Potential Chemical Impacts of CO₂ Leakage on Underground Source of Drinking Water Assessed by Quantitative Risk Analysis

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Abstract

Many geologic carbon storage site options include not only excellent storage reservoirs bounded by effective seal layers, but also Underground Sources of Drinking Water (USDWs). An effective risk assessment and mitigation plan provides maximum protection for USDWs, to respect not only current policy but also to accommodate likely future USDW-specific regulatory protections. The goal of this study is to quantify possible risks to USDWs, specifically risks associated with chemical impacts on USDWs. Reactive transport models involve tremendous computational expense. Therefore, a secondary purpose of this study is to develop, calibrate and test reduced order models specifically for assessing risks of USDW chemical impacts by CO₂ leakage from a storage reservoir. In order to achieve these goals, a geochemical model was developed to interpret changes in water chemistry following CO₂ intrusion. A response surface methodology (RSM) based on these geochemical simulations was used to quantify associated risks. The case study example for this analysis is the Ogallala aquifer overlying the Farnsworth unit (FWU), an active commercial-scale CO₂-enhanced oil recovery field. Specific objectives of this study include: (1) to understand how CO₂ leakage is likely to influence geochemical processes in aquifer sediments; (2) to quantify potential risks to the Ogallala groundwater aquifer due to CO₂ leakage from the FWU oil reservoir; and (3) to identify water chemistry factors for early detection criteria.

Results indicate that the leakage rate would most likely range between 10^{-14} – 10^{-10} kg/(m²·year) for typical and likely leakage pathway permeability ranges. Within this range of CO₂ leakage rate, groundwater quality is not likely to be significantly impacted. The worst-case scenario yields trace metal concentrations approximately twice as much as the initial value, but these predicted concentrations are still less than one-fifth of regulation-stipulated maximum contamination levels and do not exceed the no-impact thresholds. Finally, the results of this analysis suggest that pH may be an effective geochemical indicator of CO₂ leakage.

1. Introduction

Enhanced Oil Recovery (EOR) with CO₂ (CO₂-EOR) offers the potential economic benefit of increased oil production, which may offset some costs of CO₂ capture and storage (IPCC, 2005). Most CO₂-EOR sites are overlain by groundwater aquifers (DOE/NETL, 2010; USGS Map of the Principal Aquifers of the United States: <http://water.usgs.gov/ogw/aquifer/map.html>). Although the possibility of CO₂ leakage from a sequestration site is very low (Bachu and Watson, 2009; Gaus, 2010), regulatory policy generally includes protections against CO₂ leakage to potable aquifers through wellbores or faults, including water quality impacts by acidification and trace metal mobilization (Gaus, 2010; IPCC, 2005). Multiple environmental variables such as aquifer geology, mineralogy, and groundwater chemistry also play an important role in controlling groundwater quality (Bacon et al., 2014, 2015; Dai et al., 2014a, 2014c; Frye et al., 2012; Wilkin and Diguilio, 2010). These geological variables suggest site-specific, quantitative risk assessment is essential for safe and effective application of carbon sequestration (Wilkin and Diguilio, 2010) and early leak detection criteria (Little and Jackson, 2010). To date, most research on assessment of chemical impact risks (from CO₂ leakage) rely on lab-scale and small, short-term site-scale experiments to obtain early detection of aquifer quality changes in non-storage formations (Frye et al., 2012; Little and Jackson, 2010; Lu et al., 2010; Qafoku et al., 2013; Viswanathan et al., 2012; Wells et al., 2007; Yang et

al., 2014; Zheng et al., 2012, 2015). However, uncertainty analysis with numerical simulations becomes a key tool for forecasting long-term groundwater quality changes by CO₂ leakage.

In this study, a response surface methodology (RSM) was conducted to quantify uncertainty and risks. Response surface methods are statistical and mathematical techniques used for developing, improving, and optimizing model building and model exploitation (Box and Draper, 1987; Myers and Montgomery, 1995). Such RSM is becoming more widely used than computationally-expensive and time-intensive processes of “traditional” risk and uncertainty analysis methods (e.g. the basic Monte Carlo method). The National Risk Assessment Partnership (NRAP) is pioneering application of RSM specifically for geologic carbon sequestration (Carroll et al., 2014; Dai et al., 2014b, Pawar et al., 2014). For example, Dai et al. (2014b) developed a generic integrated framework for optimizing CO₂ sequestration with RSM. Results suggest that, in order to maximize both oil production and CO₂ injection, the distance between injection and production wells should approach 300 m. Additionally, the best value of water alternating gas (WAG) ratio should be 5-6.5. Other recent work detailing RSM, as applied in carbon sequestration research, includes Rohmer and Bouc (2010) and Li and Zhang (2014).

An active CO₂-EOR field was selected for this study, the Farnsworth Unit (FWU) in Ochiltree County, Texas (Fig. 1), operated by Chaparral Energy, L.L.C. (CELLC). The FWU site is the subject of the Southwest Regional Partnership on Carbon Sequestration (SWP) Phase III, a program sponsored and facilitated by the U.S. Department of Energy and its National Energy Technology Laboratory. The FWU includes an overlying underground source of drinking water (USDW) aquifer, the Ogallala formation, located in the northern Anadarko basin. For this site, our primary goal is to quantify potential risks to groundwater quality due to CO₂ leakage through wellbores. We selected the FWU for case study because: (1) there are considerable brine/water and mineralogy data available for both the FWU and the Ogallala aquifer; and (2) the Ogallala aquifer is one of the largest USDWs in North America (George et al., 2011), which represents a typical drinking water resource in the USA. The main objectives of this study include: (1) to understand how CO₂ leakage is likely to influence geochemical processes in aquifer sediments; (2) to quantify potential risks to the Ogallala groundwater aquifer associated with changes in groundwater chemistry due to CO₂ leakage from the FWU; and (3) to identify water chemistry components as indicators for early detection criteria.

This study is organized into three parts: (1) cement hydration simulations, to obtain the equilibrium composition of wellbore fluids with wellbore cements; (2) quantification of the possible range of CO₂ leakage rates from the FWU reservoir through wellbore fractures (using typical and likely permeability ranges) to the overlying USDW; and (3) quantification of potential risks to Ogallala groundwater quality due to CO₂ leakage.

Fig. 1. The Farnsworth Unit.

2. Methods

To analyze potential impacts of CO₂ on the water quality of a USDW, a series of numerical simulations was conducted. Simulation of cement hydration provides associated wellbore cement components, which are major reactants that consume CO₂ through a leakage pathway such as a fissure. Results were then used to determine the possible extent/rate of CO₂ leakage flux through the wellbore cement. Simulation of CO₂ leakage flux through wellbores suggests possible leakage rates as well as the likely probability distribution exhibited by the data. Finally, the forecasted range of CO₂ leakage fluxes was used for RSM-based quantification of risks associated with CO₂ leakage into the Ogallala formation in this case study.

