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Research Article

Keywords: Geological storage, CO₂ migration, Shallow groundwater, Chemical composition, Monitoring indicators, TOUGHREACT

Posted Date: May 5th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-446707/v1>

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Version of Record: A version of this preprint was published at Environmental Earth Sciences on January 25th, 2022. See the published version at <https://doi.org/10.1007/s12665-022-10194-2>.

Influence of CO₂ migration from geological storage on the chemical composition of groundwater and monitoring indicators

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Abstract

In the process of CO₂ geological sequestration, there is a risk that CO₂ will migrate to and dissolve in groundwater, resulting in a series of physical and chemical reactions, with influence on chemical compositions of groundwater. In this paper, numerical simulations are conducted to study the influence of CO₂ migration on the chemical composition of groundwater. The modeling results show that when CO₂ migrates to the groundwater, gaseous CO₂ 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, chlorite and hematite, and precipitation of quartz, kaolinite, smectite-Na, siderite and smectite-Ca. The porosity of the formation increases. The concentrations of K⁺ and Fe²⁺ in groundwater gradually increase, the concentrations of Ca²⁺ and HCO₃⁻ basically remain unchanged after increasing to a certain value, the concentrations of Mg²⁺ and AlO₂⁻ first increase and then decrease, and the concentrations of Na⁺, Cl⁻ and SO₄²⁻ first decrease slightly and then gradually increase, but the change in concentration is small. Therefore, Fe²⁺, Mg²⁺, Ca²⁺, K⁺ and pH can be used as important monitoring indicators of whether CO₂ migrates to groundwater during geological storage.

Keywords Geological storage • CO₂ migration • Shallow groundwater • Chemical composition • Monitoring indicators • TOUGHREACT

1 Introduction

With the increasing concerns on global warming, CO₂ geologic sequestration has been considered to be one of the most effective ways to reduce CO₂ emissions and alleviate global warming (Kharaka et al. 2011). However, due to the uncertainty in geological conditions, the risk of CO₂ leaking during geological storage has to be considered (Aines et al. 2009; Oldenburg et al. 2011). For example, sequestered CO₂ may migrate into groundwater along faults, fractures and

recovery wells (Du et al. 2012; Xie et al. 2017). Once CO₂ 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 CO₂ migration from geological storage on the quality of groundwater is an important part of the environmental risk assessment and development of early warning in CO₂ geological storage.

Although the evaluation of the impact of CO₂ geological storage on water quality has been studied long ago (Meer et al. 1992), systematic study of the impact of CO₂ on shallow groundwater quality began in 2004. Wang et al. (2004) used numerical simulation for the first time to study the impact of CO₂ 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 mg/L 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. (2009, 2013) studied the impact of CO₂ geological storage on the hydrochemistry of shallow groundwater in sandstone aquifers in New Mexico, USA. The study showed that high alkalinity and carbonate minerals mitigate the effects of CO₂ intrusion on pH, and no migration of trace elements in the aquifer was observed, but the migration of As, U and Pb was observed in other saline aquifers. Therefore, they suggested that geochemical conditions determine the changes in the water quality of the aquifer and also affect the effectiveness of detecting CO₂ migration. Cheng (2013) studied the Ordos region of China and used the TOUGHREACT numerical simulation software to simulate the leakage of CO₂ into shallow aquifers, and studied its impact on water quality. The results showed the migration of CO₂ causes the migration of certain metals in the ore, which in turn affected the total amount of metal ions in the water.

Lu et al. (2009) conducted CO₂ injection experiments on actual water-bearing media in the Gulf Coast area of 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 concentration of some metal elements such as Ca, Mg, Zn, etc. increased rapidly when CO₂ was just injected, and then tended to stabilize. The concentration of other metal elements such as Fe, Al, Cu, etc. increased at the beginning of the injection, and then began to decrease and became lower than before the test. Little and Jackson (2010, 2011) conducted more than 300 days of indoor injection experiments using aqueous media in 17 regions of the United States. The results showed that the H⁺ concentration in all aqueous 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. (2010) 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 ($\delta^{13}\text{C}_{\text{DIC}}$, ⁸⁷Sr/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 shallow groundwater, it is necessary to couple the hydrodynamic and chemical reaction processes that may occur during the movement of multiphase fluids in the formation. In this paper, the Yanchang Oilfield in China was studied with numerical simulations 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 in shallow groundwater, we can screen out monitoring indicators that are more sensitive to changes of CO₂ migration, and provide basis for similar CO₂ geological storage monitoring programs, and reduce the possible risks in carbon capture and storage (CCS) projects.

