Influence of CO$_2$ migration from geological storage on the chemical composition of groundwater and monitoring indicators

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Abstract
In the process of CO$_2$ geological sequestration, there is a risk that CO$_2$ will leak into groundwater, resulting in a series of physical and chemical reactions, with influence on chemical compositions of groundwater. In this work, numerical simulation is conducted to study the influence of CO$_2$ migration on the chemical composition of groundwater. The modeling results indicated that when CO$_2$ leaks into groundwater, gaseous CO$_2$ will migrate upward and diffuse laterally under the effect of buoyancy. The acidity of groundwater is enhanced and the pH is significantly reduced, leading to dissolution of calcite, illite, oligoclase, K-feldspar, chloride and hematite, and precipitation of quartz, kaolinite, smectite-Na, siderite and smectite-Ca. The porosity of the formation increases. The concentrations of K$^+$ and Fe$^{2+}$ in groundwater gradually increase, the concentrations of Ca$^{2+}$ and HCO$_3$$^-$ basically remain unchanged after increasing to a certain value, the concentrations of Mg$^{2+}$ and AlO$_2$$^-$$^-$ first increase and then decrease, and the concentrations of Na$^+$, Cl$^-$ and SO$_4$$^{2-}$ first decrease slightly and then gradually increase, but the change in concentration is small. Therefore, Fe$^{2+}$, Mg$^{2+}$, Ca$^{2+}$ and pH can be used as important monitoring indicators of whether CO$_2$ leakage into groundwater during geological storage.

Keywords Geological storage · CO$_2$ migration · Groundwater · Chemical composition · Monitoring indicators · TOUGHREACT

Introduction
With the increasing concerns on global warming, CO$_2$ geological sequestration has been considered to be one of the most effective ways to reduce CO$_2$ emissions and alleviate global warming (Cao et al. 2021). However, due to the uncertainty in geological conditions, the risk of CO$_2$ leaking during geological storage has to be considered (Aines et al. 2009; Oldenburg et al. 2011). For example, sequestered CO$_2$ may migrate into groundwater along faults, fractures and recovery wells (Du et al. 2012; Xie et al. 2017). Once CO$_2$ migrate into groundwater, it will break the original hydrochemical equilibrium in groundwater and cause a series of problems on groundwater quality (Apps et al. 2010). Therefore, studying the impact of CO$_2$ migration from geological storage on the quality of groundwater is an important part of the environmental risk assessment and development of early warning in CO$_2$ geological storage.

Although the evaluation of the impact of CO$_2$ geological storage on water quality has been studied long ago (Meer 1992), systematic study of the impact of CO$_2$ on shallow groundwater quality began in 2004. Wang and Jaffe (2004) used numerical simulation for the first time to study the impact of CO$_2$ migration on shallow groundwater. The results showed that if the monitored trace metal indicators
were abnormal, it could be an indicator of CO₂ leakage to shallow aquifers. Carroll et al. (2009) conducted reactive migration modeling on the impact of CO₂ intrusion into American plateau aquifers, and showed that CO₂ migration in aquifers can be detected by pH and carbonate chemical changes, and pointed out that the most appropriate monitoring location was the bottom of the waterproof roof. Fahrner et al. (2011) used Phreeqc to simulate the impact of CO₂ migration to shallow groundwater on the electrical conductivity (EC) of groundwater, analyzed the impact of CO₂ intrusion on the EC change of groundwater, and explored the use of monitoring groundwater EC changes to identify leakage. Kharaka et al. (2010) monitored the concentration changes of the main components, minor components, trace components and organic components in groundwater after CO₂ injection, and the results showed that with CO₂ injection, the concentrations of chemical components in groundwater changed significantly. Among them, pH dropped from 7.0 to 5.6, alkalinity increased from 400 to 1330 mg/L. The main components and trace components (including Pb, As, etc.) in groundwater increased significantly, but were lower than the Environmental Protection Agency (EPA) drinking water limit in the US. Keating et al. (2010, 2013) studied the impact of CO₂ geological storage on the hydrochemistry of water limit in the United States. The results showed the pH in the water decreased sharply (by about 3 units) at the beginning of CO₂ injection, and then gradually recovered to a stable value. The main components and trace components in individual media samples increased by 1 to 2 orders of magnitude. The concentration of alkali elements, alkaline earth elements, Mn, Co, Ni, and Fe in the water increased by more than 2 orders of magnitude. The concentration of U and Ba in individual media samples increased significantly. The migration of trace metal elements, the buffering effect of carbonate minerals, and the redox conditions of shallow aquifers control the effect of CO₂. Because the concentrations of Mn, Fe, and Ca tend to increase at the beginning of the experiment, their concentrations can be used as the basis for monitoring CO₂ leakage. Zhang et al. (2016) studied the impacts on pH value, DO, HCO₃⁻ and COD of surface water by changing the leakage time, leakage rate, and the temperature of carbon dioxide. They suggested that pH, DO and HCO₃⁻ could be used as the surface water monitoring indicators for CO₂ geological storage.

