using the calculation models. Then, we established a THM coupled model for CO₂ in gas, liquid and supercritical states. Based on the THM coupled model, the injection pressure and spatial distribution of CO₂ under the coupled THM effect were then determined.

**Thermodynamic properties of CO₂**

**Calculation model for density of CO₂**

At present, cubic EoSs is mainly used to determine the phase state of fluids, among which the Peng–Kwong (PK) EoS, Soave–Redlich–Kwong (SRK) EoS, Peng–Robinson EoS, and experience Redlich–Kwong (EXP-RK) EoS are relatively typical. Comparative analysis shows that the Peng–Robinson EoS has the highest accuracy for calculating density of CO₂ under different temperatures and pressure\(^\text{18,19}\). The Peng–Robinson EoS is expressed as follows\(^\text{20}\).

\[
P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)},
\]

where

\[
\begin{align*}
a(T) &= 0.457235R^2\tau_{\text{cri}}^2 \alpha(T) / P_{\text{cri}}, \\
\alpha(T) &= [1 + 0.37646 + 1.5426w - 0.26992w^2)(1 - \sqrt{\frac{T}{T_{\text{cri}}}})]^2, \\
b &= 0.077796RT_{\text{cri}}/P_{\text{cri}}, \\
T_r &= T/T_{\text{cri}}. 
\end{align*}
\]

Here R is the universal gas constant (8.314 J/(mol K)), a and b are parameters of the EoS, \(P_{\text{cri}}\) the critical pressure of the CO₂ phase, \(T_{\text{cri}}\) the critical temperature of the CO₂ phase, \(w\) the eccentric factor (0.239) and \(T_r\) is the reduced temperature.

By substituting the CO₂ density \(\rho_c = m/V\) into eq. (1) it can be simplified as follows

\[
(b^2P + b^2RT - ab)\rho_c^3 - (3b^2P + 2b^2RT - a)M_c\rho_c^2 \\
+ (Pb - RT)M_c^2\rho_c + PM_c^3 = 0,
\]

where \(\rho_c\) is the CO₂ density and \(M_c\) is the molar mass of CO₂.

Equation (3) is a simple cubic equation of \(\rho_c\) with three roots by which the phase state of CO₂ can be determined\(^\text{21}\). If the roots of eq. (3) consist of a real number and two imaginary numbers, the phase of CO₂ is gas or liquid, determined by the temperature and pressure. If the roots of eq. (3) are three different real numbers, two phases of gas and liquid of CO₂ exist at the same time. The maximum root is the density of liquid CO₂, the minimum root is the density of gaseous CO₂, and the middle root has no physical significance. If the three roots are equal, the CO₂ fluid is in a supercritical phase, and the root value is the density of the supercritical CO₂. Figure 1 a shows the density of CO₂ in gaseous, liquid and supercritical states calculated by the Peng–Robinson EoS. The figure illustrates that the density of CO₂ is highly sensitive to changes of temperature and pressure. Near the critical point, the density of CO₂ changes drastically with change in temperature and pressure because the phase of CO₂ changes near the critical point.

**Calculation model for dynamic viscosity of CO₂**

The dynamic viscosity of CO₂ is a function of temperature and pressure. The phases of CO₂ are different under different temperatures and pressures, and the dynamic viscosities of gaseous and liquid CO₂ are usually calculated using different models. In the continuous transition of CO₂ from gas to liquid, conventional methods of
calculation are no longer applicable for the dynamic viscosity of CO2. Based on the Peng–Robinson EoS, a new calculation model for dynamic viscosity was established, which can be used to calculate the dynamic viscosity of CO2 in the gas, liquid and supercritical phases. The formula for CO2 dynamic viscosity can be expressed as follows:

\[ T \mu_c^2 + (2bT - b'T - r'P)\mu_c^2 = \]
\[ (2b'T + Tb^2 + 2r'bP - a)\mu_c + (Tb' b^2 + r'Pb^2 - ab') = 0, \] (4)

where

\[ a = 0.45724a_c^2P_c^2/T_c^2, \quad b = 0.07780a_c^2P_c^2/T_c^2, \]
\[ \mu_c = 7.77T_c^{-1.6}M^{0.5}P_c^{2/3}, \]
\[ r' = r\tau(T_c, P_c), \quad b' = b\phi\tau(T_c, P_c), \quad \tau(T_c, P_c) \]
\[ = [1 + Q_1(\sqrt{P_c/T_c} - 1)]^{-2}, \]
\[ P_c = P/T_c, \quad T_r = T/T_c, \]
\[ Q_1 = 0.829599 + 0.350867w - 0.747680w^2, \]
\[ \mu_c \] is the dynamic viscosity of CO2, and \( \phi \) is the pore ratio.