2.1. Response surface methodology

Stages in the application of RSM employed in this study include: (1) determining major independent parameters and experimental design; (2) conducting numerical experiments according to the selected experimental matrix with verification of the RSM model equation; and (3) obtaining the response surface model and conducting further analysis (e.g. determination of early detection indicators).

Choosing of experimental design has a large influence on the accuracy of the approximation of the response surface. Common designs include the full three-level factorial design, central composite design, and Box-Behnken design (Bezerra et al., 2008). These are widely used for symmetrical second-order experiments (Fig. 2). In this study, the Box-Behnken design was applied because of its mathematical efficiency.

Fig. 2. Symmetrical second-order experimental designs: (a) full three-level factorial design; (b) central composite design; and (c) Box-Behnken design (Adopted from Bezerra et al., 2008).

The model equation is defined with a polynomial function,

$$\eta = f(x_1, x_2, \dots, x_n) + \varepsilon,$$

where η is the response, f is the function of response, $x_1, x_2, \dots, x_n$ are the independent parameters, n is the number of the independent parameters, and ε is the statistical error.

The units and/or ranges are usually different in the experimental domain, thus potentially having different levels of effects for the response. To overcome uneven impacts and render the units of the parameters irrelevant to responses, the parameters are normalized to the range from -1 to 1. Usually the equation of normalization is written as

$$X = \frac{x - (x_{max} + x_{min})/2}{(x_{max} - x_{min})/2},$$

where X is the normalized parameter, x is the natural variable, and x_{max} and x_{min} are maximum and minimum values of the natural variables.

To account for and quantify curvature, usually a second-order equation is used for RSM, written as

$$y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i < j} \beta_{ij} X_i X_j + \sum_{i=1}^n \beta_{ii} X_i^2 + \varepsilon,$$

where $\beta_0, \beta_i, \beta_{ij}$, and β_{ii} represent the regression coefficients of constant, linear, interaction, and quadratic terms, respectively; X_i and X_j are normalized independent parameters.

The matrix notion of this model is written as

$$\begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_k \end{bmatrix} = \begin{bmatrix} 1 & X_{11} & X_{12} & \dots & X_{1n} \\ 1 & X_{21} & X_{22} & \dots & X_{2n} \\ \vdots & \vdots & \vdots & \dots & \vdots \\ 1 & X_{k1} & X_{k2} & \dots & X_{kn} \end{bmatrix} \begin{bmatrix} \beta_0 \\ \beta_1 \\ \vdots \\ \beta_n \end{bmatrix} + \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \vdots \\ \varepsilon_k \end{bmatrix} \text{ or } = X\beta + \varepsilon.$$

The regression coefficient β is solved by using the method of least squares (MLS), which assumes errors are random, independent of each other, and profile with a zero mean and a common unknown variance; β should minimize the sum of the squares of the errors (SSE), or

$$\varepsilon = y - \hat{y} = y - X\beta,$$

$$SSE = \sum_{i=1}^n \varepsilon_i^2 = \varepsilon^T \varepsilon = (y - X\beta)^T (y - X\beta),$$

where y is the observed value and $\hat{y}$ is the fitted value. The derivative of SSE may be used to yield β , or

$$\frac{\partial}{\partial \beta} (SSE) = -2X^T (y - X\beta) = 0 \Rightarrow \beta = (X^T X)^{-1} X^T y.$$

After the regression coefficients are obtained, model adequacy may be evaluated by several techniques.

Usually, coefficient of determination R^2 ($R^2 = 1 - \frac{\sum (y_i - \hat{y}_i)^2}{\sum (y_i - \bar{y})^2}$, $\bar{y} = \frac{1}{n} \sum y_i$), and/or coefficient of variation

of the root mean square error ($CVRMSE = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{n}} / \bar{y}$) are used to check how well the model fits with the observed data.

2.2. Simulation of cement hydration

Wells in the FWU are completed with Portland cement. When the cement mixes with water, it starts hydration with chemical reactions, and causes microstructure formations to form a harder structure (Li, 2011; Mehta and Monteiro, 2014). Chemical reactions during hydration involve:

(1) Hydration of aluminates:

where Al^{3+} in ettringite and monosulfate can also be substituted by Fe^{3+} (Taylor, 1997);

(2) Hydration of the silicates:

where *CSH* doesn't have a confirmed formula, and the ratio of *Ca/Si* of *CSH* varies. It is the primary binding material of the cement. Saturated *CSH* has the approximate formula $(CaO)_{1.7} \cdot SiO_2 \cdot (H_2O)_4$ (Baur et al., 2004);

(3) Hydration of ferrite:

The major cement component that reacts with CO_2 is portlandite ($Ca(OH)_2$):

Most of the reactions take place during a few hours and release a significant amount of heat. After a few days, the chemical reactions and hardening rates decelerate. However, hydration processes may take decades to reach an equilibrium state. To predict the equilibrium wellbore cement composition for the field environment, a batch simulation of cement hydration was conducted with an arbitrary and lengthy time period of 100 years. To avoid vigorous chemical reactions and heat release during the initial several hours, the initial Portland cement composition for this simulation (Table 1) was adopted from Scrivener et al. (2011), and specifically their cement hydration experimental results at the end of the 1st day. Water chemistry was adapted from the average brine chemistry data of the FWU reservoir, which was conducted by the New Mexico Institute of Mining and Technology, part of SWP Phase III.

Table 1 Initial mineral composition of cement hydration simulation (Scrivener et al., 2004).

Name	Volume fraction: %	Name	Volume fraction: %
Alite	19.8	Belite	7.5
Ferrite	5.6	Aluminate	2.7
Portlandite	17.8	Ettringite	7.0
CSH	35.0		