Natural isotope tracers are an important way to detect CO₂ leakage. Sr isotopes were used to record the dissolution of carbonate rocks at CO₂-enhanced oil recovery sites (Quattrocchi et al. 2005), and were coupled with carbon isotopes to track the movement of CO₂ plumes during a controlled leak of CO₂ into a shallow aquifer (Newell et al. 2014). Kim et al. (2020) evaluated the application of ²²²Rn in groundwater as a tracer for monitoring CO₂ plume migration on shallow groundwater, and the results indicated that ²²²Rn could be used as a sensitive tracer to directly monitor CO₂ leakage. Gardiner et al. (2021) demonstrated that multiple isotope system (δ¹³C, δ¹⁸O, Sr/⁸⁶Sr, ²³⁴U/²³⁸U) could be used to identify and measure the impact of CO₂ leakage at sequestration sites.

CO₂ storage involves the flow of multi-phase and multi-component fluids in geological media, and processes such as mechanical and chemical reactions. To accurately simulate the effects of CO₂ migration on the chemical composition of groundwater, it is necessary to couple the hydrodynamic and chemical reaction processes that may occur during the movement of multi-phase fluids in the formation. In this work, the Yanchang Oilfield in China was studied with numerical simulation to establish the reaction transport model of CO₂ migration to groundwater during geological storage. By analyzing the influence of CO₂ migration during geologic sequestration on the chemical components of groundwater, we can screen out monitoring indicators that are more sensitive to changes of CO₂ leakage, and provide basis for similar CO₂ geological storage monitoring programs, and reduce the possible risks in carbon capture and storage (CCS) projects.
Model setup

Modeling code and conceptualization

The non-isothermal reactive geochemical transport code TOUGHREACT V3.32-OMP (Xu 2001; Xu et al. 2006, 2014) was used in this work. TOUGHREACT is an extension of TOUGH2 (Pruess et al. 1999) and the fluid property module ECO2N was used for H$_2$O–CO$_2$–NaCl mixtures (Pruess et al. 2004).

The depth of groundwater in the Yanchang Oilfield in China is 10 m, and the aquifer is sandstone. It is assumed that CO$_2$ is leaking into the groundwater through cracks in the formation (Fig. 1). The vertical thickness of the groundwater is 60 m, which is divided into 6 grids, and the length in the horizontal direction is 500 m, which is divided into 50 grids (Fig. 2). The volume of the lateral boundary mesh is set to infinity. The annual average ground temperature in this area is 10.8 °C, the temperature gradient is about 3.1 °C/100 m, and the hydrostatic pressure gradient is 10 bar/100 m. Therefore, the bottom temperature of the model is about 13 °C and the pressure is 8 bar. The CO$_2$ leakage point is set at $X = 250$ m, the CO$_2$ leaking time and simulation time are set to 100 years. The constant leakage rate of CO$_2$ is 0.0001 kg/s, which is estimated by the following formula.

$$Q_G = C_dAPY \sqrt{MK \left(\frac{2}{K + 1}\right)^{\frac{K + 1}{K - 1}}}$$

where $Q_G$ is the gas leakage rate, kg/s; $C_d$ is the gas leakage coefficient, and $C_d = 1$ when the shape of the crack is round, $C_d = 0.95$ when the shape of the crack is triangular, $C_d = 0.9$ when the shape of the crack is rectangular; $A$ is the area of the crack, $m^2$; $P$ is the pressure, MPa; $Y$ is the outflow coefficient; $M$ is the relative molecular mass, and the relative molecular mass of CO$_2$ is 0.044 kg/mol; $K$ is the adiabatic index; $R$ is the gas constant, the value is 8.314, J/(mol·K); $T$ is the temperature, K.

For the hydrogeologic parameters of groundwater, the porosity and permeability values are from geological surveys of the Yanchang oilfield in China, and the other hydrogeological parameters are from Xu et al. (2010). The hydrogeologic parameters are shown in Table 1.