Figure 1 shows the results of applying eq. (4) to calculate the dynamic viscosity of CO2 fluid under different temperatures and pressures.

**Calculation model for specific heat capacity of CO2**

The calculation models for CO2 specific heat capacity can be classified into two categories: models for gaseous CO2 and those for liquid CO2. The Sterling–Brown equation is generally used to calculate the specific heat capacity of liquid CO2. Because of the phase change of CO2, a calculation model for the specific heat capacity of CO2 in different phases should be selected. We used the calculation model for specific heat capacity of CO2 based on the Peng–Robinson EoS; it can be used to calculate the specific heat capacity of CO2 in any phase and is expressed as follows:

\[ C_{pc} = C_p^* + DC_p = C_p^* + (Z - 1)R \]
\[ + \frac{0.6766P}{ZRT^2 + 29.7903 \times 10^{-6} PT}, \] (5)

where \( C_{pc} \) is the specific heat capacity of the fluid at constant pressure, \( \Delta C_p \) the deviation of specific heat capacity
at constant pressure, \( Z \) the compressibility factor \( (Z = PV/RT) \), \( T \) the temperature and \( C_p^\ast \) is the specific heat capacity of an ideal gas under constant pressure, given by \( C_p^\ast = A + BT + CT^2 + DT^3 \), where \( A = 4.728 \), \( B = 1.754 \times 10^{-2} \), \( C = -2.338 \times 10^{-5} \), and \( D = 4.079 \times 10^{-8} \).

In general, the injection pressure of \( CO_2 \) is 5–35 MPa, and the injection temperature is 253–393 K. Figure 1c shows the calculated specific heat capacities of \( CO_2 \) under different pressures and temperatures using eq. (5). The figure illustrates that a peak point of the specific heat capacity of \( CO_2 \) occurs near the critical region. This indicates that the phase change of \( CO_2 \) has a great effect on its specific heat capacity.

**Calculation model for heat conductivity coefficient of \( CO_2 \)**

The heat conductivity coefficient of \( CO_2 \) is a function of temperature and pressure. Under different temperatures and pressures, the heat conductivity coefficient changes with the \( CO_2 \) phase. We used the calculation model for heat conductivity of \( CO_2 \) as follows:

\[
(\lambda_\infty - \lambda_{CO}) \Gamma Z_c^5 \left[ 1.22 \times 10^{-2} (e^{0.55p_t} - 1), \rho_t < 0.5, \\
1.14 \times 10^{-2} (e^{0.67p_t} - 1.069), 0.5 \leq \rho_t \leq 2.0, \\
2.60 \times 10^{-3} (e^{1.155p_t} + 2.016), 2.0 < \rho_t < 2.8, \\
0 \right] \rho_t < 0.5, \]

where \( \lambda_\infty \) is the heat conductivity of supercritical \( CO_2 \) at atmospheric pressure

\[
\lambda_\infty = 10^{(3.07 \log_e T - 0.5)} \quad \text{and} \quad \Gamma = 1.431 \times 10^7 (T_{\text{cr}} M^3 / \rho_{\text{cr}}^4)^{1/6}. 
\]

Figure 1d shows the calculation model for heat conductivity coefficient of \( CO_2 \). The figure indicates that temperature and pressure have significant effects on the heat conductivity of \( CO_2 \). The heat conductivity coefficient of \( CO_2 \) in the energy conservation equation should be modified by the calculation model of eqs (6) to (7) account for changes in temperature and pressure in the reservoir during the migration of \( CO_2 \) in saline aquifers.

**Solubility of \( CO_2 \) in saline water**

The solubility of \( CO_2 \) in brine is non-negligible with an increase in temperature and pressure\(^28\). We used the calculation model for solubility of \( CO_2 \) in brine as follows:

\[
\rho_{CO} = \frac{0.178094}{A_1 \rho_w^A (1.87 + 459.67)^{A_1} + A_2 (1.87 + 459.67)^{A_2} \exp[-145.0377 A_1 \rho_w + A_0 (145.0377 \rho_w)]}, 
\]

where \( \rho_{CO} \) is the \( CO_2 \) solubility in brine and \( A_1, A_2, A_3, A_4, A_5, A_6 \) and \( A_7 \) are the parameters of the calculation model, whose values are 0.004934, 4.0928, 5.71 \times 10^{-7}, 1.6428, 6.763 \times 10^{-4}, 781.334 and –0.2499 respectively.