2.3. Simulation of CO_2 leakage flux through wellbores

To assess the most likely value of CO_2 leakage rate through wellbore fractures, a vertical 1-D simulation was conducted over a time period of 100 years. The resulting mineralogy of the cement hydration batch model was then utilized for subsequent simulations. Based on the sizes of wells in the FWU, the diameter of the simulated well was set as 17 cm, and the thickness of the wellbore was assigned 2.5 cm. The bottom of the reservoir was assigned at 3,000 m depth, and the thickness was assigned 30 m. The overlying aquifer was assigned a thickness of 100 m, and the upper surface boundary was assigned atmospheric pressure. Hydrostatic pressure was set as the initial pressure of the domain, and the initial temperature was set as 20 °C at the top of the domain with a 25 °C/km gradient. Hydrogeological and geochemical parameters of the reservoir were assigned using monitoring/characterization data as much as was possible. Cement permeability was set based on results of previous studies by Bachu and Bennion (2009) and Rimmelé et al. (2008). The Ogallala USDW formation is a typical sand aquifer, and its hydrogeological parameters (i.e. porosity and permeability) were assigned based on its sand properties (Cronin, 1969). The initial chemical parameters were assigned according to monitoring data from the Ogallala formation. A dual permeability domain was utilized for fracture and matrix flow, implemented using the multiple interacting continua (MINC) in the TOUGH2 code (Pruess et al., 2012) for simulation

of micro fractures within the cement casing. The major hydrogeological parameters are summarized in Table 2. Saturation of CO₂ and reservoir pressure were chosen as independent parameters, given that the FWU is an active oil production field. It is widely believed that wells used for CO₂ injection would pose less risk because of frequent attention and care (Bachu and Watson, 2009), but micro fractures/cracks can occur when the wells are in use (Bachu and Bennion, 2009). Consequently, wellbore fractures proportion was chosen as another uncertainty parameter. A selected range of these independent uncertainty parameters are summarized in Table 3. The uncertainties of leakage flux were quantified by RSM on the basis of these three parameters.

Table 2 Hydrogeological parameters.

Property	Value	Property	Value
Reservoir (Morrow)		USDW aquifer	
Thickness	30 m	Thickness	100 m
Permeability	$4.52 \times 10^{-14} \text{ m}^2$	Permeability	$5.0 \times 10^{-13} \text{ m}^2$
Porosity	0.1453	Porosity	0.30
Rock density	2650 kg/m ³	Rock density	2600 kg/m ³
Salinity	6%	Salinity	0.35%
Cement		Fracture	
Permeability	$5.0 \times 10^{-20} \text{ m}^2$ *	Permeability	$1.0 \times 10^{-14} \text{ m}^2$ *
Porosity	0.08 **	Porosity	0.40 **
Rock density	2400 kg/m ³	Rock density	2400 kg/m ³

* Bachu and Bennion, 2009

** Rimmelé et al., 2008

Table 3 Independent parameters for CO₂ leaking rate simulation.

Parameter name	Low (-1)	Mid (0)	High (+1)	Distribution
CO ₂ saturation	0.1	0.5	0.9	Uniform
Reservoir pressure: bar	300	325	350	Uniform
Wellbore fracture proportion	0.01	0.055	0.10	Uniform

2.4. Quantification of risks associated with CO₂ leakage into the Ogallala formation

2.4.1. Model domain and assumptions

A 2-D radial model was assembled and simulated to analyze the potential risks to groundwater quality due to CO₂ leakage (Fig. 3). Regional groundwater flow may dilute potential contaminants, but this was neglected for simplicity in this study, because regional flow velocities in this basin that are maximum ~10 m/year (Nativ and Smith, 1987) is not significant for our simulations to achieve such dilution. In the initial simulation step to quantify CO₂ leakage rate, all simulations assumed that CO₂ dissolves in water instantly when it was injected with gaseous CO₂ injected into the system at a constant rate. Water chemistry results in the Ogallala aquifer were examined for a simulated time duration of 200 years. Based on more than 100 fresh-water well drilling records on/near the FWU (TWDB database), the thickness of the aquifer was assigned 100 m, and the bottom depth was set as 150 m. The distance between monitoring wells of the FWU is around 1,000 m; consequently, the dimension of the model was set as 1,000 m × 100 m with a total of 230 grid cells. A regression model was created with RSM to assess the impacts to the Ogallala USDW aquifer. Permeability, CO₂ leakage rate, cation exchange capacity (CEC) and absorbent specific surface area (SSA) were chosen as independent parameters (Table 4). The range of CO₂ leakage rate was determined by the results of the previous section, the permeability range was assigned according to typical sand measurements (Beard and Weyl, 1973). Additionally, the ranges of the remaining two parameters are discussed in section 2.4.3.

Fig. 3. Simplified conceptual model.

Table 4 Independent parameters for simulations of CO₂ leaking into USDW aquifer.

Parameter name	Low (-1)	Mid (0)	High (+1)	Distribution
Permeability: m ²	10 ⁻¹⁴	10 ⁻¹³	10 ⁻¹²	Lognormal
Leaking rate: kg/(s·m ²)	10 ⁻²¹	10 ⁻¹⁹	10 ⁻¹⁷	Lognormal
CEC: meq/100g	1	6.5	12	Uniform
Absorbent SSA: m ² /g	1	50.5	100	Uniform

2.4.2. Model parameters and boundary conditions

A constant temperature of 25 °C and hydrostatic pressure were assigned as initial conditions. A homogeneous porosity value of 0.3 was used, and heterogeneity neglected (Beard and Weyl, 1973). The initial water chemistry was based on the average composition of more than 100 water analyses of FWU groundwater samples (Table 5), which was conducted by the New Mexico Institute of Mining and Technology, part of SWP Phase III. For the water indexes not available with the water samples, their values were adopted from Hopkins (1993). Total dissolved solids (TDS) was calculated by the sum of concentrations of all ions included and resulting in the simulations.

Table 5 Initial water chemistry of the Ogallala aquifer.

Name	Concentration (mg/L)	Balanced Concentration (mol/kg)	Name	Concentration (mg/L)	Balanced Concentration (mol/kg)
H ⁺	pH 7.73	10 ^{-7.52}	Ca ²⁺	51.8	1.04 × 10 ⁻³
Mg ²⁺	29.8	1.14 × 10 ⁻³	Na ⁺	47.9	2.07 × 10 ⁻³
K ⁺	5.55	1.42 × 10 ⁻⁴	Fe ²⁺	2.00 × 10 ^{-3*}	1.49 × 10 ⁻⁸
SiO ₂ (aq)	18.6 (as Si)	6.65 × 10 ⁻⁴	HCO ₃ ⁻	263*	3.70 × 10 ⁻³
NO ₃ ⁻	15.2	2.45 × 10 ⁻⁴	SO ₄ ²⁻	58.9	5.22 × 10 ⁻⁴
Cl ⁻	60.7	1.71 × 10 ⁻³	AlO ₂ ⁻	1.00 × 10 ⁻³ (as Al ³⁺)	2.05 × 10 ⁻¹⁰
H ₂ AsO ₄ ⁻	2.40 × 10 ⁻³ (as As)	3.41 × 10 ⁻⁹	Ba ²⁺	7.20 × 10 ⁻²	5.12 × 10 ⁻⁷
Cd ²⁺	3.44 × 10 ⁻⁵	2.18 × 10 ⁻¹⁰	Cr(OH) ₂ ⁺	2.00 × 10 ⁻³ (as Cr)	3.28 × 10 ⁻⁸
Pb ²⁺	8.70 × 10 ⁻⁴	2.78 × 10 ⁻⁹	Cu ²⁺	1.40 × 10 ⁻²	9.19 × 10 ⁻⁸
F ⁻	1.73	9.12 × 10 ⁻⁵	HSeO ₃ ⁻	3.00 × 10 ⁻³ (as Se)	1.10 × 10 ⁻⁸
Ag ⁺	3.61 × 10 ⁻⁵	8.78 × 10 ⁻¹¹	Mn ²⁺	7.70 × 10 ⁻³	1.17 × 10 ⁻⁷
Zn ²⁺	4.50 × 10 ⁻¹	5.03 × 10 ⁻⁶	ORP	437 mV	
TDS	570	548 mg/L	O ₂ (aq)	--	1.48 × 10 ⁻⁴⁰