The liquid relative permeability and capillary pressure models applied in this model are the Van Genuchten model (Van Genuchten 1980), and the gas relative permeability model is the Corey model (Corey 1954). The specific parameters are extracted from Xu et al. (2010). The models

| Physical property parameter | Value  |
|----------------------------|--------|
| Porosity                   | 0.2    |
| Permeability ($m^2$)       | $k_h$  | $0.5 \times 10^{-13}$ |
|                            | $k_v$  | $0.5 \times 10^{-14}$ |
| Thermal conductivity (W/(m° C)) | 2.51  |
| Rock grain density (kg/m$^3$) | 2600  |
| Coefficient of compressibility (1/pa) | $4.5 \times 10^{-10}$ |
| Aqueous diffusion coefficient ($m^2$/s) | $1.0 \times 10^{-9}$ |
| Rock specific heat (J/(kg °C)) | 920   |
The mineral composition of the formation

The primary mineral composition of the aquifer and the possible secondary minerals are shown in Table 3, extracted from Xu et al. (2014).

The volume fractions of primary mineral, possible secondary mineral, and their reaction kinetics parameters are shown in Table 4. Since the reaction rate of calcite is fast, it is assumed at equilibrium throughout the simulations. The dissolution and precipitation of other minerals are controlled by kinetics, and the kinetic parameters are extracted from Lasaga et al. (1994).

Kinetic rates could be functions of non-basis species as well. Usually the species appearing in rate laws happen to be basis species. TOUGHREACT (Xu et al. 2006) uses a general form of rate expression (Lasaga et al. 1994).

\[
   r_n = f(c_1, c_2, \ldots, c_N) = \pm k_n A_n \left[ 1 - \Omega_n \right]^\theta \quad n = 1, 2 \ldots N_q, \tag{2}
\]

where positive values of \( r_n \) indicate dissolution, and negative values precipitation, \( k_n \) is the rate constant, \( A_n \) is the specific reactive surface area per kg \( \text{H}_2\text{O} \), \( \Omega_n \) is the kinetic mineral saturation ratio. \( \theta \) and \( \eta \) are usually taken equal to one.

The temperature dependence of the reaction rate constant can be expressed reasonably well via an Arrhenius equation (Lasaga, 1984; Steefel and Lasaga, 1994). Because many rate constants are reported at 25 °C, it is convenient to approximate rate constant dependency as a function of temperature, thus

\[
   k = k_{25} \exp \left[ \frac{-E_a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right], \tag{3}
\]

where \( k_{25} \) is the rate constant at 25 °C; \( R \) is gas constant; \( E_a \) is the activation energy; \( T \) is absolute temperature.

The reaction rate constant calculated using the above formula is usually considered only with pure water (neutral mechanism), while the dissolution and precipitation of minerals are often catalyzed by \( \text{H}^+ \) (acid mechanism) and \( \text{OH}^- \) (base mechanism). The kinetic rate constant \( k \) includes each of these three mechanisms (Lasaga et al. 1994; Palandri and Kharaka 2004).
where superscripts or subscripts nu, H, and OH indicate neutral, acid and base mechanisms, respectively; $E_a$ is the activation energy, (KJ/mol); $k_{25}$ is the rate constant at 25 °C, (mol/(m$^2$ s)); $R$ is gas constant, (KJ/(mol K)); $T$ is absolute temperature, (K); $a$ is the activity of the species; and $n$ is power term (constant). Notice that parameters $\theta$ and $\eta$ are assumed the same for each mechanism.

The reaction surface area $A$ changes as the reaction progresses. In TOUGHREACT, the reaction surface area is approximated as a spherical model.

$$A = \frac{(1 - \phi)}{\phi} \frac{3}{r},$$

where $\phi$ is porosity, $r$ is the particle radius of a particular porous medium.

$k = k_{25}^{nu} \exp \left[ \frac{-E_{nu}}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right]$

$\quad + k_{25}^{H} \exp \left[ \frac{-E_{H}}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] a_{H}^{nu}$

$\quad + k_{25}^{OH} \exp \left[ \frac{-E_{OH}}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] a_{OH}^{nu},$  

(4)

where $E_{nu}$, $E_{H}$, and $E_{OH}$ are the activation energies for the neutral, acid, and base mechanisms, respectively.

