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

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Carbon dioxide (CO₂) sequestration in saline aquifers is considered to be one of the most viable measures to control its emissions. During the process of CO₂ injection, phase changes of gas, liquid, and supercritical CO₂ will lead to changes in the density, dynamic viscosity, specific heat capacity, and CO₂ heat conductivity and solubility in water, which will influence the injection pressure and spatial distribution of CO₂. To study the characteristics of injection pressure and spatial distribution of CO₂ 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 CO₂. 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 CO₂ 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 CO₂ 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 CO₂ 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 (CO₂) is considered to be one of the main greenhouse gases (GHGs) that results in global warming of the earth’s atmosphere. Methods to effectively dispose of man-made CO₂ is important now. CO₂ capture and storage (CCS) is one of the most effective methods to reduce massive CO₂ emissions into the atmosphere. 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 CO₂, which is equivalent to the total man-made CO₂ production in the next 20 years, can be stored in saline aquifers of the Utzira sandstone reservoirs of the Sleipner field in Norway.

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. According to the research statistics, seven billion tonnes of CO₂ worldwide, needs to be disposed of yearly by geologic sequestration to effectively control man-made CO₂ emissions. A series of physical and chemical changes will occur with massive CO₂ injection into saline aquifers, including multiphase fluid flow, change in effective stresses in the saline aquifers, dissolution of CO₂ in brine and chemical reactions in brine, reservoir rock minerals and CO₂.

CO₂ 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. Numerical simulation is considered as the most suitable method to study the complex relation among different fields during CO₂ sequestration. By solving the coupled equations of numerical simulation, the mechanism of CO₂ sequestration can be better understood. Moreover, CO₂ storage locations can be properly selected by accurate calculation of storage capacity, and the CO₂ injection pressure and its spatial distribution in the aquifers can be effectively predicted. CO₂ injection pressures can also be controlled to prevent cap rock fracture, which would lead to sequestrated CO₂ leaking into the atmosphere.

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 CO₂ density, dynamic viscosity, specific
heat capacity, thermal conductivity coefficient and solubility of CO$_2$ in water are used in these three equations. The physical parameters of CO$_2$ will change with changes in environmental temperature and pressure.

Under standard conditions, CO$_2$ can be considered an ideal gas with a density of 1.872 kg/m$^3$. The pressure and temperature in saline aquifers are usually higher than the critical temperature (304.25 K) and critical pressure (7.39 MPa) of CO$_2$. Under such conditions, the density of CO$_2$ is similar to that of a liquid, whereas its dynamic viscosity is close to that of a gas. This CO$_2$ state is called the supercritical state. During injection of CO$_2$ from the ground into deep saline aquifers, the CO$_2$ phase will change from gas to liquid and then to the supercritical state. Therefore, it is impractical to consider CO$_2$ density as a constant. Moreover, the ideal equation of state (EoS) of a gas can be used to calculate the density of CO$_2$ in the gaseous state. To calculate density of CO$_2$ 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$^{18}$. 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 CO$_2$ in different states. However, other physical parameters, such as dynamic viscosity, specific heat capacity, thermal conductivity coefficient and solubility of CO$_2$ in water cannot be calculated.

To study the effects of changing physical parameters on the CO$_2$ injection process, we first studied the calculation models for CO$_2$ density, dynamic viscosity, specific heat capacity, thermal conductivity coefficient and CO$_2$ solubility in brine. The physical parameters of CO$_2$ in different states were then calculated using the calculation models. Then, we established a THM coupled model for CO$_2$ in gas, liquid and supercritical states. Based on the THM coupled model, the injection pressure and spatial distribution of CO$_2$ under the coupled THM effect were then determined.

### Thermodynamic properties of CO$_2$

#### Calculation model for density of CO$_2$

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 CO$_2$ under different temperatures and pressure$^{18,19}$. The Peng–Robinson EoS is expressed as follows$^{20}$

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)},$$  \hspace{1cm} (1)

where

$\begin{align*}
   a(T) &= 0.457235R^2T^2\alpha(T)/P_{ci}, \\
   \alpha(T) &= [1 + 0.37646 + 1.5426\omega - 0.26992\omega^2](1 - \sqrt{T/T_c})^2, \\
   b &= 0.077796RT_{ci}/P_{ci}, \\
   T_r &= T/T_c.
\end{align*}$  \hspace{1cm} (2)$

Here $R$ is the universal gas constant (8.314 J/(mol K)), $a$ and $b$ are parameters of the EoS, $P_{ci}$ the critical pressure of the CO$_2$ phase, $T_{ci}$ the critical temperature of the CO$_2$ phase, $\omega$ the eccentric factor (0.239) and $T_r$ is the reduced temperature.