* Hopkins, 1993

Selected maximum contaminant levels (MCLs) of drinking water contaminants by Texas and the U.S. E.P.A. (Environmental Protection Agency) are listed in Table 6. All element concentrations except Se do not exceed the Texas MCL; Se does not exceed the EPA standard. TDS exceeds EPA MCL values but not the Texas MCL; NO₃⁻, As and Mn are more than 1/10 of the standard value. Former studies suggest that pH is an important indicator for CO₂ intrusion in groundwater. Therefore, this study considered TDS, nitrate, As, Se, Mn and pH as potential water contaminants. The initial dissolved oxygen was calculated

using the oxidation reduction potential (ORP) value. A water-mineral equilibrium condition was obtained by performing the simulation without any injection for 100 years (Table 5). The initial mineralogy was set up based on geological data of the High plains aquifer (Qafoku et al., 2013), shown in Table 7. The radius of mineral grain was set to 1 mm, according to the results of our size distribution tests for the Ogallala sand samples. Specific surface area (SSA) of each mineral was calculated by $SSA = A \cdot v / (V \cdot MW)$, where A is sphere area, v is molar volume, V is sphere volume, and MW is molecular weight (Labus and Bujok, 2011). Molar volume and molecular weight were obtained from EQ3/6 database (Wolery, 1992).

Table 6 Selected MCLs for inorganic contaminants of Texas and EPA

Name	Texas (mg/L)	EPA (mg/L)	Name	Texas (mg/L)	EPA (mg/L)
NO ₃ ⁻	10 (as N)	10 (as N)	pH	>7.0 (unitless)	6.5-8.5 (unitless)
As	0.01	0.01	Mn	0.05	0.05
Se	0.002	0.05	TDS	1000	500
Cd	0.005	0.005	Al	0.05 to 0.2	0.05 to 0.2
Cr	0.1	0.1	SO ₄ ²⁻	300	250

2.4.3. Chemical reactions

Previous analyses suggest that cation exchange capacity (CEC) and sorption processes with dissolution of carbonates might be the main factors driving the geochemical response to CO₂ injection (Zheng et al., 2012). Aqueous complexation, cation exchange, adsorption/ desorption and mineral dissolution/precipitation were considered for chemical reactions. The thermodynamic parameters for aqueous and mineral reactions were taken from the EQ3/6 database (Wolery, 1992). The parameters for the kinetic rate law of minerals were taken from Palandri and Kharaka (2004). For minerals not include in these sources, the kinetic parameters were assumed to be the same as similar minerals in the same category (Table 7).

Table 7 List of initial mineral abundance and possible secondary mineral phases

Mineral	Volume fraction (% of solid)	Reactive SSA (cm ² /g)	Kinetic rate law							
			Neutral		Acid			Base		
			k25 (mol/(m2·s))	Ea (kJ/mol)	k25	Ea	n (H ⁺)	k25	Ea	n (H ⁺)
Primary										
Quartz	60.9	11.328	1.259 × 10 ⁻¹⁴	87.5						
Calcite	5.0	11.071	1.600 × 10 ⁻⁶	23.5	0.501	14.4	1.0			
Kaolinite	8.5	11.565	6.918 × 10 ⁻¹⁴	22.2	4.898 × 10 ⁻¹²	65.9	0.777	8.912 × 10 ⁻¹⁸	17.9	-0.472
K-feldspar	23.0	11.735	3.890 × 10 ⁻¹³	38.0	8.710 × 10 ⁻¹¹	51.7	0.5			
Muscovite	2.5	10.598	3.020 × 10 ⁻¹³	22.0	7.762 × 10 ⁻¹²	22.0	0.5			
Fe(OH) ₃ (HFO)	0.1	9.646	1.000 × 10 ⁻¹¹	61.2						
Secondary										
Illite	0.0	10.858	1.660 × 10 ⁻¹³	35.0	1.047 × 10 ⁻¹¹	23.6	0.34	3.020 × 10 ⁻¹⁷	58.9	-0.40
Smectite-Na	0.0	10.854	1.660 × 10 ⁻¹³	35.0	1.047 × 10 ⁻¹¹	23.6	0.34	3.020 × 10 ⁻¹⁷	58.9	-0.40
Smectite-Ca	0.0	10.880	1.660 × 10 ⁻¹³	35.0	1.047 × 10 ⁻¹¹	23.6	0.34	3.020 × 10 ⁻¹⁷	58.9	-0.40
Dolomite	0.0	10.471	2.951 × 10 ⁻⁸	52.2	6.456 × 10 ⁻⁴	36.1	0.5			
Greenrust	0.0	13.483	1.500 × 10 ⁻⁹	73.0						
Goethite	0.0	7.030	1.148 × 10 ⁻⁸	86.5						

For adsorption/desorption reactions, the Gouy-Chapman double diffuse layer model was used (Smith, 1999). Hydrrous ferric oxide (HFO) was assumed to be the sorbent, because it is a widely existing mineral as a sorbent in shallow natural systems, with the approximate formula Fe(OH)₃ used in this model. Constants and sorbent properties were taken from Dzombak and Morel (1990), with the strong site density 9.0×10^{-8} mol sites/m², and the weak site density 3.0×10^{-6} mol sites/m². Adsorption/desorption reactions are controlled by the total amount of sorption sites (product of amount of sorbent and sorbent SSA). The model sensitivity to the total amount of sorbent sites could be evaluated by varying one of these parameters (Zheng et al., 2012). Sorbent fraction of the total mineral volume was assigned at 0.1%, and sorbent SSA was treated as an independent uncertainty parameter. Pure sorbent SSA is 600 m²/g; yet the actual (Ogallala) value is far less. Based on tests of Fe concentrated clay surface areas (Fontes and Weed, 1996) and BET surface area tests for our Ogallala sand samples, 1 – 100 m²/g sorbent SSA was used in our study. Adsorption/desorption reactions considered in this study are shown in Table 8.