2 Model Setup

2.1 Modeling code and conceptualization

The non-isothermal reactive geochemical transport code TOUGHREACT V3.32-OMP (Xu and Pruess 2001; Xu et al. 2006; Xu et al. 2014) was used in this study. TOUGHREACT is an extension of TOUGH2 (Pruess et al. 1991) and the fluid property module ECO2N was used for H₂O-CO₂-NaCl mixtures (Pruess et al. 2004).

The depth of groundwater in the Yanchang Oilfield in China is 10m, the vertical thickness of the groundwater is 60m, which is divided into 6 grids, and the length in the horizontal direction is 500m, which is divided into 50 grids. 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/100m, and the hydrostatic pressure gradient is 10 bar/100m. Therefore, the bottom temperature of the model is about 13°C and the pressure is 8bar. The CO₂ migration point from geological storage was set at X=250 m, the constant leaking rate of CO₂ is 0.0001 kg/s, and the CO₂ leaking time and simulation time were set to 100 years.

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

Table 1 Hydrogeological parameters

Physical property parameter	Value
Porosity	0.2
Permeability (m ²)	k_h
	k_v
Thermal conductivity (W/(m·°C))	2.51
Rock grain density (kg/m ³)	2600
Coefficient of compressibility (pa ⁻¹)	4.5×10^{-10}
Aqueous diffusion coefficient (m ² /s)	1.0×10^{-9}
Rock specific heat (J/(kg·°C))	920

The water relative permeability and capillary pressure models applied in this model are the Van Genuchten-Mualem model ([Van et al. 1980](#)), and the gas relative permeability model is the Corey model ([Corey et al. 1954](#)). The specific parameters are taken from [Xu et al. \(2010\)](#). The models of relative permeability and capillary pressure are shown in Table 2.

Table 2 Models of relative permeability and capillary pressure

Relative permeability	
Intrinsic permeability (Van Genuchten-Mualem, 1980)	Gas relative permeability (Corey, 1954)
$k_{lr} = \sqrt{S^*} \{1 - (1 - [S^*]^{1/m})^m\}^2$ with $S^* = (S_l - S_{lr}) / (1 - S_{lr})$	$k_{rg} = (1 - \hat{S})^2 (1 - \hat{S}^2)$ with $S = (S_l - S_{lr}) / (S_l - S_{lr} - S_{gr})$
S_{lr} : Residual water saturation, $S_{lr}=0.30$ m: Index, m=0.457	S_{gr} : Residual gas saturation, $S_{gr}=0.50$
Capillary pressure function (Van Genuchten, 1980)	
$P_{cap} = -P_0 ([S^*]^{-1/m} - 1)^{1-m}$	
$S^* = (S_l - S_{lr}) / (1 - S_{lr})$	
$P_0 = \rho_w / \alpha$	
S_{lr} : Residual water saturation, $S_{lr}=0.00$ m: Index, m=0.457 P_0 : Coefficient of strength, $P_0=19.61\text{kPa}$	

2.2 The mineral composition of the formation

The major mineral compositions in the shallow groundwater, the possible secondary minerals and their volume fractions are shown in Table 3, extracted from the TOUGHREACT V3.0-OMP Sample Problems (Xu et al. 2014).