Chemical composition of shallow groundwater

The initial chemical composition is measured using groundwater samples collected from the Yanchang Oilfield in China. The salinity of groundwater is about 0.867 g/L and the density is $1 \times 10^3$ kg/m$^3$. The groundwater is reacted with aquifer minerals listed in Table 3 to obtain equilibrium concentration. The initial and equilibrium concentrations are given in Table 5.

| Mineral          | $A$ (cm$^2$/g) | Parameters for kinetic rate law                                                                 |
|------------------|---------------|-----------------------------------------------------------------------------------------------|
|                  |               | Neutral mechanism | Acid mechanism | Base mechanism | Neutral mechanism | Acid mechanism | Base mechanism |
|                  | $K_{25}$ (mol/m$^2$s) | $E_a$ (KJ/mol) | $K_{25}$ (mol/m$^2$s) | $E_a$ (KJ/mol) | $n$ (H$^+$) | $K_{25}$ (mol/m$^2$s) | $E_a$ (KJ/mol) | $n$ (H$^+$) |
| Primary mineral  |               | $E_a$ (KJ/mol) | $K_{25}$ (mol/m$^2$s) | $E_a$ (KJ/mol) | $n$ (H$^+$) | $K_{25}$ (mol/m$^2$s) | $E_a$ (KJ/mol) | $n$ (H$^+$) |
| Calcite          | Assumed at equilibrium |               |               |               |               |               |               |
| Quartz           | 9.8           | 1.023 × 10$^{-14}$ | 87.7         |               |               |               |               |
| Kaolinite        | 151.6         | 6.918 × 10$^{-14}$ | 22.2         | 4.898 × 10$^{-12}$ | 65.9 | 0.777 | 8.813 × 10$^{-18}$ | 17.9 | −0.472 |
| Illite           | 151.6         | 1.660 × 10$^{-13}$ | 35           | 1.047 × 10$^{-11}$ | 23.6 | 0.34  | 3.020 × 10$^{-17}$ | 58.8 | −0.4    |
| Oligoclase       | 9.8           | 1.445 × 10$^{-13}$ | 69.8         | 2.138 × 10$^{-11}$ | 65.0 | 0.457 | 6.310 × 10$^{-22}$ | 94.1 | −0.823 |
| K-feldspar       | 9.8           | 3.890 × 10$^{-13}$ | 38           | 8.710 × 10$^{-11}$ | 51.7 | 0.5   | 3.020 × 10$^{-17}$ | 58.8 | −0.4    |
| Chlorite         | 9.8           | 3.020 × 10$^{-13}$ | 88           | 7.762 × 10$^{-12}$ | 88  | 0.5   | 3.020 × 10$^{-17}$ | 58.8 | −0.4    |
| Smectite-Na      | 151.6         | 1.660 × 10$^{-13}$ | 36           | 1.047 × 10$^{-11}$ | 23.6 | 0.34  | 3.020 × 10$^{-17}$ | 58.8 | −0.4    |
| Hematite         | 12.9          | 2.512 × 10$^{-13}$ | 66.2         | 4.074 × 10$^{-10}$ | 66.2 | 1     |               |       |  |
| Secondary mineral|               | $E_a$ (KJ/mol) | $K_{25}$ (mol/m$^2$s) | $E_a$ (KJ/mol) | $n$ (H$^+$) | $K_{25}$ (mol/m$^2$s) | $E_a$ (KJ/mol) | $n$ (H$^+$) |
| Magnesite        | 9.8           | 4.571 × 10$^{-10}$ | 23.5         | 4.169 × 10$^{-7}$ | 14.4 | 1     |               |       |  |
| Siderite         | 9.8           | 1.260 × 10$^{-9}$ | 62.76        | 6.457 × 10$^{-4}$ | 36.1 | 0.5   |               |       |  |
| Pyrite           | 12.87         | 2.818 × 10$^{-5}$ | 56.9         | 3.020 × 10$^{-9}$ | 56.9 | 0.5   | 3.020 × 10$^{-8}$ | 56.9 | −0.5    |
| Albite           | 9.8           | 2.754 × 10$^{-10}$ | 69.8         | 6.918 × 10$^{-11}$ | 65.0 | 0.457 | 2.512 × 10$^{-16}$ | 71  | −0.572 |
| Smectite-Ca      | 151.6         | 1.660 × 10$^{-13}$ | 35.0         | 1.047 × 10$^{-11}$ | 23.6 | 0.34  | 3.020 × 10$^{-17}$ | 58.8 | −0.4    |
| Dolomite         | 9.8           | 2.951 × 10$^{-8}$ | 52.2         | 6.457 × 10$^{-4}$ | 36.1 | 0.5   |               |       |  |
| Ankerite         | 9.8           | 1.260 × 10$^{-9}$ | 62.76        | 6.457 × 10$^{-4}$ | 36.1 | 0.5   |               |       |  |
| Dawsonite        | 9.8           | 1.260 × 10$^{-9}$ | 62.76        | 6.457 × 10$^{-4}$ | 36.1 | 0.5   |               |       |  |