Table 8 Surface complexation reactions and surface complexation constants on HFO

Surface complexation reaction	logK
$\text{HFO_sOH} + \text{H}^+ = \text{HFO_sOH}_2^+$	7.29
$\text{HFO_wOH} + \text{H}^+ = \text{HFO_wOH}_2^+$	7.29
$\text{HFO_sOH} = \text{HFO_sO}^- + \text{H}^+$	-8.93
$\text{HFO_wOH} = \text{HFO_wO}^- + \text{H}^+$	-8.93
$\text{HFO_sOH} + \text{SO}_4^{2-} + \text{H}^+ = \text{HFO_sSO}_4^- + \text{H}_2\text{O}$	7.78
$\text{HFO_wOH} + \text{SO}_4^{2-} + \text{H}^+ = \text{HFO_wSO}_4^- + \text{H}_2\text{O}$	7.78
$\text{HFO_sOH} + \text{SO}_4^{2-} = \text{HFO_sOHSO}_4^{2-}$	0.79
$\text{HFO_wOH} + \text{SO}_4^{2-} = \text{HFO_wOHSO}_4^{2-}$	0.79
$\text{HFO_sOH} + \text{Ag}^+ = \text{HFO_sOAg} + \text{H}^+$	-1.72
$\text{HFO_wOH} + \text{Ag}^+ = \text{HFO_wOAg} + \text{H}^+$	-5.3
$\text{HFO_sOH} + \text{Cd}^{2+} = \text{HFO_sOCd}^+ + \text{H}^+$	0.47
$\text{HFO_wOH} + \text{Cd}^{2+} = \text{HFO_wOCd}^+ + \text{H}^+$	-2.91
$\text{HFO_sOH} + \text{HSeO}_3^- = \text{HFO_sSeO}_3^- + \text{H}_2\text{O}$	4.29
$\text{HFO_wOH} + \text{HSeO}_3^- = \text{HFO_wSeO}_3^- + \text{H}_2\text{O}$	4.29
$\text{HFO_sOH} + \text{H}_2\text{AsO}_4^- + \text{H}^+ = \text{HFO_sH}_2\text{AsO}_4 + \text{H}_2\text{O}$	10.17
$\text{HFO_wOH} + \text{H}_2\text{AsO}_4^- + \text{H}^+ = \text{HFO_wH}_2\text{AsO}_4 + \text{H}_2\text{O}$	10.17
$\text{HFO_sOH} + \text{Fe}^{2+} = \text{HFO_sOFe}^+ + \text{H}^+$	-0.95
$\text{HFO_wOH} + \text{Fe}^{2+} = \text{HFO_wOFe}^+ + \text{H}^+$	-2.98
$\text{HFO_wOH} + \text{Fe}^{2+} + \text{H}_2\text{O} = \text{HFO_wOFe(OH)} + 2\text{H}^+$	-11.55
$\text{HFO_sOH} + \text{Cu}^{2+} = \text{HFO_sOCu}^+ + \text{H}^+$	2.43
$\text{HFO_wOH} + \text{Cu}^{2+} = \text{HFO_wOCu}^+ + \text{H}^+$	0.14
$\text{HFO_sOH} + \text{Cr(OH)}_2^+ = \text{HFO_sOCr(OH)}^+ + \text{H}_2\text{O}$	11.63
$\text{HFO_sOH} + \text{CrO}_4^{2-} + \text{H}^+ = \text{HFO_sCrO}_4^- + \text{H}_2\text{O}$	10.85
$\text{HFO_wOH} + \text{CrO}_4^{2-} + \text{H}^+ = \text{HFO_wCrO}_4^- + \text{H}_2\text{O}$	10.85
$\text{HFO_sOH} + \text{CrO}_4^{2-} = \text{HFO_sOHCrO}_4^{2-}$	3.9
$\text{HFO_wOH} + \text{CrO}_4^{2-} = \text{HFO_wOHCrO}_4^{2-}$	3.9
$\text{HFO_sOH} + \text{Mn}^{2+} = \text{HFO_sOMn}^+ + \text{H}^+$	-0.4
$\text{HFO_wOH} + \text{Mn}^{2+} = \text{HFO_wOMn}^+ + \text{H}^+$	-3.5
$\text{HFO_sOH} + \text{Pb}^{2+} = \text{HFO_sOPb}^+ + \text{H}^+$	4.65
$\text{HFO_wOH} + \text{Pb}^{2+} = \text{HFO_wOPb}^+ + \text{H}^+$	0.3
$\text{HFO_sOH} + \text{Zn}^{2+} = \text{HFO_sOZn}^+ + \text{H}^+$	0.99
$\text{HFO_wOH} + \text{Zn}^{2+} = \text{HFO_wOZn}^+ + \text{H}^+$	-1.99
$\text{HFO_sOH} + \text{Ca}^{2+} = \text{HFO_wOHCa}^{2+}$	4.97
$\text{HFO_wOH} + \text{Ca}^{2+} = \text{HFO_wOCa}^+ + \text{H}^+$	-5.85
$\text{HFO_wOH} + \text{Mg}^{2+} = \text{HFO_wOMg}^+ + \text{H}^+$	-4.60

The CEC of a sediment could often be considered constant (Appelo and Postma, 1994). However, no measured data of the Ogallala formation overlying FWU is available, so CEC was treated as an uncertainty independent parameter. Based on CEC values for various minerals, 1 – 12 meq/100g was assigned for this study, which could cover typical values for sands (Ming and Dixon, 1987). The exchange reactions and their selectivity coefficients are shown in Table 9 (Appelo and Postma, 1994).

Table 9 Cation exchange reactions and selectivity coefficients

Equation: $\text{Na}^+ + 1/i \text{M-X}_i \longleftrightarrow \text{Na-X} + 1/i \text{M}^{i+}$ with $K_{\text{Na/M}} = [\text{Na-X}] [\text{M}^{i+}]^{1/i} / ([\text{M-X}_i]^{1/i} [\text{Na}^+])$					
Ion	$K_{\text{Na/M}}$	Ion	$K_{\text{Na/M}}$	Ion	$K_{\text{Na/M}}$
H^+	1	Mg^{2+}	0.5	Ca^{2+}	0.4
K^+	0.2	Fe^{2+}	0.6	Mn^{2+}	0.55
Cu^{2+}	0.5	Zn^{2+}	0.4	Pb^{2+}	0.3
Ba^{2+}	0.35	Cd^{2+}	0.4	Cr^{3+}	0.08

2.4. Simulation tool

All simulations were performed with TOUGHREACT V2 (Xu et al., 2012) and an equation of state for multiphase CO₂ and brine, ECO2N (Pruess, 2005). TOUGHREACT V2 is enhanced with surface complexation and cation exchange to compute the adsorption and ion exchange processes on mineral surfaces. Although ECO2N doesn't include a liquid CO₂ phase, the temperature and pressure conditions for the Ogallala suggest only supercritical and dissolved CO₂ phases can exist, indicating that ECO2N is appropriate for this study.