Table 3 List of mineral composition

	Mineral	Chemical composition	Volume fraction(%)
Primary mineral	Calcite	CaCO_3	1.929
	Quartz	SiO_2	57.888
	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	2.015
	Illite	$\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{1.8}(\text{Al}_{0.5}\text{Si}_{3.5}\text{O}_{10})(\text{OH})_2$	0.954
	Oligoclase	$\text{CaNa}_4\text{Al}_6\text{Si}_{14}\text{O}_{40}$	19.795
	K-feldspar	KAlSi_3O_8	8.179
	Chlorite	$\text{Fe}_{2.5}\text{Mg}_{2.5}\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$	4.556
	Smectite-Na	$\text{Na}_{0.290}\text{Mg}_{0.26}\text{Al}_{1.77}\text{Si}_{3.97}\text{O}_{10}(\text{OH})_2$	3.897
Secondary mineral	Hematite	Fe_2O_3	0.497
	Magnesite	MgCO_3	0
	Siderite	FeCO_3	0
	Pyrite	FeS_2	0
	Albite	$\text{NaAlSi}_3\text{O}_8$	0
	Smectite-Ca	$\text{Ca}_{0.145}\text{Mg}_{0.26}\text{Al}_{1.77}\text{Si}_{3.97}\text{O}_{10}(\text{OH})_2$	0
	Dolomite	$\text{CaMg}(\text{CO}_3)_2$	0
	Ankerite	$\text{CaMg}_{0.3}\text{Fe}_{0.7}(\text{CO}_3)_2$	0
	Dawsonite	$\text{NaAlCO}_3(\text{OH})_2$	0

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. The mineral abundances are from the TOUGHREACT V3.0-omp Sample Problems in the software manual (Xu et al. 2014), and the kinetic parameters are extracted from Lasaga et al. (1994).

Table 4 Mineral composition and reaction kinetics parameters in the model

Mineral	A (cm ² /g)	Parameters for kinetic rate law							
		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									
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	0.457			
K-feldspar	9.8	3.890×10 ⁻¹³	38	8.710×10 ⁻¹¹	51.7	0.5	6.310×10 ⁻²²	94.1	-0.823
Chlorite	9.8	3.02×10 ⁻¹³	88	7.762×10 ⁻¹²	88	0.5			
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 ⁻¹⁵	66.2	4.074×10 ⁻¹⁰	66.2	1			
Secondary mineral									
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			2.8184×10 ⁻⁵	56.9	0.5	3.02×10 ⁻⁸	56.9	-0.5
Albite	9.8	2.754×10 ⁻¹⁰	69.8	6.918×10 ⁻¹¹	65	0.457	2.512×10 ⁻¹⁶	71	-0.572
Smectite-Ca	151.6	1.660×10 ⁻¹³	35	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			

Note that: (1) all rate constants are listed for dissolution; (2) A is the reactive surface area, k₂₅ is the kinetic constant at 25 °C, E_a is activation energy, and n is the power; (3) the power terms n for both acid and base mechanisms are with respect to H⁺.

2.3 Chemical composition of shallow groundwater

The initial water chemical composition is measured using groundwater samples collected from the Yanchang Oilfield in China in September 2019. The groundwater is reacted with aquifer minerals listed in Table 3 to obtain equilibrium fluid compositions. The initial and equilibrium concentrations are given in Table 5.

Table 5 Initial concentration of chemical compositions in shallow groundwater

Component	Measured initial concentration	Equilibrium concentration
	(mol/L)	(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 ²⁺	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

3 Results and discussion

3.1 Change of CO₂ concentration in groundwater

As shown in Fig. 1, after CO₂ migrates to shallow 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. CO₂ basically diffuses into the entire study area and gather at the top of shallow groundwater (Fig. 1(f)). 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. 2). The dissolved CO₂ concentration increases gradually at the point source of CO₂ injection. By 10 years the concentration of dissolved CO₂ at the point source of CO₂ migration changes little. By 100 years, the concentration of CO₂ dissolved at the point source of CO₂ is about 0.38 mol/L (Fig. 3(b)).

