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Sequentially coupled THMC model for CO₂ geological sequestration into a 2D heterogeneous saline aquifer





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ABSTRACT

The significance of thermal-hydrological-mechanical-chemical (THMC) interactions is well recognized in the operation of CO₂ geo-sequestration. Geo-mechanical and geochemical effects may significantly affect aqueous phase composition, porosity and permeability of the formation, which in turn influence flow and transport. The TOUGHREACT simulator has the capability to quantitatively simulate fluid flow, solute transport and geochemical reaction in CO₂ geo-sequestration using sequential coupling. Using a mean stress formulation, geomechanical effects such as stresses, displacements, and rock deformation in CO₂ sequestration have been simulated by the recently developed TOUGH2_CSM. Based on these simulators, in this paper a novel mathematical model of the THMC processes is developed. A sequentially coupled computational framework is proposed and used to simulate reactive transport of water, CO₂ gas and species in subsurface formation with geomechanics. The novel frameworks are designed to keep a generalized computational structure for different THMC processes. The coupled THMC simulators focus on: (1) fluid and heat flow, solute transport within a three-phase mixture, (2) stresses and displacements related to the mean stress. (3) non-isothermal effects on fluid properties and reaction processes, and (4) the equilibrium and kinetics of fluid-rock and gas-rock chemical interactions. A set of partial differential equations is presented to model the THMC processes of the fluid and heat flow, solute transport in aqueous and gaseous phase, mean stress, and geochemical reactions under both equilibrium and kinetic conditions. A 2D reactive transport model with complex chemical compositions is presented to analyze the THMC processes quantitatively on the coupled effects of geochemical reaction and geomechanics during CO₂ geo-sequestration process. The model is able to analyze the long term fate of CO₂ and the efficacy of different trapping mechanism (structural, residual, solubility and mineral trapping) with respect to key minerals. The modeling algorithm can also be used to simulate CO₂ EOR and other secondary and EOR processes in petroleum reservoirs.

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1. Introduction

Based on the technical report of Intergovernmental Panel on Climate Change (IPPC), the concentration of CO_2 existing in the atmosphere was 280 parts per million by volume (ppmv) at the beginning of the Industrial Revolution in the 18th century, and it increased to around 380 ppmv in 2006. The concentration of CO_2 in the air has been increased by one third over the past 150 years, and is currently still rising by about 1.7 ppmv every year (IPCC, 2007). While CO_2 reacting with the molecules of water in the atmosphere, soil and ocean system, carbonic acid and hydrogen

* Corresponding author. E-mail address: zhangronglei@gmail.com (R. Zhang). ions are formed, leading to an acidized environment. About 35% of the CO₂ emissions in the atmosphere dissolves into the aqueous system of the oceans (Millero, 1995). The pH value of the acidized ocean system has decreased by 0.1 units since preindustrial times (IPCC, 2007). The ecosystems in the ocean are influenced by aqueous acidification and the concentration reductions of associated carbonate ion (Orr et al., 2005). Only 25% of CO₂ emissions to the atmosphere by human activities can be absorbed and utilized by the terrestrial biosphere (Feely et al., 2004), thus CO₂ emissions can increase the acidities of soil, river, lake, sea and air. Therefore, CO₂ geo-sequestration into saline aquifers is the most effective solution to reduce CO₂ emissions into the atmosphere. Saline aquifers have the largest volumetric capacity among the many options for long term geological storage of CO₂ (IPCC, 2005).

1.1. Physical mechanisms of CO₂ geo-sequestration

Saline aquifers are porous geological reservoirs with large volumes and great depths, and saturated with brine solutions, which are always rich in a certain amount of mineral ions. The sketch of CO_2 geo-sequestration is shown in Fig. 1 The most favorable sequestration sites are sealed by thick low-permeability layers of shale or clay, where to trap the immobile CO_2 permanently, to adsorb CO_2 on the surfaces of micro-pores, or to convert gaseous CO_2 into solid rock minerals. After a large amount of CO_2 is injected into the aquifers, there are several primary mechanisms controlling the percolation and ultimate fate of CO_2 (IPCC, 2005). The effectiveness of geological storage depends on a combination of the important trapping mechanisms. All kinds of the primary flow and transport mechanisms can be categorized into these three mechanisms contributing to trap CO_2 gas (IPCC, 2005):

Stratigraphic and structural trapping. The physical trapping of gaseous CO₂ below cap-rocks and above bed-rock, such as shale or clay seals with ultra low permeabilities, is the primary means to sequestrate gaseous CO₂ in geological reservoirs. CO₂ injected in the saline aquifer can be sealed between the caprock and the bedrock. Both the free CO₂ gas phase and two phase mixture are trapped in this manner. Such stratigraphic traps are often located in sedimentary basins, and are occupied by saline water, oil and gas. Structural trapping are resulted from the variations of rock types caused by changes in the way the sediments were deposited. After the CO₂ injection into the saline aquifer, two phase mixture will be formed rapidly. The pressure will increase rapidly accordingly, which results in significant geo-mechanical effects in the formation. By the maximum extent of geo-mechanical effect during the CO₂ injection period, faults can be activated as favorable leaking pathways of gaseous CO₂. This mechanism usually operates over large spatial scales (field size) but short timescales (injection period).

Solubility trapping. It occurs in the saline aquifers where fluids transport very slowly over long distances. After CO_2 is injected into the aquifer, it displaces aqueous water and migrates upwards. Under the formation pressure, gaseous CO_2 becomes equilibrated with formation water, leading to $CO_2(aq)$ in the formation water. This process follows phase and chemical equilibrium conditions under the formation pressure. Over time, a large amount of gaseous CO_2 dissolve in the aqueous water of the formation. Dispersion and fingering of aqueous CO_2 may be formed due to permeability heterogeneity, gravity override and mobility contrast between CO_2 and formation fluid. These mechanisms also operate over relatively short timescales (injection period).

Mineral trapping. After gaseous CO₂ is dissolved into formation water (separate phase may still be there), carbonic acid is released



Fig. 1. Sketch of CO_2 geo-sequestration to inject supercritical CO_2 into subsurface (IPCC, 2007).

to dissolve certain amount of rock minerals, leading to a rise of the pH value. Dissolved ions and minerals may further react to form stable carbonate and silicate minerals. Reaction of dissolved CO₂ with minerals can be very rapid (days) for some carbonate minerals, but very slow (hundreds to thousands of years) for others (silicate minerals). Precipitation of carbonate minerals leads to the continuous reaction of bi-carbonate ions with metal ions (e.g. ion, calcium, and magnesium), which are released by the dissociation of the silicate minerals (e.g. clay, chlorite, feldspar and mica). This mechanism operates over long timescales (thousand years) and relatively small site scale (formation scale).

1.1.1. Important rock minerals for trapping CO₂

From the existing reactive transport simulations (Audigane et al., 2007; Balashov et al., 2013; Gaus et al., 2005; Gunter et al., 2000; Johnson et al., 2001; Ketzer et al., 2009; Kihm et al., 2012; Knauss et al., 2005; Liu et al., 2011; Mito et al., 2008; Raistrick et al., 2009; White et al., 2005; Wigand et al., 2008; Xu et al., 2003, 2004a, 2004b, 2005, 2007; Zerai et al., 2006), I can summarize that the general mineralogy composition that could be present in the potential CO₂ geo-sequestration sites can be categorized into two kind: carbonate minerals (i.e., calcite, magnesite, dawsonite, siderite, ankerite, etc.) and silicate minerals (i.e., quartz, oligoclase, smectite, feldspar). Among these previous numerical simulations, the contribution of mineral trapping is significant when plagioclase feldspar minerals and chlorite minerals present in the chemical reaction system, especially for the reactive transport simulations by Xu et al. (2003, 2004a, 2004b, 2005). It is obvious that the quartz, plagioclase feldspar minerals, chlorite minerals, kaolin minerals and illite minerals are the common minerals selected for the numerical simulation of mineral trapping in Fig. 2. Among the precipitated minerals by mineral trapping in Fig. 3, eighteen of these twenty numerical models mentioned the generation of dawsonite as secondary mineral. Sixteen of these twenty numerical models mentioned siderite and ankerite as secondary minerals. Twelve of them mentioned smectite as a secondary mineral. Since the chlorite has been concluded as a key minerals for the mineral trapping of CO₂ in formation rock (Kihm et al., 2012), other minerals such as oligoclase that may play a significant role for the mineral trapping will be studied in this research. The general mineralogy investigated in this study is selected from the key minerals with high frequency of presence in these twenty numerical simulations.