**The THM coupled modelling framework**

**Mass conservation equation**

During the flow of water and \( CO_2 \) in saline aquifers, the dissolution of water and \( CO_2 \) in each other will occur. If the dissolution of water in \( CO_2 \) is ignored and only the mass conservation equations for water and \( CO_2 \) can be written as follows:

\[
\begin{align*}
\frac{\partial (\phi S_w \rho_w)}{\partial t} + \nabla \cdot (\rho_w \nu_w) &= 0, \\
\frac{\partial (\rho(1-S_w) \rho_c) + \nabla \cdot (\rho_c \nu_c) + \partial (\rho S_w \rho_w)}{\partial t} + \nabla \cdot (\rho_w \nu_w) &= 0,
\end{align*}
\]

where \( \phi \) is the porosity of the saline aquifer, \( S_w \) the water saturation, \( \rho_w \) the density of water, \( \rho_c \) the velocity of water, \( t \) the time, \( \rho_c \) is the density of \( CO_2 \), which is determined by the reservoir temperature and pressure and can be calculated by eq. (3), \( \nu_c \) is the velocity of \( CO_2 \) and \( \rho_{CO} \) is the dissolution of \( CO_2 \) in water which is calculated by eq. (7).

The flow of water and \( CO_2 \) in porous media is governed by the generalized Darcy’s law. The corresponding formula for fluid velocity is as follows:

\[
\nu_w,c = -\frac{k k_w,c}{\mu_w,c} \nabla (p_{w,c} - p_w - p_c g),
\]

where \( k \) is the intrinsic permeability of rock, \( k_w \) and \( k_c \) the relative permeability of water and \( CO_2 \) respectively, \( \mu_w \) the dynamic viscosity of water, \( \mu_c \) the dynamic viscosity of \( CO_2 \), which can be calculated by eq. (4), and \( g \) is the acceleration due to gravity.

The density of water is influenced by pressure and temperature. The relationship of water density \( \rho_w \) with pressure and temperature can be expressed as follows:

\[
\rho_w = \rho_{w0} \exp\left[c_{wp}(p_w - p_{wef}) - c_{wT}(T_w - T_{wef})\right],
\]

and

\[
\begin{align*}
\rho_{w} &= \frac{1}{\rho_w} \frac{\partial \rho_w}{\partial p}, \\
c_{wp} &= -\frac{1}{\rho_w} \frac{\partial \rho_w}{\partial T}, \\
c_{wT} &= -\frac{1}{\rho_w} \frac{\partial \rho_w}{\partial T},
\end{align*}
\]
where $p_{w,\text{ref}}$ is the reference pressure whose value is 101.325 kPa under standard conditions, $T_{\text{w,ref}}$ the reference temperature, whose value is 273 K under standard conditions and $\rho_{w,0}$ is the density of water under reference pressure and reference temperature.

Energy conservation equation

Heat exchange occurs within the system composed of water, CO$_2$ and saline aquifers by convection and heat transfer. To more accurately simulate the effect of the temperature field on CO$_2$ sequestration, the physical properties of CO$_2$, such as specific heat capacity and heat conductivity were considered in this study. Based on the law of energy conservation, the energy balance equation of the temperature field can be written as follows:

$$\frac{\partial}{\partial t} \left[ (\rho C_p) \varepsilon T \right] + (\nabla \cdot (\rho_w C_p w \varepsilon + \rho_c C_p c \varepsilon)) \nabla T = \nabla \cdot (\lambda \nabla T) = Q_f, \tag{12}$$

and

$$\begin{align*}
\lambda_c &= \phi(S_w \rho_w C_p w + S_p \rho_c C_p c) + (1 - \phi) \rho_c C_p c \\
\lambda_s &= \phi(S_w \lambda_w (1 - S_w) \lambda_c) + (1 - \phi) \lambda_s \\
Q_f &= \phi Q_w + (1 - \phi) Q_s, \tag{13} \\
\tilde{v}_{w,c} &= \frac{k w_r c}{\mu_{w,c}} (\nabla P_{w,c} - \rho_{w,c} g) 
\end{align*}$$