Fig. 1 Spatial distribution of CO₂ gas saturation

Fig. 2 Spatial distribution of dissolved CO_2

Fig. 3 Change in CO₂ concentration at the leaking point over time

3.2 Chemical reaction in groundwater and change of mineral volume fraction

With the gradual migration of CO₂, the amount of CO₂ dissolved in shallow groundwater continues to increase, and the spatial distribution of pH gradually expands (Fig. 4), resulting in a significant decrease in the pH value of groundwater. By 100 years, the pH of shallow groundwater has decreased from 6.67 to about 5.3 (Fig. 6(a)), and the chemical composition of groundwater is greatly affected. The formation porosity increases (Fig. 5). 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. 6(b)). The main reason for the decrease in pH value of groundwater is that CO₂ dissolves in shallow groundwater to form carbonic acid, which is unstable and decomposes into H⁺ and HCO₃⁻. The reaction equations are as follows:

Fig. 4 Spatial distribution of pH

Fig. 5 Spatial distribution of porosity

Fig. 6 Changes in pH and porosity at the leaking point over time

CO₂ migration to shallow groundwater changes the acidity of the groundwater and the

original water chemistry, leading to dissolution of calcite, illite, oligoclase, K-feldspar, chlorite and hematite (Fig. 7(a)). The volume fraction of calcite remains almost unchanged after 10 years. The volume fractions of oligoclase, K-feldspar and chlorite gradually decrease, while illite begins to precipitate after 10 years (Fig. 7(b)). The dissolution reactions are as follows:

The dissolution of minerals consumes H^+ in the groundwater, alleviating the pH change 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. Fig. 7(c) 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 1.65×10^{-5} , while the volume fraction of hematite remains almost unchanged. The precipitation reactions occur as follows:

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. 7(d), 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 3.29×10^{-8} . The reactions that occur are as follows:

(a) Dissolved primary minerals

(b) Illite

(c) Precipitated primary minerals

(d) Secondary minerals

Fig. 7 Changes in mineral volume fraction (Note: negative value represents mineral dissolution, positive value represents mineral precipitation)

3.3 Changes in the concentration of chemical components in groundwater

Fig. 8(a) 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 point source of CO_2 leaking is 1.67×10^{-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 migration, the concentration of Ca^{2+} increases significantly. By 10 years, the concentration of Ca^{2+} is 2.09×10^{-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 2.18×10^{-3} mol/L (Fig. 8(b)) at the leaking point. Comparing Fig. 7(a) and Fig. 7(c), it can be seen that the volume fractions of oligoclase and smectite-Ca have a small change, and 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-Na consumes part of Na^+ .

Fig. 7(a) and Fig. 7(b) shows that by 100 years, the volume fraction change of oligoclase is about 2.07×10^{-5} , and the volume fraction of smectite-Na is about 1.65×10^{-5} . Since the initial volume fraction of oligoclase is much larger than that of smectite-Na, the concentration of Na^+ gradually increases (Fig. 8(c)).

Fig. 8(d) 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. 7(b) and Fig. 7(c) 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. 8(e) the concentration of Fe^{2+} gradually increases. The dissolution of chlorite provides a large amount of Fe^{2+} for the precipitation of siderite. Comparing Fig. 7(a) and Fig. (c), 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 the initial time. Due to the increase in the amount of siderite precipitation and the consumption of part of Fe^{2+} , the increase in the concentration of Fe^{2+} began to slow down.

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. 8(f), 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. Fig. 7 shows 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. 8(g), 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^- , 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 SO_4^{2-} and Cl^- change is very small, the main reason is the small changes caused by the changes in the concentration of other chemical components during the migration of the reaction solute, the concentration of SO_4^{2-} and Cl^- basic maintained at the initial value (Fig. 8(h), (I)).