1.1.2. Chemical reaction pathway

The chemical reaction pathway depends upon rock compositions. According to the mineral compositions of the CO2 geosequestration sites, the most common formations are categorized into three kinds: sandstone, carbonate and clay. In terms of the rock type, the rock minerals in these three formations are quite similar, but the volume fractions of the rock minerals vary significantly. These formations are always composed of quartz, carbonate minerals, plagioclase feldspar minerals, clay minerals, and minor other components. Calcite represents the carbonate minerals. Oligolcase and K-feldspar represent the plagioclase feldspar minerals. Clay minerals includes kaolin group (kaolinite), illite group (illite), smectite group (smectite-Na and smectite-Ca) and chlorite group (chlorite). Furthermore, the chemical reaction pathway after supercritical CO₂ injection can be described in terms of rates of the kinetic reactions. Based on the parameters of the kinetic rates by Xu et al. (2003, 2004a, 2004b, 2005), the kinetic reactions rates are small and vary significantly for different rock minerals. Carbonate minerals have the fastest kinetic reaction rates (in the magnitude of 10^{-7} mol/m²s), then plagioclase feldspar minerals have the kinetic reaction rates in the magnitude of 10^{-12} mol/m² s, illite minerals and smectite minerals have the kinetic reaction rates in the



Fig. 2. The frequency and contribution of different original rock minerals present in the geochemistry system modeled previously.



Fig. 3. The frequency and contribution of different secondary rock minerals present in the geochemistry system modeled previously.

magnitude of 10^{-13} mol/m² s, kaolin minerals and quartz have the kinetic reaction rates in the magnitude of 10^{-14} mol/m² s. The kinetic chemical reaction rates are also related to the reactive surface area of rock, the acid or base mechanism involved in the aqueous phase, the activation energy and temperature.

In terms of the rock mineral compositions and kinetic rates, the chemical reaction pathway can be described in Fig. 4. Every small pore can be treated as a batch reactor when supercritical CO₂ invades into it. The CO₂ dissolution is the fastest chemical reaction, the chemical equilibrium of CO₂ dissolution is reached simultaneously with the injection of supercritical CO₂. It releases large amounts of hydrogen ion, leading to an acidized aqueous environment. This process is an acidized process. Secondly, the carbonate minerals such as calcite, dolomite, magnesite start to dissolve into the aqueous phase. Various iron species and bicarbonate species are releasing into the aqueous phase. The rates of

the carbonate mineral dissolution are in the magnitude of 10^{-7} mol/m² s, and the dissolution of carbonate minerals reaches the equilibrium state rapidly. Thirdly, the rock minerals from plagioclase group, kaolin group, illite group, smectite group and chlorite group starts to dissolve into the aqueous phase under the effects of chemical species H⁺. This process is defined as pH buffering. The minerals break into large amounts of different chemical species in aqueous phase. K-feldspar and chlorite are taken as examples to illustrate how the minerals dissociate into different chemical species in Fig. 4. It may take thousands of years for the minerals dissolutions. These three processes are dissolutions of gas and minerals. After this, the new minerals precipitate into the solid phase on the surface of the formation. The new minerals are mainly composed of stable carbonate mineral such as dawsonite, ankerite and siderite. The precipitation of the new minerals are relatively fast in the magnitude of 10^{-8} mol/m² s after the mineral



Fig. 4. The sketch for the chemical reaction pathway in the THMC processes during CO₂ geo-sequestration.

dissolution. Finally, the slowest reaction is the precipitation of quartz in the magnitude of 10^{-14} mol/m² s. The last two processes lead to the mineral trapping of supercritical CO₂ in solid phase, and continue to buffer pH value and consume the chemical species of H⁺. Based on the analysis above, the chemical reaction pathway of supercritical CO₂ with rock minerals is complicated due to the key factors (rock type, rock composition, reaction rate, etc.)

1.2. Numerical simulation scheme and algorithm for THMC processes

For the numerical simulations of the THMC processes, THM processes and THC processes are always coupled separately to solve different problems in both systems. Among many factors of the THMC processes to be considered in the numerical models, the geomechanical effects take place immediately after the working fluid injection, leading to pore structure change and land subsidence. The geochemical reactions that take place between injected working fluid (i.e., CO₂ gas), formation water and the rock minerals are much more complex than the others, and are more important to determine the long term fate of supercritical CO₂ in saline aquifers. These geochemical reactions have a significant role in the related transport processes, for example, through chemical precipitations in the pore or fracture spaces affecting porosity and permeability, or dissolved CO₂ decreasing the density of formation fluid resulting in buoyant flow fluxes. It is a challenging issue to model the THMC processes within a coupled procedure mathematically, because of the complexity of multiphase fluid and heat flow, geomechanics, geochemical reactions of water-gas-rock, and the strong nonlinearities in the mass, energy and momentum conservation equations. Among the four processes, THM processes and THC processes are always coupled separately to solve for CO₂ geosequestration, but these coupled processes don't have capabilities to address the mutual effects of thermal gradients, geomechanics and geochemistry quantitatively. It is necessary for us to develop a THMC model. There are few numerical studies to couple the THMC processes together. Among the THMC processes, the geochemical reaction process is much more complex than the others. Many numerical studies have addressed the coupled methods for THC processes. The numerical scheme and algorithm for THMC processes can be based on that of THC processes. There are two major methods widely used to solve the fluid flow, solute transport, and geochemical reactions together, i.e. direct substitution approach and sequential iteration approach. In the two approaches, the second one solves the fluid transport and the geochemistry individually and sequentially in an iterative manner (Cederberg et al., 1985; Yeh and Tripathi, 1991; Engesgaard and Kipp, 1992; Šimůnek and Suarez, 1994; Walter et al., 1994; Zysset et al., 1994; Xu, 1996; Wei, 2012). Furthermore, a modified sequential noniterative approach was proposed to solve solute transport and chemistry only once without iteration (Liu and Narasimhan, 1989; Ague and Brimhall, 1989; Appelo, 1994). By means of sequential iteration approach, a set of geochemical codes such as SOLMINEQ (Kharaka et al., 1989), EQ3/6 (Wolery, 1992), PHREEQE (Parkhurst et al., 1991), PATHARC (Hitchon, 1996), PHREEQC V2.0 (Parkhurst et al., 1999), GEOCHEMIST'S WORKBENCH (Bethke, 2002), TOUGHREACT (Xu et al., 1997), and UTCHEM (Delshad et al., 1996; Najafabadi et al., 2009) are designed to couple the fluid flow, solute transport, and geochemical reaction sequentially. Among them, SOLMINEQ, EQ3/6, PHREEQC, PATHARC, GEOCHEMIST'S WORKBENCH are for batch reaction systems or 1D geochemistry transport problems, and majority of these simulators track the database of geochemical reaction parameters at the every iteration. This may be not efficient or realistic to simulate a field-scale multidimensional reactive transport problems. TOUGHREACT and UTCHEM are developed to solve the multi-dimensional and multiphase fluid flow, solute transport, and chemical reactions in groundwater and petroleum systems, respectively. UTCHEM does not consider the kinetic reactions. The second method, direct substitution approach, substitutes the geochemical reaction into the fluid flow equations directly, forming a fully coupled reactive solute transport model. There are few studies of the fully coupled approach (Zhang et al., 2012a, 2012b; Zhang, 2013; Xiong et al., 2013; Wu et al., 2014), it solves the fluid flow, solute transport, and geochemical reactions simultaneously with a high accuracy, but it might consume lots of computer resources than the sequential iteration approach. Therefore, the sequential iteration approach is sufficient for us to couple THMC processes together, in order to avoid the calculation complexity.