| Component  | Measured initial concentration (mol/L) | Equilibrium concentration (mol/L) |
|------------|----------------------------------------|----------------------------------|
| $K^+$      | 4.462 × 10$^{-5}$                     | 4.3634 × 10$^{-5}$               |
| $Ca^{2+}$  | 2.156 × 10$^{-3}$                     | 3.2542 × 10$^{-4}$               |
| $Na^+$     | 5.111 × 10$^{-3}$                     | 5.0622 × 10$^{-1}$               |
| $Mg^{2+}$  | 2.295 × 10$^{-3}$                     | 3.7282 × 10$^{-13}$              |
| $Fe^{3+}$  | 1.893 × 10$^{-5}$                     | 2.4642 × 10$^{-12}$              |
| $HCO_3^-$  | 4.025 × 10$^{-4}$                     | 5.4955 × 10$^{-1}$               |
| $SO_4^{2-}$| 2.515 × 10$^{-3}$                     | 2.3002 × 10$^{-3}$               |
| $AlO_2^{-}$| 5.085 × 10$^{-7}$                     | 1.0286 × 10$^{-10}$              |
| $Cl^-$     | 3.364 × 10$^{-3}$                     | 3.0714 × 10$^{-3}$               |
| pH         | 7.95                                  | 6.67                             |
Results and discussion

Change of CO₂ concentration in groundwater

As shown in Fig. 3, after CO₂ migrates to groundwater, because the density of CO₂ is smaller than the density of water, CO₂ will migrate upward under buoyancy and gradually diffuse to the surroundings. As CO₂ gradually diffuses, the CO₂ gas saturation in the groundwater formation gradually increases. By 100 years, the CO₂ gas saturation at the leaking point is about 0.36 (Fig. 5a). CO₂ basically diffuses into the entire area and gather at the top of groundwater (Fig. 3f). A fraction of CO₂ will dissolve in groundwater and participate in water–rock interactions. As CO₂ gradually migrates, the region with dissolved CO₂ in groundwater gradually expands (Fig. 4). The dissolved CO₂ concentration increases gradually at the point source of CO₂ injection. By 10 years the concentration of dissolved CO₂ changes little at the leaking point. By 100 years, the concentration of CO₂ dissolved at the point source of CO₂ is about 0.38 mol/L (Fig. 5b).

Chemical reaction in groundwater and change of mineral volume fraction

With the gradual migration of CO₂, the amount of CO₂ dissolved in groundwater continues to increase, and the spatial distribution of pH gradually expands (Fig. 6), resulting in a significant decrease in the pH value of groundwater and an increase in formation porosity (Fig. 7). By 100 years, the pH of groundwater has decreased from 6.67 to about 5.3 (Fig. 8a), and the chemical composition of groundwater is greatly affected. The porosity of the formation increases in 0–10 years, and when the mineral dissolution and precipitation reach a steady state, the porosity basically remains unchanged. By 100 years, formation porosity is approximately 0.20027 (Fig. 8b). The main reason for the decrease in pH value of groundwater is that CO₂ dissolves in groundwater to form carbonic acid, which is unstable and decomposes into H⁺ and HCO₃⁻. The reaction equations are as follows.

\[
CO_2(gas) \rightleftharpoons CO_2(aq),
\]
\[
CO_2(aq) + H_2O \rightleftharpoons H_2CO_3,
\]
\[
H_2CO_3 \rightleftharpoons H^+ + HCO_3^-.\]
The change in volume fraction (abundance) of mineral is defined by the following formula. 

\[
HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}
\]  

(9)

\[
V_1 - V_0, \quad \frac{V_1 - V_0}{V_0}
\]  

(10)  

where \(V_0\) is the initial volume fraction of mineral, \(V_1\) is the volume fraction of mineral at a given time \(t\). Negative values indicate dissolution, positive values indicate precipitation.