By substituting the CO$_2$ density $\rho_c = m/V$ into eq. (1) it can be simplified as follows

$$\begin{align*}
   (b^2P + b^2RT - ab)\rho_c^3 - (3b^2P + 2bRT - a)M_c\rho_c^2 \\
   + (Pb - RT)M_c^2\rho_c + PM_c^3 = 0,
\end{align*}$$  \hspace{1cm} (3)

where $\rho_c$ is the CO$_2$ density and $M_c$ is the molar mass of CO$_2$.

Equation (3) is a simple cubic equation of $\rho_c$ with three roots by which the phase state of CO$_2$ can be determined$^{21}$. If the roots of eq. (3) consist of a real number and two imaginary numbers, the phase of CO$_2$ 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 CO$_2$ exist at the same time. The maximum root is the density of liquid CO$_2$, the minimum root is the density of gaseous CO$_2$, and the middle root has no physical significance. If the three roots are equal, the CO$_2$ fluid is in a supercritical phase, and the root value is the density of the supercritical CO$_2$. Figure 1a shows the density of CO$_2$ in gaseous, liquid and supercritical states calculated by the Peng–Robinson EoS. The figure illustrates that the density of CO$_2$ is highly sensitive to changes of temperature and pressure near the critical point.

#### Calculation model for dynamic viscosity of CO$_2$

The dynamic viscosity of CO$_2$ is a function of temperature and pressure. The phases of CO$_2$ are different under different temperatures and pressures, and the dynamic viscosities of gaseous and liquid CO$_2$ are usually calculated using different models. In the continuous transition of CO$_2$ 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:

\[
T\mu^c + (2bT - b'T - r'P)\mu^c - (2bb'T + Tb^2 + 2rbP - a)\mu^c + (Tb'b^2 + r'Pb^2 - ab') = 0,
\]

where

\[
av = 0.45724r_c^2P_c^2/T_c^2,
b = 0.07780r_c^2P_c^2/T_c^2,
\]

\[
\mu^c = 7.777^{-1/6}M^{0.5}P_c^{2/3},
\]

\[
r' = r\tau(T_c, P_c), b' = b\phi\tau(T_c, P_c), \tau(T, P)
\]

\[
= [1 + Q_1(\sqrt{P_c/T_c} - 1)]^{-2},
\]

\[
P_i = P_i/P_c, T_i = T/T_c,
\]

\[
Q_1 = 0.829599 + 0.350867w - 0.747680w^2,
\]

\[
\mu^c \text{ is the dynamic viscosity of CO}_2, \quad \phi \text{ is the pore ratio.}
\]

Figure 1 a–e. Relationship between thermodynamic parameters of carbon dioxide (CO₂) and pressure and temperature.

Figure 1 b 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:

\[
C_{pc} = C_p^0 + DC_p = C_p^0 + (Z - 1)R
\]

\[
+ \frac{0.6766P \times 29.7903 \times 10^{-6}PT}{ZRT^2 + 29.7903 \times 10^{-6}PT},
\]

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 \( C_p^* \) is the specific heat capacity of an ideal gas under constant pressure, given by \( C_p^* = A + BT + CT^2 + DT^3 \), 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 \( \text{CO}_2 \) is 5–35 MPa, and the injection temperature is 253–393 K. Figure 1c shows the calculated specific heat capacities of \( \text{CO}_2 \) under different pressures and temperatures using eq. (5). The figure illustrates that a peak point of the specific heat capacity of \( \text{CO}_2 \) occurs near the critical region. This indicates that the phase change of \( \text{CO}_2 \) has a great effect on its specific heat capacity.

**Calculation model for heat conductivity coefficient of \( \text{CO}_2 \)**

The heat conductivity coefficient of \( \text{CO}_2 \) is a function of temperature and pressure. Under different temperatures and pressures, the heat conductivity coefficient changes with the \( \text{CO}_2 \) phase. We used the calculation model for heat conductivity of \( \text{CO}_2 \) as follows:

\[
(\lambda_c - \lambda_{c0})Z^5_c = \begin{cases} 
1.22 \times 10^{-2} \left( e^{0.535 \rho_t} - 1 \right), & \rho_t < 0.5, \\
1.14 \times 10^{-2} \left( e^{0.67 \rho_t} - 1.069 \right), & 0.5 \leq \rho_t \leq 2.0, \\
2.60 \times 10^{-3} \left( e^{1.155 \rho_t} + 2.016 \right), & 2.0 < \rho_t < 2.8,
\end{cases} \tag{6}
\]

where \( \lambda_{c0} \) is the heat conductivity of supercritical \( \text{CO}_2 \) at atmospheric pressure \( \lambda_{c0} = 10^{(1.307 \log_{10} T - 0.5)} \) and \( \Gamma = 1.431 \times 10^{7} (T/c_m M^3/\rho_c^4)^{1/6} \).