There are many developments for the algorithm of THM models

(Settari et al., 2001; Longuemare et al., 2002; Minkoff et al., 2003; Tran et al., 2004; Samier et al., 2008). The procedures of coupling algorithm can be categorized into three kinds: loosely coupled, iteratively coupled and fully coupled. Basically, there are two sets of equations (heat and fluid flow, geomechanics) to be solved in the algorithm. The loosely coupled method solves the geomechanics after a certain number of time steps of fluid flow. A certain amount of THM simulators employ the loosely coupled procedure to solve fluid flow and geomechanics, e.g., TOUGH-FLAC (Rutqvist and Tsang, 2002; Rutqvist et al., 2002), ATH2VIS (Longuemare et al., 2002), and IPARS-JAS3D (Minkoff et al., 2003). Secondly, the iteratively coupled procedure solves the primary variables for heat and fluid flow, and primary variables for geomechanics individually and sequentially. The solutions are delivered into equations of heat, fluid flow and geomechanics back and forth in both directions at a specific time point. Then the THM procedures are coupled iteratively at the end of each time step (Longuemare et al., 2002). In this procedure, either the equations of heat and fluid flow or the equations of geomechanics are solved initially, and then the other equations can be solved sequentially and iteratively by substituting the intermediate solutions, e.g., GEOSIM (Settari et al., 2001), Rocflow (Wang and Kolditz, 2007). A typical example of this iteratively coupled method is explicitly coupled method. It only allows one iteration per one time step, e.g., ROCMAS (Noorishad et al., 1984), FRACture (Kohl et al., 1995) and FRACON (Nguyen, 1996). Furthermore, the fully coupled procedure solves a set of nonlinear partial differential equations, which represents all the related physical mechanisms (Minkoff et al., 2003). Thus, the equations of heat flow, fluid flow and geomechanics are solved simultaneously at each time step. TOUGH_CSM (Winterfeld and Wu, 2012) is a successful implementation of fully coupled procedure, which solves the fluid flow and mean stress equation simultaneously.

In this paper, a novel mathematical model of the THMC processes is developed based on the TOUGHREACT simulator (Xu et al., 2004c) and TOUGH2_CSM simulator (Winterfeld and Wu, 2012). A sequentially coupled computational framework is proposed and used to simulate reactive transport of water, CO₂ gas and chemical species in subsurface formation with geomechanics. The novel frameworks are designed to keep a generalized computational structure for different THMC processes. The coupled THMC simulators focus on: (1) fluid and heat flow, solute transport within a three-phase mixture, (2) stresses and displacements related to the mean stress, (3) non-isothermal effects on fluid properties and reaction processes, and (4) the equilibrium and kinetics of fluidrock and gas-rock chemical interactions. A set of partial differential equations is presented to model the THMC processes of the fluid and heat flow, solute transport in aqueous and gaseous phase, mean stress, and geochemical reactions under both equilibrium and kinetic conditions. A 2D reactive transport model with complex chemical compositions are presented to analyze the THMC processes quantitatively on the coupled effects of geochemical reaction and geomechanics during CO₂ geo-sequestration process. The model is able to analyze the long term fate of CO₂ and the efficacy of different trapping mechanism (structural, residual, solubility and mineral trapping) with respect to key minerals.

2. Numerical scheme and algorithm of THMC model

2.1. Assumptions

A brief description of the assumptions is given as follows: The THMC model is developed for multi-dimensional porous media with heterogeneous physical and chemical properties. The gaseous, aqueous and solid phases are involved in heat flow, fluid flow, geomechanics and geochemical reactions. The effects of heat, pressure and stress are taken into account for the calculation of physical, geomechanical and geochemical properties. Multiphase Darcy flow formulation is applied for the fluid flow in porous media. A simplified mean stress formulation is used in this THMC model. Transport of aqueous and gaseous species by advection is taken into account. Any kind of chemical species in liquid, gas, and solid phases can be simulated in this model. Thermodynamic equilibrium are considered between gaseous species and the corresponding aqueous species. Aqueous complexation and gas dissolution are considered under the local equilibrium assumption. Thermodynamic and chemical equilibrium are attained instantly within each grid cell. Mineral dissolution and precipitation predefined in the model can occur either under local equilibrium or kinetic conditions.

For the sequentially coupled THMC model, it has three main parts to solve the THMC processes. The first part is fluid flow, heat flow and geomechanics. The second part is solute transport. The last part is chemical reaction module. The first part is an independent procedure, which is solved in a fully coupled process. After this, the second part of solute transports for gaseous species and aqueous species are solved to obtain the total concentrations of primary chemical species. Finally, the chemical reactions are solved to obtain the geochemical compositions in the geochemical system in every grid cell. Among these three main parts, the solute transport and chemical reaction is solved in a sequential manner with an iterative procedure. The mathematical equations for numerical algorithm are described as below.

2.2. Fluid flow, heat transfer and geomechanical equations

The mathematical equations for fluid flow, heat flow and geomechanics are described in the following part.

2.2.1. Mass conservation equation

In the sequentially coupled procedure, the first part only solve the mass balance for a certain number of primary components (i.e., H₂O, NaCl, and CO₂), mass loss or gain of primary components in chemical reactions are considered in the equation. The mass balance for primary components κ in accordance to Darcy's law can be written in the following form:

$$\frac{\mathrm{d}M^{\kappa}}{\mathrm{d}t} = \nabla \cdot F^{\kappa} + q^{\kappa} + R^{\kappa} \tag{1}$$

The quantity *M* is the accumulation term, representing mass of a primary components or species, with $\kappa = 1, ..., N_k \kappa$ is the primary components or species (H₂O, NaCl, and CO₂). *F* is the mass flux based on the Darcy's Law, and *q* is sinks and sources of primary components. *R* denotes mass or loss for H₂O and CO₂ due to chemical reactions, which are the feedbacks from the third part of geochemical reaction module.

2.2.2. Energy conservation equation

The energy balance equation is derived under the assumptions that energy is a function of temperature only and energy flux in the porous media occurs by advection and heat conduction only.

$$\frac{\mathrm{d}U}{\mathrm{d}t} = \nabla \cdot F + q_{\mathrm{h}} \tag{2}$$

where *U* is the heat accumulation term of rock and fluid, F_{β} is the heat flux, and q_h is the heat sink and source by heat injection and withdraw.

2.2.3. Mean stress equation

The mean stress equation in this THMC model is based on the

equation by Winterfeld et al. (Winterfeld et al., 2012), which is to solve the normal mean stress. The mean stress equation is given below.

$$\frac{3(1-\nu)}{1+\nu}\nabla^2\tau_m - \frac{2(1-2\nu)}{1+\nu}\left(\alpha\nabla^2 p + 3\beta K\nabla^2 T\right) + \nabla\cdot\overline{F} = 0$$
(3)

where *v* is the Poisson's ratio, τ_m is the normal mean stress, α is the Biot's coefficient, *p* is the pore pressure, β is the linear thermal expansion coefficient, *K* is the bulk modulus, *F* is body force, λ is the Lame's constant, *G* is the shear modulus, *T* is the temperature, and subscript *m* is the label of mean stress.