(a) K^+

(b) Ca^{2+}

(c) Na^+

Fig. 8 changes in ion concentration at the leaking point over time

3.4 Safety monitoring indicators

According to the above simulation results, due to the small changes in mineral volume fraction and formation porosity, they are not suitable safety monitoring indicators. As AlO_2^- has a strong ability to bind H^+ , it is very easy to form $\text{Al}(\text{OH})_3$ precipitation, making it is not suitable as a monitoring indicator. The pH value of shallow groundwater changes significantly and is easy to detect. Therefore, if CO_2 migrates to shallow groundwater during the geological storage, the pH value can be used as an important monitoring indicator. In addition, we analyzed the relative change of ion concentration in shallow groundwater according to formula (17).

$$R = \frac{C_1 - C_0}{C_0} \quad (17)$$

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

Fig. 9 shows that the concentrations of Fe^{2+} , Mg^{2+} and Ca^{2+} in shallow 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 use the pH value as an important monitoring indicator of CO_2 migration and to monitor the changes of Fe^{2+} , Mg^{2+} , Ca^{2+} , K^+ and HCO_3^- . These six 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, monitoring indicators 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.

Fig. 9 CO₂ geological storage safety monitoring indicators

4 Summary and conclusions

In this work, the multiphase reaction transport code TOUGHREACT-OMP/ECO2N is used to model the effect of CO₂ migration on shallow groundwater. The following conclusions are made from our simulations:

(1) After CO₂ migrates to shallow groundwater, it migrates upward due to buoyancy in gaseous form and gradually diffuses to the surroundings, and the CO₂ gas saturation in shallow groundwater gradually increases. A fraction of CO₂ will be dissolved in the groundwater. As the dissolved CO₂ gradually increases, the acidity of the groundwater is significantly increased and the pH value 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 Fe²⁺ in the groundwater gradually increase. The concentrations of Ca²⁺ and HCO₃⁻ remain basically unchanged after increasing to a certain value. The concentration of Mg²⁺ and AlO₂⁻ increase first and then decrease, but is still higher than the initial value. The concentration of Na⁺, SO₄²⁻ and Cl⁻ do not change much.

(4) It is recommended to choose pH value as an important indicator of whether CO₂ migrates to shallow groundwater during geological storage. At the same time, the changes of Fe²⁺, Mg²⁺, Ca²⁺ and K⁺ can be monitored. These five indicators could provide early warning of CO₂ leakage.

Declarations

Conflicts of interest All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

Acknowledgements

This work was supported by National Key Research and Development Program of China (Grant No.2018YFB0605504).

References

1. Kharaka YK, Thordsen JJ, Kakouros E, Ambats G, Herkelrath WN, Beers SR, Birkholzer JT, Apps JA, Spycher NF, Zheng L (2010) Changes in the chemistry of shallow groundwater related to the 2008 injection of CO₂ at the ZERT field site, Bozeman, Montana. *Environ Earth Sci* 60(2): 273-284. <http://doi.org/10.1007/s12665-009-0401-1>
2. Aines RD, Leach MJ, Weisgraber TH, MD Simpson, Friedmann SJ, Bruton CJ (2009) Quantifying the potential exposure hazard due to energetic releases of CO₂ from a failed sequestration well. *Energy Procedia* 1(1), 2421-2429. <http://doi.org/10.1016/j.egypro.2009.02.003>
3. Oldenburg CM, Jordan PD, Nicot JP, Nicot JP, Mazzoldi A, Gupta AK, Bryant SL (2011) Leakage risk assessment of the In Salah CO₂ storage project: Applying the certification framework in a dynamic context. *Energy Procedia* 4: 4154-4161. <http://doi.org/10.1016/j.egypro.2011.02.360>
4. Du SH, Su XS, Zheng LG (2012) Advances in deep CO₂ leakage impact on shallow groundwater quality. *Adv Water Sci* 023(006):875-880. <http://doi.org/10.14042/j.cnki.32.1309.2012.06.013>
5. Xie J, Wei N, Wu LZ, Zhang KN, Xu M (2017) Progress in leakage study of geological CO₂ storage. *Rock Soil Mech* S1:187-194. <http://doi.org/10.16285/j.rsm.2017.S1.021>
6. Apps JA, Zheng L, Zhang Y, Xu TF, Birkholzer JT, Evaluation of Potential Changes in Groundwater Quality in Response to CO₂ Leakage from Deep Geologic Storage. *Transport in Porous Med* 82(1): 215-246 (2010). <http://doi.org/10.1007/s11242-009-9509-8>
7. Meer L (1992) Investigations regarding the storage of carbon dioxide in aquifers in the netherlands. *Energ Convers Manage* 33(5-8), 611-618. [http://doi.org/10.1016/0196-8904\(92\)90063-3](http://doi.org/10.1016/0196-8904(92)90063-3)
8. Wang S, Jaffe PR (2004) Dissolution of a mineral phase in potable aquifers due to CO₂ releases from deep formations; effect of dissolution kinetics. *Energ Convers Manage* 45(18-19): 2833-2848. <http://doi.org/10.1016/j.enconman.2004.01.002>
9. Carroll S, Hao Y, Aines R (2009) Geochemical detection of carbon dioxide in dilute aquifers. *Geochem T.* <http://doi.org/10.1186/1467-4866-10-4>
10. Fahrner S, Schaefer D, Dahmke A (2011) Reactive transport modeling to assess geochemical monitoring for detection of CO₂ intrusion into shallow aquifers. *Energy Procedia* 4: 3155-3162. <http://doi.org/10.1016/j.egypro.2011.02.230>
11. Kharaka YK, Thordsen JJ, Kakouros E, Ambats G, Herkelrath WN, Beers SR, Birkholzer JT, Apps JA, Spycher NF, Zheng L (2010) Changes in the chemistry of shallow groundwater related to the 2008 injection of CO₂ at the ZERT field site, Bozeman, Montana. *Environ Earth Sci* 60(2): 273-284. <http://doi.org/10.1007/s12665-009-0401-1>
12. Keating EH, Fessenden J, Kanjorski N, Koning DJ, Pawar R (2010) The impact of CO₂ on shallow groundwater chemistry: observations at a natural analog site and implications for