\(\text{CO}_2\) migration to groundwater changes the acidity of the groundwater and the original water chemistry, leading to dissolution of calcite, oligoclase, K-feldspar, chlorite and hematite (Fig. 9a). The volume fraction of calcite remains almost unchanged after 10 years. The volume fractions of oligoclase, K-feldspar and chlorite gradually decrease, while...
Fig. 6 Spatial distribution of pH

Fig. 7 Spatial distribution of porosity

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Fig. 8 Changes in pH and porosity at the leaking point over time

Fig. 9 Changes in mineral volume fraction (Note: negative value represents mineral dissolution, positive value represents mineral precipitation)
illite begins to precipitate after 10 years (Fig. 9b). The dissolution reactions are as follows:

$$\text{CaCO}_3(\text{Calcite}) + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-, \quad (11)$$

$$\text{K}_0.4\text{Mg}_{0.25}\text{Al}_{1.8} (\text{Al}_{0.5}\text{Si}_{3.5}\text{O}_{10}) (\text{OH})_2 (\text{Illite}) + 8\text{H}^+ \rightarrow 5\text{H}_2\text{O} + 0.6\text{K}^+ + 0.25\text{Mg}^{2+} + 2.3\text{Al}^{3+} + 3.5\text{SiO}_2(\text{aq}), \quad (12)$$

$$\text{CaNa}_3\text{Al}_{6}\text{Si}_{14}\text{O}_{40}(\text{Oligoclase}) + 24\text{H}^+ \rightarrow \text{Ca}^{2+} + 4\text{Na}^+ + 6\text{Al}^{3+} + 14\text{SiO}_2(\text{aq}) + 12\text{H}_2\text{O}, \quad (13)$$

$$\text{KAlSi}_3\text{O}_8 (\text{K-feldspar}) + 4\text{H}^+ \rightarrow \text{K}^+ + \text{Al}^{3+} + 3\text{SiO}_2(\text{aq}) + 2\text{H}_2\text{O}. \quad (14)$$

$$2\text{Mg}_{2.3}\text{Fe}_{2.7}\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 (\text{Chlorite}) + 20\text{H}^+ \rightarrow 5\text{Mg}^{2+} + 5\text{Fe}^{2+} + 4\text{Al}(\text{OH})_3 + 6\text{H}_4\text{SiO}_4. \quad (15)$$

$$\text{Fe}_2\text{O}_3 (\text{Hematite}) + 6\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 3\text{H}_2\text{O}. \quad (16)$$

The dissolution of minerals consumes H$^+$ in the groundwater, alleviating the pH value of the groundwater, and leads to precipitation of secondary minerals. When the dissolved CO$_2$ in groundwater gradually increases, K-feldspar is gradually transformed into kaolinite. In addition, due to the massive dissolution of oligoclase and chlorite, the concentration of Na$^+$ and Mg$^{2+}$ in the groundwater increases significantly, resulting in the precipitation of smectite-Na. Figure 9c shows that the mineral volume fraction of quartz, kaolinite and smectite-Na increases gradually, and the amount of mineral precipitation increases accordingly, among which the volume fraction of smectite-Na changes the most. By 100 years, the volume fraction of smectite-Na changes by about $1.65 \times 10^{-5}$, while the volume fraction of hematite remains almost unchanged. The precipitation reactions occur as follows:

$$\text{H}_2\text{SiO}_4 \rightarrow \text{SiO}_2 (\text{Quartz}) + 2\text{H}_2\text{O}, \quad (17)$$

$$2\text{KAlSi}_3\text{O}_8 (\text{K-feldspar}) + 2\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{Kaolinite}) + 4\text{SiO}_2 + 2\text{K}^+ + 2\text{HCO}_3^-, \quad (18)$$

The dissolution and precipitation of the initial minerals lead to significant changes in the concentration of chemical components in the groundwater, which then recombine to form secondary minerals. In 100 years, the secondary minerals are mainly smectite-Ca and siderite. As shown in Fig. 9d, the volume fraction of smectite-Ca and siderite gradually increases, and the volume fraction of siderite changes the most. By 100 years, the volume fraction of siderite changes about $3.29 \times 10^{-5}$. The reactions that occur are as follows:

$$0.26\text{Mg}^{2+} + 0.29\text{Na}^+ + 1.77\text{Al(OH)}_3 + 3.97\text{H}_2\text{SiO}_4 \rightarrow \text{Na}_{0.329}\text{Mg}_{0.26}\text{Al}_{1.77}\text{Si}_{3.97}\text{O}_{10}(\text{OH})_2(\text{Smectite-Ca}) + 0.81\text{H}^+ + 9.19\text{H}_2\text{O}. \quad (19)$$