2.3. Discretization and solution method for fluid and heat flow, geomechanics

The mass balance equation, energy balance equation and mean stress equation are discretized as follows:

2.3.1. Mass balance

The mass balance equations (Eq. (1)) are discretized in space using the integral finite difference method. Introducing appropriate volume averages, then

$$\frac{\mathrm{d}M_n^{\kappa}}{\mathrm{d}t} = \frac{1}{V_n} \sum_m A_{nm} F_{nm}^{\kappa} + q_n^{\kappa} + R_n^{\kappa} \tag{4}$$

where M_n is the average value of M over V_n . Surface integrals are approximated as a discrete sum of averages over surface segments A_{nm} , F_{nm} denotes mass flux between two volume elements V_n and V_m , and q_n denotes sinks and sources by mass injection or withdraw at element n.

2.3.2. Energy conservation equation

The energy balance equation (Eq. (2)) are discretized in space using the integral finite difference method. Introducing appropriate volume averages, then

$$\frac{\mathrm{d}U_n}{\mathrm{d}t} = \frac{1}{V_n} \sum_m A_{nm} F_{nm} + q_{\mathrm{h,n}} \tag{5}$$

2.3.3. Mean stress equation

Eq. (3) expresses the mean stress in terms of the pressure and body forces. The Integral Finite Difference method is employed to discretize the mean stress equation over the volume of grid cell Vtowards the outer surface. The discretized form of mean stress in terms of surface integral is expressed as:

$$M_{n}(\tau, p, T) = \sum_{m} \left[\frac{3(1-\nu)}{1+\nu} \nabla \tau_{nm} - \frac{2(1-2\nu)}{1+\nu} (\alpha \nabla p_{nm} + 3\beta K \nabla T_{nm}) + \overline{F}_{nm} \right] A_{nm} = 0$$
(6)

2.3.4. Equation system in residual form

For the fully coupled approach to solve the THM processes in first part, the mathematical equations for fluid flow, heat flow and geomechanics are solved simultaneously. The equation system for THM model can be written as follows:

$$R_{n}^{\kappa,k+1} = M_{n}^{\kappa,k+1} - M_{n}^{\kappa,k} - \frac{\Delta t}{V_{n}} \left[\sum_{m} A_{nm} F_{nm}^{\kappa,k+1} + V_{n} q_{n}^{\kappa,k+1} + V_{n} R_{r,n}^{\kappa,k+1} \right]$$
$$+ V_{n} R_{req,n}^{\kappa,k+1} + V_{n} R_{r,n}^{\kappa,k+1} \right]$$
$$\kappa = 1, \dots, N_{C}$$
(7)

$$M^{k+1} = M(X_{j,k+1}) \quad j = 1, ..., N_C + N_p + N_g$$
(8)

For each control volume V_n , there are N_{eq} equations to describe the THM processes. The total number of the non-linear equations representing the THM system with N_{el} grid blocks is $N_{el} \times N_{eq}$. The unknown primary variables has the same number as the equations, X_{j} , $j = 1, ..., N_{el} \times N_{eq}$, which define the state of the THM system at a specific time step t^{k+l} . The method of Newton–Raphson iteration is employed to solve the equation system. A NR iteration index p is used to expand the residuals R at iteration step p+1 by means of Taylor series expansion. The Taylor series expansions of residual equations in terms of primary variables are as follows:

$$\sum_{j=1}^{N_{C}} \frac{\partial R_{n}^{\kappa,k+1}}{\partial X_{j}} \Big|_{p} (X_{j,p+1} - X_{j,p}) = -R_{n}^{\kappa,k+1} (X_{j,p}) \quad \kappa = 1, \dots, N_{C}$$
(9)

$$\sum_{j=1}^{N_{c}} \frac{\partial M^{k+1}}{\partial X_{j,p}} \Big|_{p} (X_{j,p+1} - X_{j,p}) = -M^{k+1} (X_{j,p})$$
(10)

For the fully coupled approach in this part, the equations for fluid flow, heat flow and geomechanics are solved simultaneously until the prescribed convergence criteria are satisfied.

2.4. Solute transport for gaseous and aqueous species

After the first part is solved, the Darcy velocity for each is used to solve the second part: solute transport for gaseous and aqueous species. The governing equation for solute transport is derived from the mass conservation equation. The aqueous species are transported in the liquid phase, and they are released by the chemical reactions with gaseous, aqueous and solid phases. Transport equations are written in terms of total dissolved concentrations of primary chemical components. Advection and diffusion of chemical species are considered in the reactive transport processes, and the coefficients of diffusion are set to be the same for different chemical species. The source or sink terms from the chemical reactions are quantified in the reactive transport equations.

2.4.1. Solute transport equation

The equation of reactive solute transport is a mole balance equation, which has the same expression of the general mass conservation of Eq. (1). The mass conservation equation become mole balance equation, and the accumulation term becomes

$$M_j = \phi S_l C_j \quad j = 1, 2, \cdots, N_c \tag{11}$$

the flux term becomes

$$F_j = u_\beta C_j - (\tau \phi S_\beta D_\beta) \nabla C_j \quad j = 1, 2, \cdots, N_c$$
(12)

and the sink/source term becomes

$$q_i = q_{il} + q_{ig}$$
 $j = 1, 2, \cdots, N_c$ (13)

where N_c is the total number of the primary chemical components (species), u_{β} is the Darcy velocity of phase β , D_{β} is the diffusion coefficient of phase β . For the primary aqueous chemical species, C_i is the total concentration of the *i*th primary species in aqueous phase. The concentrations of the secondary species can be calculated by means of a linear combination of the concentrations of primary species. Therefore, all the moles of the secondary species can be transferred to the moles of primary chemical species. For the primary gaseous chemical species, C_i is the concentration of the *i*th species in gaseous phase, which is related to its partial pressure in gaseous phases, $C_i = p_g/RT$, P_g is the gaseous species partial pressure, R is the gas constant, and T is the absolute temperature. q_i denotes sinks and sources for primary chemical species. q_{il} denotes sinks and sources for primary chemical species in aqueous phase. q_{ig} denotes sinks and sources for primary chemical species in gaseous phase. R_i denotes chemical reactions for primary chemical species, which are the feedbacks from the third part.

2.5. Discretization and solution method for solute transport

Finite difference is employed to discretize the solute transport equations for gaseous and aqueous species, then a generalized form of discretized solute transport equation is as follows:

$$\frac{\Delta t}{V_n} \sum_m A_{nm} \left[u_{nm}^{k+1} C_{nm}^{i,k+1} + D_{nm} \frac{C_m^{j,k+1} - C_n^{j,k+1}}{d_{nm}} \right]$$
$$= \Delta M_n^{j,k+1} - q_n^{j,k+1} \Delta t - R_n^{j,k+1} \Delta t \quad j = 1, 2, \cdots, N_c$$
(14)

where *n* labels the grid block, *j* labels the chemical component, N_c is the total number of chemical components, *k* labels the number of the time step, u_{nm} is the liquid volumetric flux or Darcys' velocity (m/s), D_{nm} is the effective diffusion coefficient (including effects of porosity, phase saturation, tortuosity and weighting factors between the two grid blocks), d_{nm} is the nodal distance, $R_n^{j,k+1}$ are the overall chemical reaction source/sink terms.

According to Eq. (14), the concentration of primary chemical species and the partial pressure of the gaseous species are the unknown variables in the solute transport equation. Every unknown variable is solved once for every primary chemical species in aqueous and gaseous phases.