where $(\rho C_p)_{\text{eff}}$ is the effective heat capacity of the porous medium, $C_{w,c}$, $C_p$ and $C_{ps}$ are the specific heat capacity of water specie, CO$_2$ specie and porous media respectively, and $C_{pc}$ can be calculated by eq. (5), $\lambda_c$ is the effective heat conductivity coefficient, $\lambda_w$, $\lambda_s$ and $\lambda_c$ are the heat conductivity coefficient of water specie, CO$_2$ specie and porous media respectively, and $\lambda_c$ can be calculated by eq. (6) and $Q_f$ and $Q_s$ are the heat source and heat sink of fluid and porous medium respectively, and $Q_f = Q_s = 0$ when the heat source and heat sink of rock are ignored.

Equation of mechanical balance

Reservoirs are usually porous media, the mechanical properties of which are influenced by pore characteristics, pore fluid pressure and reservoir temperature. Porous medium is generally considered to be a linearly elastic material. According to the generalized Hooke’s law, the control equation of the stress field expressed by the displacement, pore fluid pressure $p$ and change in temperature $T$ can be written as follows:

$$G_{ij} u_{i,j} + (G + \lambda) u_{i,j} + \alpha_p p_j + \alpha_T T_j + F_i = 0, \tag{14}$$

and

$$\begin{align*}
G &= E /[2(1 + \nu)] \\
\lambda &= E \nu /[1 + (1 - 2\nu)] \\
p &= S_w p_w + (1 - S_w) p_c \\
F_i &= \rho g \\
\rho &= (1 - n) \rho_c + n S_w \rho_w + n(1 - S_w) \rho_c 
\end{align*}$$

where $G$ is the shear modulus, $u_i$ the displacement component in the $i$th direction ($i = x, y, z$), $\lambda$ the lame constant, $\alpha_p$ ($\leq 1$) the corresponding Biot effective stress coefficient of the pore, $p_j$ the pore pressure, $\alpha_T$ is the thermal expansion coefficient, $T_i$, the change of the reservoir temperature, $F_i$ the volume force in the $i$th direction, $E$ the elastic modulus of the reservoir and $\nu$ is the Poisson ratio.

Dynamic evolution model of porosity and permeability

The porosity and permeability of a reservoir are key factors to describe fluid flow within the rock strata, which are closely related to the stress state and intrinsic properties of the rocks. The porosity and permeability of rock strata are influenced by ground stress, pore pressure and temperature. Considering the volume deformation caused by change in the framework particles and temperature, dynamic evolution models for porosity and absolute permeability respectively, can be represented as follows:

$$\varphi = 1 - \frac{(1 - \varphi_0)(1 - \Delta p/K_s + \alpha_T \Delta T)}{1 + \epsilon_v}, \tag{16}$$

$$k = k_0 \left[ 1 + \frac{\epsilon_v - (1 - \varphi_0)(\alpha_T \Delta T + \Delta p/K_s)}{\varphi_0} \right]^3, \tag{17}$$

where $\varphi_0$ is the initial porosity of the reservoir, $\epsilon_v = \epsilon_x + \epsilon_y + \epsilon_z$ the volume strain of the reservoir, $\Delta p$ the increment of the pore pressure, $\Delta T$ the increment of temperature, $K_s$ the volume modulus of the reservoir framework, and $k_0$ the initial absolute permeability of the strata.

Currently, the relative permeability models for porous media include the Van Genuchten Mulaem/Buridine (VGM&VGB) model, the Brooks and Corey Mulaem/Buridine (BCM&BCB) model, the lognormal distribution–Mualem (LNM) model, the Brutsaert–Buridine (BRB) model, and the Gardner–Mulaem model (GDM), among others. Among these, the VGM and BCB models are popular. The BCB model was selected to calculate relative permeability of water and CO$_2$ phase in this study, and the corresponding equations are given below:

$$k_{r,w} = k_{r,0} \left( \frac{S_w - S_{r,w}}{1 - S_{r,w}} \right)^{3/2} \left( \frac{S_w - S_{r,w}}{S_{r,w} - S_{r,e}} \right)^{3/2}, \tag{18}$$
where $k_{r,w0}$ is the initial relative permeability of the water phase, $k_{r,c0}$ the initial relative permeability of the CO$_2$ phase, $S_{r,w}$ residual saturation of the water phase, $S_{r,c}$ residual saturation of the CO$_2$ phase and $\lambda$ is a parameter representing the characteristics of pore structure in the reservoir.