3. Results and discussion

3.1. Cement hydration

The solid phase changes during cement hydration are shown in Fig. 4. With the consumption of alite, belite, ferrite and aluminate, CSH, portlandite and ettringite precipitate as main products, and porosity decrease because of precipitation. These results are consistent with known cement hydration mechanisms (Li, 2011). The composition of cement become stable after 0.1 year, but there are still slight changes for decades of simulated time. Although CSH doesn't have a confirmed formula, in these simulations the average Ca/Si ratio is about 1.7, corresponding to former studies (Allen et al., 2007). Portlandite (Ca(OH)₂) as the major reactant with CO₂ in the wellbore makes up to 40% of the volume of the hydrated cement.

Fig. 4. Composition changes during cement hydration.

3.2. CO₂ leakage flux through wellbore

The simulated CO₂ leakage rate to the overlying groundwater formation (the Ogallala) during the 100 year time period was of particular interest. The correlation between the original (full reservoir model) simulated CO₂ leakage rates and RSM forecasted rates are above 0.95, which suggests that the RSM forecasts are sufficient. Additional results show that CO₂ leakage rate increase during the first year, but then it maintains a stable value for the remainder of the 100 years. Simulations indicate that no gaseous phase CO₂ leaks, instead only dissolved (aqueous) CO₂ enter the simulated Ogallala. Similar results were also found by Elison et al. (2012). With the relatively low permeability of wellbore cement, diffusion is assumed to be the main CO₂ leakage mechanism. For CO₂ leakage through wellbore cement obtained in this study, more than 95% is trapped by cement. Only 0.4 – 4.3% of CO₂ leaks into the USDW formation, at least for the prescribed fracture proportion, reservoir pressure and CO₂ saturation conditions. The cumulative distribution function (CDF) of log CO₂ leakage rate after 100 years fits a normal distribution curve with P value < 0.005 by the Anderson-Darling test (Fig. 5). More than 90% probability suggests that the leakage rate for the assigned hydrologic properties range between 10⁻²¹ – 10⁻¹⁷ kg/(m²·s), or about 10⁻¹⁴ – 10⁻¹⁰ kg/(m²·year). This leakage rate is far less than other estimations by former studies (Carroll et al., 2009, 2014; Elison et al., 2012). However, other studies assumed a much higher wellbore permeability (e.g. 10⁻¹⁴ – 10⁻¹⁰ m² used by Carroll et al., 2014) and leaky wells have been assumed to fully penetrate the

caprock and connect the storage reservoir and the shallow aquifer (Carroll et al., 2014). Under such conditions, convection would be dominant and result in a much higher leakage flux. If reactive transport within wellbore cement is not considered, CO₂ leakage is also likely to be overestimated – at least in the beginning stages of CO₂ intrusion before cement (portlandite) is consumed. Other studies also confirmed that wellbore cement plays an important role for preventing CO₂ leakage (Carey et al., 2007; Kutchko et al., 2008). Specifically, model simulations with higher permeability (homogeneous 10⁻¹⁴ m²) and without chemical reactions were also executed in this study. Gas phase CO₂ leakage breakthrough occurs much faster than that with chemical reactions, and leakage rate increases significantly up to as high as 10⁻⁶ kg/(m²·s), which is similar to the results of other studies. Generally, the model results suggest that these resulting small flux values are due to (1) the scenarios are for non-penetrated micro fractures that naturally occur in the wellbore cement; and (2) the reactions between CO₂ and portlandite (Ca(OH)₂) of wellbore cement largely consume CO₂. Note that although porosity decreases due to precipitation of CaCO₃, permeability is not considered to be reduced as well; these simulated flux reduction results found in this study are due only to CO₂ consumption by chemical reaction. The reduction in flux rate would be even greater if a permeability-porosity relationship (such as Kozeny-Carman relationships; Carman, 1956) were utilized. We are evaluating such permeability-porosity impacts in more detail in a separate study.

Fig. 5. CDF of CO₂ leakage rate after 100 year.

3.3. Risk assessments of CO₂ leakage into the Ogallala formation

3.3.1. Polynomial response surface model and validation of the equations

Generally, the coefficient of determination (R^2) between simulation results and the responses of the regression (RSM) model for all of the water indexes examined exceed 0.9, average values exceed 0.96, and the coefficient of variation of the root mean square error (CVRMSE) is no more than 10%, averaging less than 3% (Table 10). All trace metals (Mn, As, and Se) show similar R^2 and CVRMSE values, thus the table only shows Mn's model adequacy to represent the model adequacy for all trace metals. The high R^2 and low CVRMSE values (Table 10) suggest that the resulting trained ROMs sufficiently fit the original (full reservoir model) simulation outcomes, and the ROMs are adequate for predicting outcomes of interest for full-scaled (non-ROM) simulations within the given range.

To verify the adequacy of the regression models for all the cases in this experimental domain, a total of 50 randomized simulations were conducted. Each independent parameter ranged from -1 to +1, following their distributions. The correlation between simulated outcomes and regression models was calculated for all water indexes of interest. The R^2 and CVRMSE values between these two series of results are shown in Table 11. It shows a nearly linear correlation between simulation and ROM results with an R^2 value that exceeds 0.7 after one year, and exceeds 0.85 afterwards. In the first few years, all water indexes examined do not show significant changes due to CO₂ leakage, which could explain the lower values of R^2 for the first year's results. On the other hand, CVRMSE is no more than 1% for the results after one year, and averaged 5% over a 200 year period. Lower correlations between the response surface model

and the verification simulation results are observed for TDS, pH, N, Mn, As and Se, but the regression model can represent the full-scale simulation results with a high confidence level.

Table 10 Model adequacy between simulation results and ROM responses.