2.6. Chemical reaction equation

The chemical equations are solved on a grid block by grid block basis at the same time. The main equations for chemical reactions are mole balance equations for each primary chemical species and saturation index for mineral and gas species. The chemical reaction of primary species leads to the source (mass gain) or sink (mass lost), which are the feedbacks for the solute transport and fluid part in the next step iteration.

2.6.1. Mole balance equation

The mole balance equation for primary chemical species is as follows:

$$F_j = T_j^{t^{k+1}} - T_j^{t^k} = 0 (15)$$

where $T_j^{t^k}$ is the total concentration of primary chemical species at time step t^k , and $T_j^{t^{k+1}}$ is the total concentration of primary chemical species at time step t^{k+1} .

The mathematical expression of total concentration is as

follows:

$$T_{j} = c_{j} + \sum_{k=1}^{N_{x}} v_{kj}c_{k} + \sum_{m=1}^{N_{p}} v_{mj}c_{m} + \sum_{n=1}^{N_{q}} v_{nj}r_{n}\Delta t$$
(16)

where *c* denotes concentrations of chemical species. The subscript *j* is primary chemical species, *k* is secondary aqueous complex, *m* is mineral under equilibrium condition, and *n* is minerals under kinetic constraints, N_x is the number of the corresponding aqueous complexation for secondary chemical species. N_p is the number of corresponding reactions between solid mineral and aqueous species under equilibrium, N_q is the number of corresponding reactions between solid mineral and aqueous species under equilibrium, N_q is the number of corresponding reactions between solid mineral and aqueous species under kinetics. k_j , m_j , and n_j are stoichiometric coefficients of the primary species in the aqueous complexes, equilibrium and kinetic minerals, respectively. r_n denotes the kinetic rates, which is a function of concentrations of primary chemical species. The equation of kinetic reaction rate for minerals is given by Lasaga et al. (1994):

$$r_n = f(c_1, c_2, ..., c_{N_c}) = \pm K_n A_n | 1 - \Omega_n^{\theta} |^{\eta} \qquad n = 1, ..., N_q$$
(17)

where A_n is the specific reactive surface area, Ω_n is the saturation ratio of kinetic mineral, the definition of saturation ratio is explained later. The parameters θ and η are assumed to be one. The values of r_n could be positive and negative, which denote dissolution and precipitation of corresponding mineral respectively. k_n is the rate constant, which is a temperature dependent variable. It is expressed by an Arrhenius equation (Lasaga, 1984; Steefel and Lasaga, 1994). In terms of the different chemistry mechanism, dissolution and precipitation of minerals are not only catalyzed by pure H₂O (neutral mechanism), but also by H⁺ (acid mechanism) and OH⁻ (base mechanism). The equation of K_n in terms of the three mechanisms can be expressed by (Lasaga et al., 1994; Palandri and Kharaka, 2004):

$$k_{n} = k_{25}^{n} \exp\left[\frac{-E_{a}^{n}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] + k_{25}^{H^{+}} \exp\left[\frac{-E_{a}^{H^{+}}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] a_{H^{+}}^{n_{H^{+}}} + k_{25}^{OH^{-}} \exp\left[\frac{-E_{a}^{OH^{-}}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] a_{OH^{-}}^{n_{OH^{-}}}$$
(18)

where E_a is the activation energy, k_{25} is the rate constant at 25 °C, R is gas constant, T is absolute temperature, $a_{H^+}^{n_{H^+}}$ is the activity of H⁺, which is the product of activity coefficient (γ_{H^+}) and concentration of H⁺ (c_{H^+}), and $a_{OH^-}^{n_{OH^-}}$ is the activity of OH⁻, which is the product of activity coefficient (γ_{OH^-}) and concentration of OH⁻ (c_{OH^-}).

2.6.2. Saturation index for mineral at equilibrium condition

In a geochemical reaction system, the dissolution rate of a certain mineral (i.e., $CaCO_3$) is very fast. The reaction of the mineral is always set to be at equilibrium, the mineral saturation index controls the dissolution of the mineral, and it can be expressed as:

$$F_m = \log \Omega_m = \log X_m^{-1} \lambda_m^{-1} K_m^{-1} \prod_{j=1}^{N_c} c_j^{\nu_{mj}} \gamma_j^{\nu_{mj}} = 0$$
(19)

where *m* is the equilibrium mineral index, X_m is the mole fraction of the *mth* mineral phase, λ_m is its thermodynamic activity coefficient, K_m is the corresponding equilibrium constant of the equilibrium mineral, C_j is the concentration of related primary chemical species or components, v_{mj} is the stoichiometric coefficient of *jth* basis

species in the *mth* mineral equilibrium reaction, and γ_j is the activity coefficient of primary chemical species.

2.6.3. Saturation index for gas at equilibrium condition

The chemical reactions between aqueous and gaseous species are set to be under a condition of local equilibrium. Based on the Mass Action Law, we obtain the following expression:

$$F_g = \log \Omega_g = \log \Gamma_g^{-1} p_g^{-1} K_g^{-1} \prod_{j=1}^{N_c} c_j^{\nu_{gj}} \gamma_j^{\nu_{gj}} = 0$$
(20)

where subscript *g* represents gas index, *p* is the partial pressure of gaseous phase, Γ is the fugacity coefficient of gaseous species.

2.7. Discretization and solution method

There are N_c mole balance equations and N_p mineral and gas saturation index, which constitute a equation system with N_c+N_p primary variables. The primary variables can be defined as c_i ($i = 1, 2, ..., N_c+N_p$), by means of Newton–Raphson iteration, then the equations become:

$$\sum_{i=1}^{N_c+N_p} \frac{\partial F_j^{t^{k+1}}}{\partial c_i} \Delta c_i = -F_j^{t^k}$$
(21)

The derivatives of Eq. (21) can be calculated both analytically and numerically.

2.8. Reservoir properties calculation with THMC effects

2.8.1. Porosity

The relationship between mean stress, τ_m , and porosity, ϕ , has been investigated extensively (Ostensen, 1986; McKee et al., 1988; Davies and Davies, 2001; Rutqvist and Tsang, 2002), which we have incorporated into our mechanical model formulation. We begin with mechanical changes in porosity as follows:

$$\phi_M = \phi(\tau_m) \tag{22}$$

where subscript *M* indicates mechanical effects on porosity and τ_m is the current mean stress.

This THMC model is able to incorporate various correlations for stress-dependent porosity and permeability, but we can select an appropriate one for the specific filed. One example from the study by Davies and Davies (2001) is given as follows:

$$\phi(\tau'_m) = \phi_r + (\phi_0 - \phi_r) e^{c\phi'_m}$$
(23)

where τ'_m is the effective stress as $\tau'_m = \tau_m - \alpha p$, α is Biot coefficient, $\phi(\tau'_m)$ is the porosity at the current state of mean effective stress τ'_m , and ϕ_r is residual porosity under infinite net stress or minimum porosity, ϕ_0 is the porosity at zero mean effective stress.

The chemical reaction model incorporates porosity changes due to mineral dissolution and precipitation as follows:

$$\phi_c = 1 - \sum_{m=1}^{N_m} f_m - f_u \tag{24}$$

where N_m is the number of reactive minerals, f_m is the total mineral fraction ($V_{mineral}/V_{medium}$), and f_u is the non-reactive fraction.