**Model verification**

**Computational procedure**

Methods to calculate density, dynamic viscosity, specific heat capacity, heat conductivity coefficient, and dissolution of CO$_2$ under different temperatures and pressures are included in the proposed model. The deformation control equation of solid mechanics, the equation of motion of two-phase flow and the control equation of temperature fields based on energy conservation are also included in the model. The evaluation laws of porosity, absolute permeability, relative permeability and capillary force of rock strata at any given time are involved in the above three control equations. The pore pressure, strata deformation and fluid saturation at different times can be obtained by solving the THM coupled model using the finite element method (FEM). The fluid flow in rock strata will change the porosity, permeability and capillary force of the rocks. As a result, solution of the THM coupled model is nonlinear and an iterative method should be employed. COMSOL Multiphysics is a commercial software that can be used to numerically solve the PDE equation of the THM coupled model.

**Verification of the fully coupled model**

In CO$_2$ sequestration, migration velocity is measured by the horizontal distance between the intersection point of the CO$_2$–brine interface and the upper boundary of the aquifer to the well. The horizontal distance is referred to as the distance of the CO$_2$ migration front. The spatial distribution and distance of the CO$_2$ front in its sequestration were used to verify the THM model in this study. The parameters of the reservoir used to sequestate CO$_2$ were as follows: length of the reservoir was 1000 m, thickness was 100 m, burial depth was 1500 m, and upper and bottom boundaries of the reservoir were impermeable. CO$_2$ was injected into the reservoir at a flow rate of 1 Mt/year. Figure 2a shows the spatial distribution of CO$_2$ one year after injection$^{34}$. Figure 2b shows CO$_2$ distribution obtained by solving the THM coupled model under the same conditions. The distribution characteristics of CO$_2$ in Figure 2a and b are the same. The distance of CO$_2$ migration front calculated by the THM coupled model was 618 m, which is close to the value (620 m) calculated by Vilarrasa et al.$^{34}$. This difference between the two calculated distances of the CO$_2$ migration front is because continuous variation of density, dynamic viscosity, specific heat capacity, heat conductivity coefficient and solubility of CO$_2$ in water were considered in the THM coupled model. Figure 2 shows that the spatial distribution and migration velocity of CO$_2$ in the aquifer can be precisely predicted by the established THM coupled model. The figure also indicates that it is reliable and viable to study complex CO$_2$ injection by the THM coupled model.

**Thermodynamic effect of supercritical CO$_2$ sequestration**

**Mathematical model and calculation parameters:** The thickness of the saline aquifer was 100 m and burial depth was 1000 m. The hydrostatic pressure gradient within the aquifer was 0.01 MPa/m and the geothermal gradient was 0.01 K/m. The diameter of the CO$_2$ injection borehole was 0.1 m. As shown in Figure 3, the aquifer was located in the two-dimensional X–Z plane. The size of the aquifer was 1200 m × 100 m. The solved region

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**Figure 2.** Spatial distribution and front distance of CO$_2$ migration within the reservoir after one year of CO$_2$ injection. a, Results using the method of Vilarrasa et al.$^{34}$. b, Results using the thermo-hydro-mechanical (THM) coupling model.

**Figure 3.** Schematic diagram of the 2D calculation region.
was symmetrical about the injection borehole. To reduce the mesh element size and operational cost of the numerical simulation, a region with size $600 \text{ m} \times 100 \text{ m}$ to the right of the injection well was selected as the solution region. Table 1 shows the related parameters of the numerical simulation.