Figure 10a shows that the concentration of K$^+$ gradually increases at the point source of CO$_2$ leaking. The increase in K$^+$ concentration is mainly due to the dissolution of K-feldspar and illite. Illite begins to precipitate after 10 years, which consumes K$^+$, making the concentration of K$^+$ increase slowly after 10 years. By 100 years, the concentration of K$^+$ at the leaking point is $1.67 \times 10^{-4}$ mol/L. The dissolution of calcite and oligoclase for the generation of secondary mineral smectite-Ca offers a large amount of Ca$^{2+}$. In the initial time of CO$_2$ leakage, the concentration of Ca$^{2+}$ increases significantly. By 10 years, the concentration of Ca$^{2+}$ is $2.09 \times 10^{-3}$ mol/L at the leaking point, after 10 years, the concentration of Ca$^{2+}$ increases more slowly. By 100 years, the concentration of Ca$^{2+}$ is $2.18 \times 10^{-3}$ mol/L at the leaking point. The change trend of the concentration of Ca$^{2+}$ is basically the same as that of calcite. The dissolution of oligoclase significantly increases the concentration of Na$^+$ in groundwater, while the formation of smectite-Ca consumes part of Na$^+$. Figure 9a, c shows that the volume fraction change of oligoclase is about $2.07 \times 10^{-5}$, and the volume fraction of smectite-Na is about $1.65 \times 10^{-5}$ at 100 years. Since the initial volume fraction of oligoclase is much larger than that of smectite-Na, the concentration of Na$^+$ gradually increases (Fig. 10c). Figure 10d shows that the concentration of Mg$^{2+}$ increases first and then decreases. The dissolution of illite and chlorite significantly increase the concentration of Mg$^{2+}$ in groundwater, and the precipitation of smectite-Na and smectite-Ca consume part of Mg$^{2+}$. It can be seen from Fig. 9c, d
the volume fraction change of smectite-Na and smectite-Ca increase significantly and consume a large amount of Mg$^{2+}$. Therefore, the concentration of Mg$^{2+}$ decreases significantly after 10 years, but it is still higher than the initial value, indicating that the content of Mg$^{2+}$ produced by the dissolution of illite and chlorite is still greater than the Mg$^{2+}$ consumed by smectite-Na and smectite-Ca precipitation. It can be seen from Fig. 10e the concentration of Fe$^{2+}$ increases significantly. The dissolution of chlorite provides a large amount of Fe$^{2+}$ for the precipitation of siderite. Comparing Fig. 9a, b, it can be seen that the change in the volume fraction of chlorite is 2–3 orders of magnitude higher than the change in the volume fraction of siderite. In 10 years, the volume fraction of siderite changes significantly. Therefore, the concentration of Fe$^{2+}$ increases significantly in 0–10 years. Due to the increase in the amount of siderite precipitation and the consumption of part of Fe$^{2+}$, the increasing trend of Fe$^{2+}$ began to slow down.

### Fig. 10 Changes in chemical composition concentration with time at the leakage point

The change of HCO$_3^-$ concentration is partly caused by the decomposition of carbonic acid, and partly by the dissolution of calcite and the precipitation of siderite. According to Fig. 10f, by 10 years, the concentration of HCO$_3^-$ is 0.86 mol/L at the leaking point, and from the 10 years, the concentration of HCO$_3^-$ changes little. Comparing Fig. 9a, d, it can be seen that the variation of the volume fraction of calcite is significantly greater than that of siderite, and the variation trend of the concentration of HCO$_3^-$ is basically similar to that of the dissolved CO$_2$ and Ca$^{2+}$ in groundwater. As can be seen from Fig. 10g, the concentration of AlO$_2^-$ increases first and then decreases. The increase of AlO$_2^-$ concentration is mainly due to the precipitation of illite. In addition, the dissolved CO$_2$ in the water also reacts with part of AlO$_2^-$ (Formula (22)), leading to the decrease of AlO$_2^-$ concentration, but the concentration of AlO$_2^-$ is still higher than the initial value. Due to SO$_4^{2-}$ and Cl$^-$ in the groundwater is not involved in the mineral dissolution and precipitation reaction, therefore, the
concentration of $\text{SO}_4^{2-}$ and $\text{Cl}^-$ change very little, and basically maintain at the initial value (Fig. 10h, i).

$$\text{AlO}_2^- + \text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{HCO}_3^-.$$ (22)