	Time, yr	1	10	50	100	200
TDS	R^2	0.990 ^{+0.008} _{-0.028}	0.993 ^{+0.006} _{-0.021}	0.994 ^{+0.006} _{-0.020}	0.993 ^{+0.006} _{-0.019}	0.993 ^{+0.007} _{-0.018}
	CVRMSE, %	0.013 ^{+0.039} _{-0.013}	0.129 ^{+0.385} _{-0.100}	0.635 ^{+1.787} _{-0.498}	1.267 ^{+3.716} _{-1.019}	2.553 ^{+7.659} _{-2.142}
pH	R^2	0.964 ^{+0.029} _{-0.032}	0.993 ^{+0.007} _{-0.021}	0.993 ^{+0.006} _{-0.021}	0.993 ^{+0.006} _{-0.020}	0.994 ^{+0.005} _{-0.018}
	CVRMSE, %	0.002 ^{+0.005} _{-0.002}	0.013 ^{+0.040} _{-0.010}	0.067 ^{+0.187} _{-0.049}	0.133 ^{+0.364} _{-0.100}	0.264 ^{+0.715} _{-0.191}
N	R^2	0.981 ^{+0.019} _{-0.029}	0.993 ^{+0.006} _{-0.021}	0.994 ^{+0.006} _{-0.020}	0.994 ^{+0.006} _{-0.019}	0.994 ^{+0.005} _{-0.016}
	CVRMSE, %	0.015 ^{+0.053} _{-0.015}	0.139 ^{+0.415} _{-0.109}	0.692 ^{+1.975} _{-0.538}	1.386 ^{+4.104} _{-1.130}	2.809 ^{+8.473} _{-2.401}
Mn	R^2	0.968 ^{+0.026} _{-0.031}	0.994 ^{+0.006} _{-0.021}	0.993 ^{+0.006} _{-0.020}	0.993 ^{+0.006} _{-0.019}	0.993 ^{+0.006} _{-0.018}
	CVRMSE, %	0.019 ^{+0.055} _{-0.019}	0.132 ^{+0.391} _{-0.095}	0.677 ^{+1.870} _{-0.489}	1.356 ^{+3.902} _{-0.995}	2.727 ^{+8.025} _{-2.101}

Table 11 Model adequacy between verification simulation results and ROM responses.

	Time, yr	1	10	50	100	200
TDS	R^2	0.833 ^{+0.028} _{-0.027}	0.878 ^{+0.031} _{-0.020}	0.881 ^{+0.035} _{-0.020}	0.881 ^{+0.037} _{-0.020}	0.883 ^{+0.039} _{-0.020}
	CVRMSE, %	0.028 ^{+0.034} _{-0.021}	0.274 ^{+0.356} _{-0.213}	1.332 ^{+1.725} _{-1.016}	2.608 ^{+3.341} _{-2.044}	5.004 ^{+6.152} _{-3.614}
pH	R^2	0.766 ^{+0.109} _{-0.043}	0.876 ^{+0.027} _{-0.019}	0.877 ^{+0.018} _{-0.025}	0.879 ^{+0.005} _{-0.044}	0.885 ^{+0.005} _{-0.008}
	CVRMSE, %	0.004 ^{+0.005} _{-0.004}	0.028 ^{+0.036} _{-0.021}	0.140 ^{+0.178} _{-0.106}	0.280 ^{+0.344} _{-0.221}	0.568 ^{+0.632} _{-0.388}
N	R^2	0.815 ^{+0.069} _{-0.029}	0.879 ^{+0.030} _{-0.020}	0.881 ^{+0.035} _{-0.020}	0.883 ^{+0.038} _{-0.020}	0.889 ^{+0.037} _{-0.018}
	CVRMSE, %	0.032 ^{+0.031} _{-0.024}	0.295 ^{+0.390} _{-0.230}	1.457 ^{+1.891} _{-1.125}	2.857 ^{+3.691} _{-2.243}	5.486 ^{+6.821} _{-3.964}
Mn	R^2	0.782 ^{+0.094} _{-0.031}	0.877 ^{+0.035} _{-0.020}	0.879 ^{+0.034} _{-0.020}	0.878 ^{+0.036} _{-0.020}	0.879 ^{+0.039} _{-0.020}
	CVRMSE, %	0.035 ^{+0.042} _{-0.025}	0.283 ^{+0.362} _{-0.212}	1.398 ^{+1.810} _{-1.072}	2.737 ^{+3.495} _{-2.144}	5.232 ^{+6.363} _{-3.708}

3.3.2. Risks of CO₂ leakage into the Ogallala formation (case study) and early detection criteria

For simulations of up to 50 years of CO₂ leakage, no significant changes in TDS, trace metals or pH resulted throughout the entire domain. However, after 100 years, the changes become more obvious. After 200 years, there is more than a 10% possibility that TDS exceeds 780 mg/L (initially 540 mg/L), approaching a 50% increase compared to the initial value (Fig. 6). pH ranges between 7.2 – 7.7 through the domain (initially 7.5), which is less than 10% different (Fig. 7). Concentrations of other elements (N, Mn, As, Se) show similar trends to TDS (figures not shown).

Both Figures 6 and 7 indicate the upper layer of the domain generally exhibit stronger impacts because CO₂ buoyancy promotes more contact by CO₂. In this model, CO₂ dissolves in groundwater when it migrates into the USDW formation, increasing the density of that groundwater within the bottom layer of the Ogallala aquifer. However, the CO₂ leakage rates are small enough that the increased density has a negligible impact. Simulated head gradients dictate that dissolved CO₂ as well as some ions flow upward and laterally away from the leaky well. Horizontally, the impacts of CO₂ plume extent reaches more than 1000 m away from the leakage point following initial significant changes after 50 years. These changes facilitate detection at the monitoring wells.

The CDF of responses of TDS at 10, 50, 100 and 200 years (Figure 8) suggests that as time increases, the uncertainty increases. In the first 50 years, no significant changes of TDS resulted. Even at 100 years, simulation results suggest only about a 10% probability that TDS would exceed 600 mg/L, which is well within what would be considered normal fluctuation. After 200 years, this probability grows to 40%, and

with a 10% probability that TDS exceeds 50% variation of the initial value. However, results also suggest less than a 4% probability that TDS could exceed 1000 mg/L, which is Texas' MCL threshold.

It is usually believed that the closer test wells are located to the leaking point, the sooner that detections are rendered. However, based on this study, the CDF plots for 100, 500 and 1000 m away from the leakage point only show slight differences within 200 years. The existing monitoring wells are 1,000 m away (on average) from the injection/production wells in the FWU, and at this distance a well could detect groundwater quality changes due to CO₂ leakage at later times. This study only considered low CO₂ leakage rates. If CO₂ leakage rates were relatively high, such as those associated with the highly-over-pressured reservoir driving flow into the Ogallala aquifer, earlier detection of the leakage would be likely.

Fig. 9 illustrates concentration changes in water quality indexes examined, with different percentiles at 1,000 m away from the leakage point. Within the 95th percentile, the concentrations are not likely to exceed twice the initial values, or exceed the MCL limits. However, Se already exceeds the Texas MCL (0.002 mg/L) value initially, and these simulations forecast a 50% probability that the concentration would increase (worsen) during the 200 year period. On the other hand, Se does not exceed EPA MCL standards for drinking water (< 0.05 mg/L), and it is still ~10 times less than the EPA standard.

Fig 6. 50th and 90th percentile probabilities of TDS distribution after 50, 100, and 200 years.