### Table 1. Numerical simulation parameters

| Parameter                                      | Value               | Source |
|------------------------------------------------|---------------------|--------|
| Elastic modulus of the reservoir ($E$)        | 10 GPa              | 18     |
| Reservoir Poisson’s ratio ($\nu$)             | 0.3                 | 18     |
| Reservoir density ($\rho_0$)                  | 2200 kg/m$^3$       | 18     |
| Reservoir specific heat capacity ($C_s$)      | 0.85 kJ/(kg K)      | 18     |
| Reservoir heat conductivity coefficient ($\lambda_s$) | $1 \times 10^{-7}$ W/(m K) | 11      |
| Initial porosity of the reservoir ($\phi_0$)  | 0.2                 | 18     |
| Initial permeability of the reservoir ($k_0$) | $1 \times 10^{-16}$ m$^2$ | 18     |
| Reservoir temperature ($T$)                   | 273–373 K           | 18     |
| Hydrostatic pressure ($p_0$)                  | 5–25 MPa            | 18     |
| Biot’s coupled coefficient ($\alpha_p$)        | 1                   | 18     |
| Characteristic parameter of reservoir pore construct ($\lambda$) | 1                  | 33     |
| Density of water ($\rho_w$)                   | 1000 kg/m$^3$       | 5      |
| Dynamic viscosity of water ($\mu_w$)          | 0.283 mPa s         | 5      |
| Specific heat capacity of water ($C_{wp}$)    | 4.2 kJ/(kg K)       | 5      |
| Heat conductivity of water ($\lambda_w$)       | 0.67 W/(m K)        | 5      |
| Residual saturation of water ($S_{r,w}$)       | 0.05                | 18     |
| Compressibility factor of water ($c_{wp}$)     | $1 \times 10^{-4}$/Pa | 11     |
| Heat expansion coefficient of water ($c_{wpT}$) | $4.5 \times 10^{-3}$ 1/K | 11     |
| Density of CO$_2$ ($\rho_c$)                  | Calculated by continuous model in part 2.1 |
| Dynamic viscosity of CO$_2$ ($\mu_c$)         | Calculated by continuous model in part 2.2 |
| Specific heat capacity of CO$_2$ ($C_{pc}$)    | Calculated by continuous model in part 2.3 |
| Heat conductivity coefficient of CO$_2$ ($\lambda_c$) | Calculated by continuous model in part 2.4 |
| Solubility of CO$_2$ in water ($\rho_{dc}$)    | Calculated by continuous model in part 2.5 |
| Residual saturation of CO$_2$ ($S_{r,c}$)      | 0.05                | 18     |
| Mass flow rate of CO$_2$ ($q_c$)              | 5 kg/s              | 18     |

Injection pressure of CO$_2$ under the THM coupled model

The injection pressure of CO$_2$ is the difference in pressure at the CO$_2$ injection point and the initial hydrostatic pressure or pore water pressure. The corresponding expression is

$$p_{\text{inj}} = p_{\text{c,inj}} - p_{\text{hydr,inj}},$$  \hspace{1cm} (20)

where $p_{\text{inj}}$ is the injection pressure of CO$_2$, $p_{\text{c,inj}}$ the pressure of CO$_2$ at the injection point and $p_{\text{hydr,inj}}$ is the initial hydrostatic pressure or pore water pressure.

Figure 4 shows the comparison results of CO$_2$ injection pressure calculated by the THM coupled model and the uncoupled model established by Sasaki et al. As shown in Figure 4 $a$ and $b$, the predicted CO$_2$ injection pressure by the THM coupled model is higher than that calculated by the uncoupled model. At a constant reservoir pressure and reservoir temperatures above 380 K, the difference between the two predicted CO$_2$ injection pressures decreases with increase in reservoir temperature. At a constant reservoir temperature, the difference of the two predicted values decreases with increase in reservoir pressure. Moreover, when the reservoir condition is close to the critical point of CO$_2$, the difference between the two predicted CO$_2$ injection pressures is relatively large because the phase change of CO$_2$ affects its injection pressure.

The preceding analysis shows that: (i) the injection pressure of CO$_2$ is highly sensitive to the reservoir temperature and pressure, and this is more obvious when the reservoir condition is close to the critical point of CO$_2$ and (ii) the injection pressure of CO$_2$ calculated by the uncoupled model, which is based on the ideal gas EoS, and the Span and Wagner EoS is lower than that calculated by the THM coupled model. As a result, the calculation results of the THM coupled model should be more accurate than that of

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**Table 1.** Numerical simulation parameters