In the THMC processes, the porosity change within each time step $\Delta t = t^{k+1} - t^k$ is given in terms of the changes in mechanical and chemical properties $\Delta \phi_M = \phi_M^{k+1} - \phi_M^k$ and $\Delta \phi_c = \phi_c^{k+1} - \phi_c^k$:

$$\phi^{t^{k+1}} = \phi^{t^k} + \Delta \phi_M + \Delta \phi_c \tag{25}$$

2.8.2. Permeability

The permeability change is related to the porosity as follows:

$$k^{t^{k+1}} = k\left(\phi^{t^{k+1}}\right) \tag{26}$$

This THMC model is able to incorporate various correlations for permeability. One example from the study by Davies and Davies (2001) is given as follows:

$$k(\tau'_m) = k_i \frac{\left(1 - \phi_i^2\right)^2}{\left(1 - \phi_i\right)^2} \left(\frac{\phi}{\phi_i}\right)^3$$
(27)

where ϕ_i is porosity at initial reservoir net stress, ϕ is porosity at reservoir net stress, $k(\tau'_m)$ is the permeability at net stress τ'_m and k_i is the permeability at initial reservoir net stress.

Another associated function for permeability in terms of porosity developed by Rutqvist and Tsang (2002) is

$$\kappa = k_0 e^{c\left(\frac{\phi}{\phi_0} - 1\right)} \tag{28}$$

where k_0 is zero stress permeability and the exponent c is a parameter.

2.8.3. Capillary pressure

A change in permeability and porosity leads to a change of pore size and capillary pressure. The following J-function is included in our model to correct for capillary pressure change assuming no change in wettability of the pore surface.

$$p_c = p_{c,0} \sqrt{\frac{k_0 \phi}{k \phi_0}} \tag{29}$$

3. Code structure for sequentially coupled THMC model

The solution procedure and code structure of TOUGHREACT simulator (Xu et al., 2004c) are taken as a reference for the sequentially coupled THMC model. Fig. 5 shows the flow chart of the sequential coupled THMC model. The solving sequence of the THMC simulator is as follows: the non-isothermal multiphase flow equations and mean stress equation are solved first, which results in a procedure in the first part to solve THM processes. The resulting flow velocities and saturation are transmitted into the module of reactive transport. The solute transport in the liquid phase is based on the total dissolved concentrations of primary chemical species. In addition, the transport of gaseous species is solved in terms of their partial pressures. The resulting concentrations and partial pressures from the transport calculation are used in the chemical reaction model. The temperature distribution obtained from the solution of the multiphase flow equations is used to update physical and chemical parameters. The chemical transport equations are solved component by component, whereas the reaction equations are solved on a grid block basis. The transport and reaction equations are solved iteratively until convergence.



Fig. 5. The flow chart of the proposed sequentially coupled THMC simulator.

4. Application: chemical reaction and geomechanics in 2D layered formation

This conceptual model is based on the model presented by Rutqvist and Tsang (2002) and Winterfeld and Wu (2012). The previous two models in the literature aim at describing the THM process during the CO_2 injection into a saline aquifer. The objectives

of this case are to describe the THMC process of CO_2 injection in a large scale reservoir with different properties in different domains, and quantitatively analyze the impacts of heterogeneous domains on the CO_2 transport, geomechanics and chemical reactions. The setup for initial conditions in this conceptual model is different from those used in the previous models. The model details and result discussions are given below.

4.1. Model description

The dimension of the conceptual model is 70,000 m (x) \times 1 m $(y) \times 3000 \text{ m}(z)$. Unlike the previous THMC conceptual model, this model is not extracted from a deep saline aquifer. The depth (3000 m) is from the ground surface to the bottom of the bedrock formation. The initial pore pressure profile, temperature profile and mean stress profile for this conceptual model is based on the depth of the reservoir. The initial hydrostatic pore pressure is assigned to the whole reservoir domain from the top (0 m) to the bottom (3000 m). The initial pore pressure at the surface is set to be the ambient pressure (about 10^5 Pa), and a higher pore pressure (about 3×10^7 Pa) is obtained at the bottom of the reservoir (3000 m) based on the hydrostatic equilibrium calculation. The initial temperature calculation is based on the temperature gradient of 25 °C/ 1000 m. It is set to be ambient temperature (about 10 °C) at the surface and higher temperature (about 85 °C) at the bottom. In addition, the initial mean stress profile for the whole simulation domain is calculated by a built-in subroutine, based on the lithostatic equilibrium condition. The initial mean stress is set to be 1×10^5 Pa at the surface of the reservoir (0 m) and 5×10^7 Pa at the bottom of the reservoir (3000 m).

The grid cell number is $201 \times 1 \times 100$ in *x*, *y*, *z* directions respectively, and the detailed subdivision of the grid cells in the three directions is given in Table 1. The horizontal distance in the *x* direction is 70,000 m. The four boundaries are set to be closed boundaries for the pressure field and fixed stress boundaries for stress fields. The whole conceptual model is an isothermal domain throughout the simulation times, which means that the thermal gradient is kept as the original one. For this conceptual model of the THMC processes during supercritical CO₂ injection into the center at the saline aquifer domain, two cases are designed for the simulation: the first one is with four different rock domains and without a fault above the target saline aquifer, and the second one is with five different rock domains and with a fault apparent above the target saline aquifer.

The vertical section profiles of the two cases are shown in Figs. 6 and 7. For the first case, there are four different domains with different rock properties, including upper caprock, middle caprock, target saline aquifer, and lower bedrock in Fig. 6. The thicknesses of the four domains are 1200 m, 100 m, 200 m, and 1500 m, respectively. The upper caprock which is near the ground surface has a

 Table 1

 Detailed subdivision of the grid cell number in x, y, and z direction in the conceptual model.

Direction	Number of grid cell	Length(m)
х	10	1600
х	10	800
х	10	400
х	10	200
х	10	100
х	101	50
х	10	100
х	10	200
х	10	400
х	10	800
х	10	1600
У	1	1
Z	10	60
Z	10	40
Z	10	20
Z	30	10
Z	10	20
Z	10	40
Z	20	45

relatively higher permeability of 0.3 \times 10⁻¹⁵ m². The middle caprock and lower bedrock have the same hydrological parameters with a lower original permeability of 0.3 \times 10⁻¹⁷ m² and lower original porosity of 0.0094 to seal the potential saline aquifer for CO₂ storage. The target saline aquifer, which is located at the middle of the conceptual model, has a larger permeability of $0.3 \times 10^{-13} \text{ m}^2$ (30 mD) and a larger porosity of 0.094. This can result in a large pore volume to storage large amount of supercritical CO_2 gas in the saline aquifer. The CO₂ injection well is located at the point (33,520 m, 1495 m), which is close to the center of the conceptual model and at the bottom of the target saline aquifer. The initial temperature, pressure and mean stress at the injection point are 47.38 °C, 1.4765 \times 10⁷ Pa, and 2.40 \times 10⁷ Pa, respectively. The injection well is located the area which can keep CO₂ gas in a supercritical condition. The effective mean stress is 0.9235×10^7 Pa. For the second case, there are five different domains with five different rock properties, including upper caprock, middle caprock, fault, target saline aquifer, and lower bedrock in Fig. 7. The fault is introduced by a stress weakness zone as domain 5 in Fig. 7, which is created into the middle caprock by means of a vertical fault zone. It is located between (33,580 m, 1200 m) and (33,580 m, 1300 m) with a horizontal width of 100 m and vertical length of 100 m. The initial permeability of the fault is set to be the same as the surrounding middle caprock, and it is set to be more porous with a larger porosity of 0.05. The relationships of porosity-stress and permeability-stress are more sensitive. The hydrological and stressrelated parameters for each domain are listed in Table 2.

The injection rate of supercritical CO_2 is kept constant at 0.05 kg/ s. The supercritical CO₂ is keeping injected for 30 years in the both cases of the conceptual model. The aquifer pressure will increase significantly with time increasing, under such an injection rate. In the previous study (Rutqvist and Tsang, 2002), the supercritical CO₂ continues to be injected into the target saline aquifer till the pore pressure becomes bigger than the lithostatic stress of the target saline aquifer after about 10 years' injection. The geomechanical behavior needs to be investigated when a risk is identified to trigger fractures due to CO₂ injection. In the study, it intends to study not only the geomechanical behavior due to supercritical CO₂ injection for a short period, but also the geochemical behavior due to CO₂ storage for a long term. Therefore, the horizontal length of the conceptual model provides the supercritical CO₂ enough space to spread into the target aquifer due to 30 years' injection without the potential to induce a fracture.