Fig. 7. 10th and 90th percentile probabilities of pH distribution after 50, 100, and 200 years.

Fig. 8. CDF of TDS responses at 10, 50, 100, and 200 years.

Fig. 9. Selection of water index changes via time at current monitoring wells with 5th, 50th and 95th percentiles.

Usually groundwater chemistry varies over time due to multiple reasons including groundwater flow, experimental errors and other issues, and some differences among tests are typically acceptable. Early detection of CO₂ leakage is more difficult by water chemistry tests if the change is very small, especially if less than 10%. Consequently, suggested principles to choose indicators for early detection include: (1) ease of testing and (2) detection of significant changes due to CO₂ leakage, especially compared to existing monitoring data (Table 12) or they exceed regulatory MCLs. Carroll et al. (2014) introduced “impact thresholds” for a no-impact contaminant level based on site-specific data. This is meaningful for water chemistry change quantification, especially for those water indices that are significantly different from the MCLs. Such no-impact thresholds were also calculated based on more than 100 monitoring water samples of the Ogallala groundwater in this study (Table 12), with 5% and 95% thresholds. If a predicted concentration stays between the 5 – 95% thresholds, it may be considered “no impact” to water quality. The no-impact thresholds for this specific site are overall stricter than the MCLs (except TDS),

suggesting that the thresholds could be more sensitive to the water chemistry changes than regulatory MCLs for the sites with high water quality (a scenario described by Carroll et al., 2014).

Manganese, As and Se all exhibit a relatively large number of “no detection” (trace, minor, or none detected) values, so the detection limits are used for their 5% thresholds, respectively. Based on these results, we infer that pH is not likely to exceed EPA and Texas MCLs. However, there is ~50% probability that pH would exceed the 5% threshold in 50 years, suggesting that pH could be considered as indicator for CO₂ leakage. The selected trace metals (Mn, As and Se) exhibit greater than 50% increase of their concentrations in the worst-case scenarios, but chances are low that these would exceed the 95% thresholds or MCLs. Arsenic is the only trace metal even close to being significant, with a ~5% probability that it would exceed the no-impact threshold after 150 years. These data might be considered normal and not suggested as leakage indicators. These trace metals usually require inductively coupled plasma-mass spectrometry (ICP-MS) to be detected, which is hardly portable (current technology), and field methods increase the possibility of larger errors. This is also another reason that the trace metals are not suggested to serve as early detection water quality change indicators. Total dissolved solids is one index that is easily tested in the field, and its concentration could increase more than 50% of its initial value according to these ROM results. However, in-situ tests suggest large error bars (uncertainty) for TDS with a high no-impact threshold; so TDS is not recommended as an early detection indicator. Additionally, this study indicates that nitrate is not recommended as an indicator either. Nitrate is not a reactant with CO₂ and it is not released like trace metals in the simulations, but it usually shows slight increases when redox changes. For most of the simulated cases, nitrate concentration does not show a significant increase (no more than 50% probability). The reason for its concentration increase in the top layer in worst-case scenarios (with highest nitrate concentration increase) is both the impacts of redox changes due to CO₂ leakage and the up-flow due to slight density changes of the groundwater. In general, the Ogallala groundwater quality is not likely to be significantly impacted due to limited CO₂ leakage (e.g., rates forecasted in this study) through wellbore cement with micro fractures. The value of pH is very sensitive to the intrusion of CO₂ in the early stage (less than 50 years) compared to the no-impact threshold value, suggesting that it may be suitable as a geochemical indicator for CO₂ leakage.

Table 12 Selection of water index variations at current monitoring wells.

	pH	TDS, mg/L	N, mg/L	Mn, mg/L	As, mg/L	Se, mg/L
Average	7.7	570	3.43	0.008	0.0024	0.003
Median	7.7	415	2.69	0.001	0.0025	0.003
Minimum	7.2	160	0.00	0	0	0.000
Maximum	8.2	1946	7.69	0.147	0.004	0.008
5% threshold	7.5	244	1.20	$1.0 \times 10^{-4*}$	$1.0 \times 10^{-4*}$	$1.0 \times 10^{-4*}$
95% threshold	8.0	1757	7.52	0.03	0.0038	0.008

* Detection limit by ICP-MS (<http://www.eag.com/documents/icp-oes-ms-detection-limit-guidance-BR023.pdf>)

Conclusions

This study focuses on assessment of potential risks of CO₂ leakage through wellbores on groundwater quality using an RSM approach, as well as identification of water chemical factors to establish early detection criteria. The case study application is a commercial-scale CO₂-EOR field. Before that, we evaluated the uncertainties of the CO₂ leakage rate with consideration of CO₂-cement chemical reactions.

Major findings include:

(1) This study suggests that a greater than 90% probability of leakage rate values should range between $10^{-14} - 10^{-10}$ kg/(m²·year). This small leakage rate is explained by the relatively low permeability of wellbore cement, and chemical reactions between CO₂ and portlandite (Ca(OH)₂) that consumes CO₂ as well as further decrease the fracture porosity resisting the CO₂ pathways.

(2) RSM-based results are sufficiently robust, as indicated by coefficient of determination (R^2) and coefficient of variation of the root mean square error (CVRMSE) values calculated between simulation results and the RSM-predicted responses. R^2 and CVRMSE between 50 validation simulation results and response surface equations are > 0.8 and $< 10\%$, respectively. The high R^2 and low CVRMSE values suggest that the results of ROMs are likely sufficiently effective for representing full-reservoir model simulation results.

(3) No-impact thresholds associated with site-specific monitoring data could be a valuable reference for evaluation of CO₂ impacts.

(4) Within the range of CO₂ leakage rate, TDS, nitrate and trace metal concentrations could be twice as much as the initial value with the worst scenarios after 200 years. However, these water indices do not exceed the MCL limit, or exceed no-impact thresholds according to the in situ monitoring data, suggesting that the Ogallala groundwater quality shouldn't be significantly impacted.

(5) Water quality at 100, 500 and 1000 m away from the leakage point indicate only slight differences within 200 years, suggesting that the distance between current monitoring wells and injection/production wells is of limited impact with respect to early detection criteria.

(6) pH is suggested as a likely geochemical indicator for early detection, because it is sensitive to CO₂ leakage and is easy to detect.

This study has limitations that indicate much future work can be done on this topic. Future research may include (1) calibration of the cement hydration simulations with experiments to obtain more accurate data; (2) an improved model for the Ogallala formation could be developed with more field formation data; (3) calibration of geochemical reactions with CO₂ by laboratory experiments could be utilized to obtain site specific reaction parameters, especially for sorbent type, sorption capacity and sorbent surface areas; and (4) additional boundary conditions such as different reservoir pressure could be evaluated, depending on the specific site/location of interest.

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