| Parameter                                      | Value               | Source |
|------------------------------------------------|---------------------|--------|
| Elastic modulus of the reservoir ($E$)        | 10 GPa              | 18     |
| Reservoir Poisson’s ratio ($\nu$)             | 0.3                 | 18     |
| Reservoir density ($\rho_0$)                  | 2200 kg/m$^3$       | 18     |
| Reservoir specific heat capacity ($C_s$)      | 0.85 kJ/(kg K)      | 18     |
| Reservoir heat conductivity coefficient ($\lambda_s$) | $1 \times 10^{-7}$ W/(m K) | 11      |
| Initial porosity of the reservoir ($\phi_0$)  | 0.2                 | 18     |
| Initial permeability of the reservoir ($k_0$) | $1 \times 10^{-16}$ m$^2$ | 18     |
| Reservoir temperature ($T$)                   | 273–373 K           | 18     |
| Hydrostatic pressure ($p_0$)                  | 5–25 MPa            | 18     |
| Biot’s coupled coefficient ($\alpha_p$)        | 1                   | 18     |
| Characteristic parameter of reservoir pore construct ($\lambda$) | 1                  | 33     |
| Density of water ($\rho_w$)                   | 1000 kg/m$^3$       | 5      |
| Dynamic viscosity of water ($\mu_w$)          | 0.283 mPa s         | 5      |
| Specific heat capacity of water ($C_{wp}$)    | 4.2 kJ/(kg K)       | 5      |
| Heat conductivity of water ($\lambda_w$)       | 0.67 W/(m K)        | 5      |
| Residual saturation of water ($S_{r,w}$)       | 0.05                | 18     |
| Compressibility factor of water ($c_{wp}$)     | $1 \times 10^{-4}$/Pa | 11     |
| Heat expansion coefficient of water ($c_{wpT}$) | $4.5 \times 10^{-3}$ 1/K | 11     |
| Density of CO$_2$ ($\rho_c$)                  | Calculated by continuous model in part 2.1 |
| Dynamic viscosity of CO$_2$ ($\mu_c$)         | Calculated by continuous model in part 2.2 |
| Specific heat capacity of CO$_2$ ($C_{pc}$)    | Calculated by continuous model in part 2.3 |
| Heat conductivity coefficient of CO$_2$ ($\lambda_c$) | Calculated by continuous model in part 2.4 |
| Solubility of CO$_2$ in water ($\rho_{dc}$)    | Calculated by continuous model in part 2.5 |
| Residual saturation of CO$_2$ ($S_{r,c}$)      | 0.05                | 18     |
| Mass flow rate of CO$_2$ ($q_c$)              | 5 kg/s              | 18     |
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Figure 4. Relation between CO₂ injection pressure, and reservoir temperature and pressure. a, Comparison of injection pressure calculated by the uncoupled model based on the ideal gas equation of state (EoS) and Span and Wagner EoS. b, Comparison of injection pressure calculated by the THM coupled model and uncoupled model based on the ideal gas EoS. c, Comparison of injection pressure calculated by the THM coupled model and uncoupled model based on the Span and Wagner EoS.

Figure 5. Density and dynamic viscosity of CO₂ under different temperatures and pressures. a, Nephogram of reservoir temperature and density contour of CO₂. b, Nephogram of reservoir temperature and dynamic viscosity contour of CO₂. c, Nephogram of reservoir pressure and density contour of CO₂. d, Nephogram of reservoir pressure and dynamic viscosity contour of CO₂.

the uncoupled model. It is necessary to verify the calculation error of the THM coupled model by field tests.

Spatial distribution of CO₂ in the THM coupled model

The temperature of injected CO₂ is usually lower than the reservoir temperature, and heat transfer between CO₂ and the reservoir will occur until the thermal transfer reaches an equilibrium state. Due to the existence of a geothermal gradient and hydrostatic pressure gradient within the reservoir, the density and dynamic viscosity of the injected CO₂ in the vertical direction is significantly different (Figure 5). After CO₂ injection, the density of CO₂ at the top boundary of the reservoir is larger than at the bottom boundary, whereas the dynamic viscosity of CO₂ at the upper reservoir is smaller than at the lower reservoir (Figure 5).

It can be seen from Figure 6a that in the migration direction of CO₂, the saturation of CO₂ rapidly increases to a peak value and then slowly decreases. The saturation of CO₂ rapidly falls to the initial value, after which it is maintained at the same value. The saturation of CO₂ at the upper boundary of the reservoir was divided into four sections along the migration direction: the fast increase section, the slow decrease section, the fast decrease section and the initial saturation section. They are shown in Figure 7 as regions I, II, III and IV respectively. These four regions change with time.

The reasons for the existence of the fast increase section are as the follows: (i) CO₂ was still in a compressed state when it entered the reservoir. Since the reservoir temperature was higher than the temperature of CO₂, the compressed CO₂ would expand rapidly. (ii) The pressure of CO₂ at the bottom of the borehole was high, and compressed CO₂ was injected into the reservoir under high injection pressure. As a result, the amount of CO₂ in the reservoir around the bottom of the borehole rapidly increased in a short time. With continuous injection, the compressed supercritical CO₂ in the slow decrease region adapted to the reservoir environment. Finally, CO₂ migrated to the fast decrease region and the initial saturation region.
Figure 6 indicates that for any spatial point in the reservoir, the saturation of CO₂ at this point gradually increases with continuous migration into the reservoir. With regard to variation in the shape of the CO₂–brine interface with time, the longer the distance to the borehole, the larger is the front distance of CO₂ migration. Also, the CO₂–brine interface is correspondingly steeper because viscosity force in the lower part of the reservoir is larger than that in the upper part, and effect of viscosity force is stronger than that of gravity³³,³⁵,³⁶.