Figure 1d shows the calculation model for heat conductivity coefficient of \( \text{CO}_2 \). The figure indicates that temperature and pressure have significant effects on the heat conductivity of \( \text{CO}_2 \). The heat conductivity coefficient of \( \text{CO}_2 \) 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 \( \text{CO}_2 \) in saline aquifers.

**Solubility of \( \text{CO}_2 \) in saline water**

The solubility of \( \text{CO}_2 \) in brine is non-negligible with an increase in temperature and pressure\(^{28} \). We used the calculation model for solubility of \( \text{CO}_2 \) in brine as follows:

\[
\rho_{dc} = \rho_{dc0} \exp(1.87T - 459.67) + A_5(1.87T - 459.67)A_6 \times \exp(-145.0377A_5p + A_6/(145.0377p)) \tag{7}
\]

where \( \rho_{dc} \) is the \( \text{CO}_2 \) 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 \( \text{CO}_2 \) in saline aquifers, the dissolution of water and \( \text{CO}_2 \) in each other will occur. If the dissolution of water in \( \text{CO}_2 \) is ignored and only the dissolution of \( \text{CO}_2 \) in water is considered, the mass conservation equations for water and \( \text{CO}_2 \) can be written as follows:

\[
\begin{align*}
\frac{\partial (\phi S_w \rho_w)}{\partial t} + \nabla \cdot (\rho_w \nu_w) &= 0 \\
\frac{\partial (\phi(1-S_w) \rho_c)}{\partial t} + \nabla \cdot (\rho_c \nu_c) &= 0
\end{align*}
\tag{8}
\]

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, \( \rho_t \) is the density of \( \text{CO}_2 \), which is determined by the reservoir temperature and pressure and can be calculated by eq. (3). \( \nu_c \) is the velocity of \( \text{CO}_2 \) and \( \rho_{dc} \) is the dissolution of \( \text{CO}_2 \) in water which is calculated by eq. (7).

The flow of water and \( \text{CO}_2 \) in porous media is governed by the generalized Darcy’s law. The corresponding formula for fluid velocity is as follows:

\[
\nu_{w,c} = -\frac{k_{rw,c}}{\mu_{w,c}} \nabla (p_{w,c} - \rho_w g), \tag{9}
\]

where \( k \) is the intrinsic permeability of rock, \( k_{rw} \) and \( k_{rc} \) the relative permeability of water and \( \text{CO}_2 \) respectively, \( \mu_w \) the dynamic viscosity of water, \( \mu_c \) the dynamic viscosity of \( \text{CO}_2 \), 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:

\[
\rho_w = \rho_{w0} \exp(c_{wp}(p_w - p_w0) - c_{wT}(T_w - T_{w0})), \tag{10}
\]

and

\[
\begin{align*}
c_{wp} &= \frac{1}{\rho_w} \frac{\partial \rho_w}{\partial p} \\
c_{wT} &= -\frac{1}{\rho_w} \frac{\partial \rho_w}{\partial T}
\end{align*}
\tag{11}
\]

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where \( p_{\text{wref}} \) is the reference pressure whose value is 101.325 kPa under standard conditions, \( T_{\text{wref}} \) the reference temperature, whose value is 273 K under standard conditions and \( \rho_{w0} \) 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:\(^30\)

\[
\frac{\partial}{\partial t}[(\rho C_p)\varepsilon T] + (\nu_w \rho_w C_{pw} + \nu_c \rho_c C_{pc}) \nabla T = -\nabla \cdot (\lambda C_p \nabla T) = Q_f, \tag{12}
\]

and

\[
\begin{aligned}
\rho C_p \varepsilon &= \phi(S_w \rho_w C_{pw} + S_c \rho_c C_{pc}) + (1-\phi)\rho_s C_{ps}, \\
\lambda_c &= \phi(S_w \lambda_w + (1-S_w)\lambda_w + (1-\phi)\lambda_s), \\
Q_f &= \phi Q_w + (1-\phi)Q_s, \\
\nu_w,c &= -\frac{k}{\rho_{w,c}}(\nabla P_{w,c} - \rho_{w,c} g) \tag{13}
\end{aligned}
\]