The isotropic geomechanical rock properties are represented by functions of porosity and mean stress, permeability and porosity. The functions They are given by Eqs. (23) and (28). The function of the capillary pressure scaling is given by Eq. (29). It is a scaling of the van-Genuchtens air-entry pressure from the values at zero stress to an initial in-situ air-entry pressure given in Table 2.

In the two cases designed for the conceptual model, there are four rock domains in the first case with different values of porosity, permeability and stress-related parameters, and there are five rock domains in the second case with different values of porosity, permeability and stress-related parameters. Therefore, the heterogeneous simulation domains for geomechanical calculation are presented in the two cases of the conceptual model. Based on the number of the equations to be solved in this conceptual model, and the potential convergence problem may occur when additional geochemical heterogeneity for different domains are taken into account in the conceptual model. It is assumed that the model is a homogeneous reservoir in terms of rock compositions, which means all the five domains have the same mineral compositions. Furthermore, a generalized rock mineral composition is assigned to all the simulation domains. The initial mineral abundances are shown in Table 3. The rock minerals selected in this conceptual



Fig. 6. Conceptual model profile along the vertical section with four different simulation domains.



Fig. 7. Conceptual model profile along the vertical section with five different simulation domains.

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Material	properties	for five	simulation	domains	in the	two conce	ptual r	nodels	(Rutc	vist an	d Tsans	g, 2002).
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Domain number	1	2	3	4	5
Young's modulus, E (Pa)	5×10^9	$5 imes 10^9$	$5 imes 10^9$	$5 imes 10^9$	$2.5 imes 10^9$
Poisson's ratio, v	0.25	0.25	0.25	0.25	0.25
Biot's parameter, α	1	1	1	1	1
Rock density, ρ_s (kg/m ³)	2260	2260	2260	2260	2260
Zero stress porosity, ϕ_0	0.1	0.01	0.1	0.01	0.1
Residual porosity, ϕ_r	0.09	0.009	0.09	0.009	0.05
Original porosity, ϕ	0.094	0.0094	0.094	0.0094	0.054
Zero stress permeability, k_0 (m ²)	1×10^{-15}	1×10^{-17}	1×10^{-13}	1×10^{-17}	1×10^{-12}
Original permeability, k (m ²)	$0.3 imes 10^{-15}$	$0.3 imes 10^{-17}$	$0.3 imes 10^{-13}$	0.3×10^{-17}	0.3×10^{-17}
Corey's irreducible gas saturation, S _{rg}	0.05	0.05	0.05	0.05	0.05
Corey's irreducible liquid saturation, S _{rl}	0.3	0.3	0.3	0.3	0.3
van Genuchten's air-entry pressure, P ₀ (Pa)	1.96×10^{5}	3.1×10^{6}	1.96×10^4	3.1×10^{6}	1×10^3
van Genuchten's exponent, m	0.457	0.457	0.457	0.457	0.457

Table 3

Initial volume fractions of primary minerals in the model and potential secondary minerals.

Mineral	Chemical compositions	Volume fraction
Primary mineral		
Quartz	SiO ₂	59.181
Calcite	CaCO ₃	1.929
Oligoclase	CaNa4Al6Si14O40	10.662
Smectite-Na	Na _{0.29} Mg _{0.26} Al _{1.77} Si _{3.97} O ₁₀ (OH) ₂	8.003
Chlorite	Mg _{2.5} Fe _{2.5} Al ₂ Si ₃ O ₁₀ (OH) ₈	10.031
Kaolinite	$Al_2Si_2O_5(OH)_4$	2.015
K-feldspar	KAlSi ₃ O ₈	8.179
Secondary mineral		
Magnesite	MgCO ₃	0.0
Low-albite	NaAlSi ₃ O ₈	0.0
Siderite	FeCO ₃	0.0
Ankerite	$CaMg_{0.3}Fe_{0.7}(CO_3)_2$	0.0
Dawsonite	NaAlCO ₃ (OH) ₂	0.0
Smectite-Ca	Ca _{0.145} Mg _{0.26} Al _{1.77} Si _{3.97} O ₁₀ (OH) ₂	0.0
Total		100%

model is commonly encountered in the potential saline aquifers at North America, such as Gulf Coast sediments, Paradox basin in Colorado plateau. The initial concentrations of primary chemical species are under equilibrium condition with the rock minerals in the saline aquifer. The initial total concentrations of primary chemical species in the system are given in Table 4. Among the minerals, calcite is set to be under local equilibrium because of its fast reaction rate. Dissolution and precipitation of other minerals are under kinetic condition. The parameters related to kinetic chemical reaction rate are listed in Table 5.

4.2. Hydrological effects and mechanical effects: structural trapping

Fig. 8 presents the saturation contour profile of supercritical CO₂

Table 4Initial total concentrations for primary chemical species.

Chemical species	Concentration (mol/l)
H^+	0.4320×10^{-1}
Na ⁺	0.989
K ⁺	0.596×10^{-2}
Ca ²⁺	0.473×10^{-2}
Mg^{2+}	0.267×10^{-4}
HCO ₃	0.456×10^{-1}
Cl ⁻	1.015
SO_4^{2-}	0.132×10^{-8}
SiO ₂ (aq)	0.103×10^{-2}
AlO ₂	0.136×10^{-7}
Fe ²⁺	0.302×10^{-6}

gas for 30 years' CO₂ injection. Fig. 8 (a) indicates that the supercritical CO₂ gas starts to transport from the injection point (33,520 m, 1495 m) to the bottom of the caprock after 1 year's injection period, with a horizontal distance of 400 m for the spread. The plume of supercritical CO_2 is not formed yet at this period. The shape of the supercritical CO₂ gas phase in the saline aquifer is like a wick of a lighted candle. The supercritical CO₂ gas saturation is decreasing gradually from the inward to the outward of the wick. The largest CO₂ gas saturation in the target saline aquifer is 0.45 in the middle (Fig. 8 (a)). After 3 years, the plume of supercritical CO₂ gas is being formed gradually, and majority of the supercritical CO₂ gas tends to accumulate below the bottom of the middle caprock due to low permeability (1 \times 10⁻¹⁷ m²). The plume of the supercritical CO₂ gas has a maximum diameter of 1400 m under the bottom of the middle caprock. The intrinsic permeability of the middle caprock in the conceptual model is larger than the one used in the previous model, therefore the supercritical CO_2 gas phase may penetrate into the middle caprock. The supercritical CO₂ gas penetrates into the middle caprock about 20 m after 3 years CO₂ injection (Fig. 8 (b)). The maximum supercritical CO₂ gas saturation is about 0.6 at the injection point of the target saline aquifer, and the diameter of the CO₂ plume gradually increases from the bottom to the top of the saline aquifer. The supercritical CO_2 gas tends to transport upwards rapidly, because the low density and viscosity of CO₂ results in strong buoyant flow. Then, the plume continues to enlarge within 5 years' CO₂ injection (Fig. 8 (c)). The maximum diameter is 2300 m under the middle caprock, and the maximum CO₂ saturation is about 0.7 around the injection point. The gas saturation is about 0.6 under the bottom edge of the middle caprock, which means that the majority of the CO₂ gas accumulates under the middle caprock. The supercritical CO₂ gas penetrates into the middle caprock about 40 m after 5 years' injection (Fig. 8 (c)). At 10 years, the plume of CO₂ is under the middle caprock over 4600 m and penetrates into the caprock by about 80 m (Fig. 8 (d)). The maximum saturation is about 0.85 around the injection point in the target saline aquifer. The supercritical CO₂ gas saturation tends to be about 0.65 under the bottom edge of the middle caprock, which means that the majority of the CO₂ gas accumulates under the middle caprock and the supercritical CO₂ gas continues to transport upwards into the middle caprock domain. Furthermore, the supercritical CO₂ keeps injected for 20 years (Fig. 8 (e)), and the supercritical CO₂ has spread under the middle caprock over 8400 m, penetrated through the caprock, and escaped to the upper caprock domain about 10 m. The maximum CO₂ saturation is about 1.0 around the injection point in the target saline aquifer, and the supercritical CO₂ gas saturation tends to be about 0.75 under the bottom edge of the middle caprock. After 30 years, the spread of CO₂ has become a big mushroom under the middle caprock over

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Table 5	
Kinetic parameters for mineral dissolution and precipitation (Xu et al., 2004c).	