It can also be seen from Figure 7 that the fast decrease region is before the initial saturation region. This is because there is a mixed transition region between the injected well and the reservoir far from the well. The closer the mixed transition region to the well, less is the difference in the temperature and pressure. On the contrary, the farther the mixed transition region to the well, more is difference in the temperature and pressure between the injected CO₂ and the saline aquifer. Therefore, the fast decrease region comes before the initial saturation region.

Figure 7 also shows the spatial distribution of CO₂ saturation under geothermal gradients of 0.1, 0.4, 0.7 and 1.0 k/m. Analysis of saturability distribution curves of CO₂ at times of 1000, 3000 and 5000 d shows that a larger geothermal gradient corresponds to a greater distance of CO₂ migration front because with the increase in the geothermal gradient, the difference in dynamic viscosity of supercritical CO₂ in the upper and lower parts of the reservoir also increases. The dynamic viscosity of supercritical CO₂ in the upper reservoir is relatively small, and resistance of CO₂ flow in the upper reservoir is also small. Within the same time frame, the migration velocity as well as distance of the supercritical CO₂ migration front in the upper reservoir are larger. This phenomenon is termed the gravity over-ride effect.

Figure 7 also indicates that at the same location, a larger geothermal gradient corresponds to a greater CO₂ saturation, because the reservoir temperature and pressure affect the density of CO₂ (Figures 1a and 5a, c). At constant pressure, the density of supercritical CO₂ is inversely...
proportional to temperature. Since temperature in the upper reservoir is less than that in the lower reservoir, the density of supercritical CO$_2$ in the upper reservoir is larger than in the lower reservoir. The larger the geothermal gradient, greater is the temperature difference between the upper and lower reservoirs and the difference in CO$_2$ density is correspondingly larger. If the injection rate of CO$_2$ is constant, CO$_2$ density in the upper reservoir is larger than in the lower reservoir. As a result, more CO$_2$ could be stored in the upper reservoir compared to the lower reservoir. Within the same time-frame, the distance of CO$_2$ migration front in the upper reservoir is relatively larger.

In addition to reservoir temperature, the spatial distribution of CO$_2$ is also affected by the following factors: (i) CO$_2$ injected into the lower part of the brine aquifer with high temperature would flow upward along the CO$_2$–brine interface; (ii) brine in the upper aquifer with lower temperature would flow downwards along the CO$_2$–brine interface; (iii) the temperature of CO$_2$ will decrease because of the Joule–Thomson effect after CO$_2$ enters the reservoir from the borehole, and (iv) the dissolution of CO$_2$ in brine is a heat-release process. All these factors will slightly increase the temperature of supercritical CO$_2$ and affect the distribution.

**Conclusion**

The injection pressure of CO$_2$ is highly sensitive to reservoir temperature and pressure, and this sensitivity becomes more significant when the reservoir conditions are close to the critical point. Compared with CO$_2$ injection pressure calculated by the THM coupled model in this study, the injection pressure of CO$_2$ calculated by an uncoupled model based on the ideal gas EoS, and Span and Wagner EoS was relatively low. The THM coupled model was established based on the continuous calculation of physical property parameters of gaseous, liquid and supercritical CO$_2$. Therefore, the THM coupled model can be used to truly reflect the process of multiphase flow and heat flow, and to accurately predict the injection pressure.

Under the THM coupled function, the spatial distribution of CO$_2$ is characterized by the obvious gravity override along the vertical direction. Different CO$_2$ saturability regions occur along its migration direction at the top boundary of the saline aquifer, i.e. fast increase region, slow decrease region, fast decrease region and initial saturation region. The larger the geothermal gradient, greater is the CO$_2$ saturation at the top boundary of the reservoir; the reservoir space needed to sequester CO$_2$ is correspondingly smaller. The reason for CO$_2$ spatial distribution is that the physical property parameters such as density and dynamic viscosity of CO$_2$ are influenced by the reservoir temperature and pressure.

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