where \( (\rho C_p)_\varepsilon \) is the effective heat capacity of the porous medium, \( C_{pw}, C_{pc} \) 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, \( \lambda_w, \lambda_c \) and \( \lambda_s \) 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:\(^9\)

\[
G\varepsilon_{ij,j} + (G + \lambda)\varepsilon_{ii} + \alpha_p p_j + \alpha_T T_j + F_i = 0, \tag{14}
\]

and

\[
\begin{aligned}
G &= E/[2(1+\nu)], \\
\lambda &= E\nu/[((1+\nu)(1-2\nu))] \\
p &= S_w p_w + (1-S_w) p_c \\
F_i &= \rho g \\
\rho &= (1-n)\rho_s + nS_w \rho_w + n(1-S_w) \rho_c \\
\end{aligned} \tag{15}
\]

where \( G \) is the shear modulus, \( \nu_i \) 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:\(^31\)

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

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

where \( \varphi_0 \) is the initial porosity of the reservoir, \( \varepsilon_v = \varepsilon_c + \varepsilon_s + \varepsilon_e \) 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/Burdine (VGM&VGB) model, the Brooks and Corey Mulaem/Burdine (BCM&BCB) model, the lognormal distribution–Mulaem (LNM) model, the Brutsaert–Burdine (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:\(^32,33\)

\[
k_{r,w} = k_{r,w0} \left( \frac{S_w - S_{r,w}}{1-S_{r,w}-S_{r,e}} \right)^{3/2}, \tag{18}
\]
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 sequestrate 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 2\(a\) shows the spatial distribution of CO\(_2\) one year after injection\(^{34}\). Figure 2\(b\) shows CO\(_2\) distribution obtained by solving the THM coupled model under the same conditions. The distribution characteristics of CO\(_2\) in Figure 2\(a\) 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 \(\times\) 100 m. The solved region

![Figure 2](https://via.placeholder.com/150)

**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-hydmechanical (THM) coupling model.

![Figure 3](https://via.placeholder.com/150)

**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 m × 100 m to the right of the injection well was selected as the solution region. Table 1 shows the related parameters of the numerical simulation.

Injection pressure of CO₂ under the THM coupled model

The injection pressure of CO₂ is the difference in pressure at the CO₂ injection point and the initial hydrostatic pressure or pore water pressure. The corresponding expression is

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

where $P_{\text{inj}}$ is the injection pressure of CO₂, $P_{c,\text{inj}}$ the pressure of CO₂ at the injection point and $P_{\text{hyd, inj}}$ is the initial hydrostatic pressure or pore water pressure.

Figure 4 shows the comparison results of CO₂ injection pressure calculated by the THM coupled model and the uncoupled model established by Sasaki et al. \(^{18}\). Figure 4a shows that when the reservoir temperature is above 380 K, the CO₂ injection pressure calculated by the ideal gas EoS is close to the CO₂ injection pressure calculated by the Span and Wagner EoS. When the reservoir temperature is close to the critical temperature, the CO₂ injection pressure calculated by the ideal gas EoS is larger than that calculated by the Span and Wagner EoS.

As shown in Figure 4b and c, the predicted CO₂ 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 CO₂ 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 CO₂, the difference between the two predicted CO₂ injection pressures is relatively large because the phase change of CO₂ affects its injection pressure.

The preceding analysis shows that: (i) the injection pressure of CO₂ 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 CO₂ and (ii) the injection pressure of CO₂ calculated by the uncoupled model, which is based on the ideal gas EoS, and Span and Wagner EoS is lower than that calculated by the THM coupled model. The calculation of the physical properties of CO₂, the phase of which continuously changes, has been taken into consideration in the THM coupled model. As a result, the calculation results of the THM coupled model should be more accurate than that of