- carbon sequestration. *Environ Earth Sci* 60(3): 521-536. <http://doi.org/10.1007/s12665-009-0192-4>
13. Keating EH, Hakala JA, Viswanathan H, Carey JW, Pawar R, Guthrie GD, Fessenden-Rahn J (2013) CO₂ leakage impacts on shallow groundwater: Field-scale reactive-transport simulations informed by observations at a natural analog site. *Appl Geochem* 30(Complete):136-147. <http://doi.org/10.1016/j.apgeochem.2012.08.007>
 14. Cheng K (2013) The impact of CO₂ leakage from reservoir on the water quality of the shallow aquifer. Dissertation, Jilin University, CN.
 15. Lu J, Partin JW, Hovorka SD, Wong C (2010) Potential risks to freshwater resources as a result of leakage from CO₂ geological storage: a batch-reaction experiment. *Environ Earth Sci* 60(2): 335-348. <http://doi.org/10.1007/s12665-009-0382-0>
 16. Little MG, Jackson RB (2011) Response to Comment on "Potential Impacts of Leakage from Deep CO₂ Geo-sequestration on Overlying Freshwater Aquifers". *Environ technol* 45(7):3175-6. <http://doi.org/10.1021/es200421f>
 17. Little MG, Jackson RB (2010) Potential impacts of leakage from deep CO₂ geo-sequestration on overlying freshwater aquifers. *Environ Sci Technol* 44: 9225-9232. <http://doi.org/10.1021/es102235w>
 18. Zhang L, Parthasarathy H, Karamalidis A (2016) Investigation on arsenopyrite dissolution and As(III) migration under geologic carbon storage conditions: A numerical simulation approach. *Greenh Gases*. <http://doi.org/10.1002/ghg.1651>
 19. Quattrocchi F, Barbieri M, Bencini R, Cinti D, Durocher K, Galli G (2005) Strontium isotope (⁸⁷Sr/⁸⁶Sr) chemistry in produced oilfield waters: the Ica Weyburn CO₂ monitoring and storage project. *Greenh Gas control Technol*, 65, 2111-2114. http://doi.org/10.1007/1-4020-4471-2_20
 20. Newell DL, Larson TE, Perkins G, Pugh JD, Stewart BW, Capo RC, Trautz RC (2014) Tracing CO₂ leakage into groundwater using carbon and strontium isotopes during a controlled CO₂ release field test. *Int J Greenh Gas Con* 29, 200-208. <http://doi.org/10.1016/j.ijggc.2014.08.015>
 21. Kim J, Lee S, Ha S, Joun W, Ju YJ, Lee K (2020) Natural ²²²Rn as a tracer of mixing and volatilization in a shallow aquifer during a CO₂ injection experiment. *Hydrol Process*. <http://doi.org/10.1002/hyp.13953>
 22. Gardiner JB, Capo R C, Newell DL, Stewart BW, Hakala JA (2021), Tracking natural CO₂ migration through a sandstone aquifer using Sr, U and C isotopes: Chimayó, New Mexico, USA. *Int J Greenh Gas Con* 104, 103209. <http://doi.org/10.1016/j.ijggc.2020.103209>
 23. Xu TF, Sonnenthal E, Spycher N, Pruess K (2006) TOUGHREACT-A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: Applications to geothermal injectivity and CO₂ geological sequestration. *Comput Geosci-UK* 32(2): 145-165. <http://doi.org/10.1016/j.cageo.2005.06.014>
 24. Xu TF (2001). Modeling multiphase non-isothermal fluid flow and reactive geochemical transport in variably saturated fractured rocks: 1. Methodology. *AM J Sci* 301(1):16-33. <http://doi.org/10.2475/ajs.301.1.16>
 25. Xu TF, Sonnenthal E, Spycher N, Zheng LG (2014) TOUGHREACT V3.0-OMP Sample Problems. Earth Sciences Division, Lawrence Berkeley National Laboratory University of California, Berkeley, CA, 94720.
 26. Pruess K, Oldenburg C, Moridis G (1999) TOUGH2 User's Guide, Version 2.0. LBL-43134,