**Monitoring indicators**

As the pH of groundwater decreases significantly with CO$_2$ leakage, the acidity of groundwater increases significantly, and the monitoring of pH value is more convenient and intuitive, therefore, we should focus on monitoring the change characteristics of the pH value of groundwater. It is recommended to lay an in-situ online monitor in the target aquifer to monitor the change characteristics of the pH of groundwater. The frequency of in-situ online monitoring is recommended to be once every 10 min, and sampling monitoring is recommended to be once a month. By comprehensively improving the monitoring frequency of groundwater, the changes of groundwater monitoring indicators can be timely and accurately grasped. The data obtained from monitoring should be compared with the previous environmental background value to eliminate fluctuations in monitoring indicators caused by non-CO$_2$ leakage such as environmental factors and human activities, so as to avoid the wrong judgment of CO$_2$ leakage. If the pH of groundwater is abnormal, it is highly likely to be caused by CO$_2$ leakage, and remedial measures should be taken immediately.

Due to the small changes in formation porosity, it is not suitable as a monitoring indicators. As AlO$_2^-$ has a strong ability to bind H$, it is very easy to form Al(OH)$_3$ precipitation, making it is not suitable as a monitoring indicator. The relative change of ion concentration in groundwater is calculated by the following formula.

$$R = \frac{C_1 - C_0}{C_0},$$ (23)

where $C_1$ is the ion concentration at a given moment, (mol/L); $C_0$ is the initial ion concentration, (mol/L).

Figure 11 shows that the concentrations of Fe$^{2+}$, Mg$^{2+}$ and Ca$^{2+}$ in groundwater change significantly after 10 and 100 years of CO$_2$ leaking. The concentrations of K$^+$ and HCO$_3^-$ change slightly, while the concentrations of Na$^+$, Cl$^-$ and SO$_4^{2-}$ remain almost unchanged. Therefore, it is recommended to adopt Fe$^{2+}$, Mg$^{2+}$ and Ca$^{2+}$ as important monitoring indicators of CO$_2$ leakage. Ion concentration is mainly monitored by sampling. It is recommended to take samples once a month before CO$_2$ injection and storage, twice a month during CO$_2$ injection and storage, and once a month in the later stage of CO$_2$ injection and storage. In the monitoring process, the sampling frequency and analysis intensity should be adjusted according to the actual situation, and the CO$_2$ leakage situation should be judged jointly with the monitoring instrument.

These indicators are recommended to be monitored to detect CO$_2$ in time and provide early warnings. Once data abnormalities are found, corresponding measures should be taken. In addition, some monitoring indicators (such as conductivity, temperature and pressure, etc.) can be appropriately added based on the actual situation on site, and the monitoring indicator system can be further improved on the basis of accurate data.

**Conclusions**

In this work, the multi-phase reaction transport code TOUGHREACT-OMP/ECO2N is used to model the influence of CO$_2$ migration on shallow groundwater. The following conclusions are made from our simulations.

1. After CO$_2$ migrates to groundwater, it migrates upward due to buoyancy in gaseous form and gradually diffuses to the surroundings, and the CO$_2$ gas saturation
in groundwater gradually increases. A fraction of CO$_2$ will be dissolved in the groundwater. As the dissolved CO$_2$ gradually increases, the acidity of the groundwater is significantly increased and the pH is significantly reduced, causing dissolution/precipitation of the initial minerals, resulting in a slight increase in the porosity of the formation.

2. The dissolved minerals are calcite, illite, oligoclase, K-feldspar, chlorite and hematite; the precipitated minerals are quartz, kaolinite and smectite-Na. The secondary minerals are siderite and smectite-Ca.

3. The dissolution and precipitation of minerals change the concentration of chemical components in the groundwater. The concentrations of K$^+$ and Fe$^{2+}$ in the groundwater gradually increase. The concentrations of Ca$^{2+}$ and HCO$_3^-$ remain basically unchanged after increasing to a certain value. The concentration of Mg$^{2+}$ and AlO$_2^-$ increase first and then decrease, but is still higher than the initial value. The concentration of Na$^+$, SO$_4^{2-}$ and Cl$^-$ do not change much.

4. It is suggested to choose pH as an important indicator to judge whether CO$_2$ leakage into groundwater during geological storage. At the same time, the changes of Fe$^{2+}$, Mg$^{2+}$, and Ca$^{2+}$ should be monitored. These indicators could provide early warning of CO$_2$ leakage.

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