### Table 1. Numerical simulation parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic modulus of the reservoir ($E$)</td>
<td>10 GPa</td>
<td>18</td>
</tr>
<tr>
<td>Reservoir Poisson’s ratio ($\nu$)</td>
<td>0.3</td>
<td>18</td>
</tr>
<tr>
<td>Reservoir density ($\rho_s$)</td>
<td>2200 kg/m³</td>
<td>18</td>
</tr>
<tr>
<td>Reservoir specific heat capacity ($C_s$)</td>
<td>0.85 kJ/(kg K)</td>
<td>18</td>
</tr>
<tr>
<td>Reservoir heat conductivity coefficient ($\lambda_s$)</td>
<td>$1 \times 10^{-1}$ W/(m K)</td>
<td>11</td>
</tr>
<tr>
<td>Initial porosity of the reservoir ($\phi_0$)</td>
<td>0.2</td>
<td>18</td>
</tr>
<tr>
<td>Initial permeability of the reservoir ($k_0$)</td>
<td>$1 \times 10^{-16}$ m²</td>
<td>18</td>
</tr>
<tr>
<td>Reservoir temperature (T)</td>
<td>273–373 K</td>
<td>18</td>
</tr>
<tr>
<td>Hydrostatic pressure ($p_0$)</td>
<td>5–25 MPa</td>
<td>18</td>
</tr>
<tr>
<td>Biot’s coupled coefficient ($\alpha_p$)</td>
<td>1</td>
<td>18</td>
</tr>
<tr>
<td>Characteristic parameter of reservoir pore construct ($\bar{\lambda}$)</td>
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<td>33</td>
</tr>
<tr>
<td>Density of water ($\rho_w$)</td>
<td>1000 kg/m³</td>
<td>5</td>
</tr>
<tr>
<td>Dynamic viscosity of water ($\mu_w$)</td>
<td>0.283 mPa s</td>
<td>5</td>
</tr>
<tr>
<td>Specific heat capacity of water ($C_{pw}$)</td>
<td>4.2 kJ/(kg K)</td>
<td>5</td>
</tr>
<tr>
<td>Heat conductivity of water ($\lambda_w$)</td>
<td>0.67 W/(m K)</td>
<td>5</td>
</tr>
<tr>
<td>Residual saturation of water ($S_{r,w}$)</td>
<td>0.05</td>
<td>18</td>
</tr>
<tr>
<td>Compressibility factor of water ($c_{wp}$)</td>
<td>$1 \times 10^{-4}$ l/Pa</td>
<td>11</td>
</tr>
<tr>
<td>Heat expansion coefficient of water ($c_{wp}$)</td>
<td>$4.5 \times 10^{-4}$ l/K</td>
<td>11</td>
</tr>
<tr>
<td>Density of CO₂ ($\rho_c$)</td>
<td>Calculated by continuous model in part 2.1</td>
<td></td>
</tr>
<tr>
<td>Dynamic viscosity of CO₂ ($\mu_c$)</td>
<td>Calculated by continuous model in part 2.2</td>
<td></td>
</tr>
<tr>
<td>Specific heat capacity of CO₂ ($C_{pc}$)</td>
<td>Calculated by continuous model in part 2.3</td>
<td></td>
</tr>
<tr>
<td>Heat conductivity coefficient of CO₂ ($\lambda_c$)</td>
<td>Calculated by continuous model in part 2.4</td>
<td></td>
</tr>
<tr>
<td>Solubility of CO₂ in water ($\rho_{dc}$)</td>
<td>Calculated by continuous model in part 2.5</td>
<td></td>
</tr>
<tr>
<td>Residual saturation of CO₂ ($S_{r,c}$)</td>
<td>0.05</td>
<td>18</td>
</tr>
<tr>
<td>Mass flow rate of CO₂ ($q_c$)</td>
<td>5 kg/s</td>
<td>18</td>
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</tbody>
</table>
the uncoupled model. It is necessary to verify the calculation error of the THM coupled model by field tests.

**Spatial distribution of CO$_2$ in the THM coupled model**

The temperature of injected CO$_2$ is usually lower than the reservoir temperature, and heat transfer between CO$_2$ 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 CO$_2$ in the vertical direction is significantly different (Figure 5). After CO$_2$ injection, the density of CO$_2$ at the top boundary of the reservoir is larger than at the bottom boundary, whereas the dynamic viscosity of CO$_2$ 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 CO$_2$, the saturation of CO$_2$ rapidly increases to a peak value and then slowly decreases. The saturation of CO$_2$ rapidly falls to the initial value, after which it is maintained at the same value. The saturation of CO$_2$ 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) CO$_2$ was still in a compressed state when it entered the reservoir. Since the reservoir temperature was higher than the temperature of CO$_2$, the compressed CO$_2$ would expand rapidly. (ii) The pressure of CO$_2$ at the bottom of the borehole was high, and compressed CO$_2$ was injected into the reservoir under high injection pressure. As a result, the amount of CO$_2$ in the reservoir around the bottom of the borehole rapidly increased in a short time. With continuous injection, the compressed supercritical CO$_2$ in the slow decrease region adapted to the reservoir environment. Finally, CO$_2$ migrated to the fast decrease region and the initial saturation region.
Figure 6. Variation of spatial distribution of CO₂ with time in the THM coupled model. a, Distribution of CO₂ saturation along the top boundary of the reservoir. b, Isoline distribution of CO₂ saturation at different times.

Figure 6b 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 override 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.

**Conflicts of interest:** The authors declare no conflict of interest.


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