Lawrence Berkeley National Laboratory, Berkeley, CA.

27. Pruess K, Garcia J, Kovscek T, Oldenburg C, Rutqvist J, Steefel C, Xu T (2004) Code intercomparison builds confidence in numerical simulation models for geologic disposal of CO₂. *Energy* 29(9/10), p.1431-1444. <http://doi.org/10.1016/j.energy.2004.03.077>
28. Xu TF, Pruess K (2010) Reactive Transport Modeling to Study Fluid-Rock Interactions in Enhanced Geothermal Systems (EGS) with CO₂ as Working Fluid. *Proceedings World Geothermal Congress 2010, Bali, Indonesia*, pp25-29.
29. Genuchten V, Th. M (1980) A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *J AM Soil Sci Soc* 44(5): 892–898. <http://doi.org/10.2136/sssaj1980.03615995004400050002x>
30. Corey AT (1954) The interrelation between gas and oil relative permeabilities. *Prod Mon* 38-41.
31. Xu TF, Kharaka YK, Doughty C, Freifeld BM, Daley TM (2010) Reactive transport modeling to study changes in water chemistry induced by CO₂ injection at the Frio-I Brine Pilot. *Chem geol* 271(3-4): 0-164. <http://doi.org/10.1016/j.chemgeo.2010.01.006>
32. Lasaga AC, Soler JM, Ganor J, Burch TE, Nagy KL (1994) Chemical weathering rates and global geochemical cycles. *Geochim Cosmochim Acta* 58:2361-2368. [http://doi.org/10.1016/0016-7037\(94\)90016-7](http://doi.org/10.1016/0016-7037(94)90016-7)

Figures

Figure 1

Spatial distribution of CO2 gas saturation

Figure 2

Spatial distribution of dissolved CO₂

(a) CO₂ gas saturation

(b) CO₂(aq)

Figure 3

Change in CO₂ concentration at the leaking point over time

Figure 4

Spatial distribution of pH

Figure 5

Spatial distribution of porosity

Figure 6
 Changes in pH and porosity at the leaking point over time

Figure 7
 Changes in mineral volume fraction (Note: negative value represents mineral dissolution, positive value represents mineral precipitation)

Figure 8

changes in ion concentration at the leaking point over time

Figure 9

CO₂ geological storage safety monitoring indicators