Mineral	Α	Parameters for kinetic rate law							
	(cm^2/g)	Neutral mechanisn	ı	Acid mechanism			Base mechanism		
		K_{25} (mol/m ² ·s)	Ea (KJ/mol)	K ₂₅	Ea	<i>n</i> (H ⁺)	K ₂₅	Ea	<i>n</i> (H ⁺)
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	8.913×10^{-18}	17.9	-0.472
Calcite	9.8	1.549×10^{-6}	23.5	$5.012 imes 10^{-1}$	14.4	1.0			
Illite	151.6	1.660×10^{-13}	35.0	1.047×10^{-11}	22.6	0.34	2.020×10^{-17}	58.9	-0.4
Oligoclase	9.8	1.445×10^{-12}	69.8	$2.138 imes 10^{-10}$	65	0.457			
K-feldspar	9.8	2.890×10^{-13}	38.0	8.710×10^{-11}	51.7	0.5	6.310×10^{-12}	94.1	-0.823
Na-smectite	151.6	1.660×10^{-13}	35.0	1.047×10^{-11}	22.6	0.34	2.020×10^{-17}	58.9	-0.4
Chlorite	9.8	2.020×10^{-13}	88.0	7.762×10^{-12}	88	0.5			
Magnesite	9.8	4.571×10^{-10}	22.5	4.169×10^{-7}	14.4	1.0			
Dolomite	9.8	2.951×10^{-8}	52.2	$6.457 imes10^{-4}$	36.1	0.5			
Low-albite	9.8	2.754×10^{-13}	69.8	6.918×10^{-11}	65.0	0.457	2.512×10^{-16}	71	-0.572
Siderite	9.8	1.260×10^{-9}	62.76	$6.457 imes 10^{-4}$	36.1	0.5			
Ankerite	9.8	1.260×10^{-9}	62.76	$6.457 imes 10^{-4}$	36.1	0.5			
Dawsonite	9.8	1.260×10^{-9}	62.76	6.457×10^{-4}	36.1	0.5			
Ca-smectite	151.6	1.660×10^{-13}	35.0	1.047×10^{-11}	22.6	0.34	2.020×10^{-17}	58.9	-0.4

12,400 m and has transported upwards into the upper caprock by 50 m (Fig. 8 (f)). The maximum CO_2 saturation is about 1.0 around the injection point in the target saline aquifer, and the supercritical CO_2 gas saturation tends to be about 0.8 under the bottom edge of the middle caprock. Finally, Fig. 9 shows the plume of the CO_2 in the target aquifer and caprock for six injection periods. The stability and integrity of the caprock plays a key role as a barrier of CO_2 fluid, where the supercritical CO_2 gas would arrive after a certain amount of time.

Fig. 10 present the saturation contour profile of supercritical CO₂ gas in Case 2 for 30 years' CO₂ injection. Fig. 10 (a) indicates that the supercritical CO₂ gas starts to leak through the fault induced by CO₂ injection. After 3 years' CO₂ injection, the plume of supercritical CO₂ gas is being formed gradually, and the supercritical CO₂ continues to leak through the fault. With CO₂ injection, the pressure increases gradually below the middle caprock where the fault is located. The fault continues to open gradually. From Fig. 10 (b), it is obvious that the CO₂ gas penetrates through the fault, and transports into the upper caprock, which has a larger permeability of 1×10^{-15} m². The shape of the whole CO_2 gas saturated area is like a flower. The fault has a width of 100 m, and surrounding rocks with a lower permeability. After supercritical CO₂ reaches the upper caprock, the plume of CO₂ in the upper caprock continues to enlarge with the continuous CO_2 injection (Fig. 10 (c-f)). Fig. 11 shows the plume of the CO₂ gas in the target aquifer and caprock for 30 years' CO₂ injection.

Figs. 12 and 13 show the contour of pore pressure, mean stress and volumetric strain in the vertical direction for both Case 1 without fault and Case 2 with fault at 10 years. Based on the isopressure and iso-tress curves, the mean effective stress can be calculated. The simulation results indicate that the significant increase in pore pressure leads to the decrease of the mean effective stresses in the caprock and aquifer. The largest changes of effective stress happen at the bottom of the caprock and top of the bedrock. At the injection point, the mean effective stress has decreased by 5.6×10^6 Pa after 10 years' CO₂ injection. The change of effective stress is less than that of the pore pressure, because CO₂ injection increases the mean stress. Fig. 12 shows the simulated results for Case 1 without fault after 10 years' CO₂ injection. The pressure propagates mainly along the bottom of caprock. The pressure, the mean stress, and volumetric strain reach the peak value at the injection point and propagate into the surrounding, but do not break through the caprock before 10 years. After this, the pressure, the mean stress, and volumetric strain start to break through the middle caprock into upper caprock with the continuous CO₂ injection till 30 years. Fig. 13 shows the simulated results for Case 2 with fault after 10 years' CO₂ injection, pressure, the mean stress and volumetric strain reach the maximum value at the injection site, and then propagate to the surrounding, and more importantly, the changes are along both the bottom of middle caprock and the fault. Comparing the changes of ground uplift and pressure at the injection site with time for both cases, it is indicated that the existing of fault cause much more changes of pore pressure and much bigger ground uplift.

The changes of the mean stresses in the layered formation leads to a vertical expansion of the rock. The increases of the pore pressure changes mean stress and volumetric strain. The uplift of the formation can be calculated from volumetric strain changes by summation over z direction grid block columns and the assumption of strain isotropy. The uplifts of the formation surface are shown in Fig. 14 for Case 1 without fault and Fig. 15 for Case 2 with fault. The expansion of formation occurs in the aquifer. Fig. 14 indicates that the maximum uplift is around 1.2 m for the layered formation without faut after 30 years' CO₂ injection. In addition, the expansion of formation occurs not only in the aquifer but also in the caprock because of the fault. The uplift in Case 2 shall be greater then that in Case 1. Fig. 15 indicates that the maximum uplift is about 1.8 m for the layered formation without faut after 30 years' CO₂ injection.

4.3. Permeability and porosity change by mechanical effects

Figs. 16 and 17 show the pressured induced permeability change and porosity change for Case 1 during 30 years' CO₂ injection period. The permeability change in the formation is proportional to the pressure and stress increase, and the porosity change is proportional to permeability change. The largest changes in permeability occurs in the top boundary of the aquifer. The permeability ratio is the ratio between the pressure induced permeability and intrinsic permeability, and the porosity ratio is the ratio between the pressure induced porosity and original porosity. The permeability has increased by a factor of about 3.3 near the top boundary of the aquifer. Correspondingly, and the porosity has increased by a factor of about 1.06 near the top boundary of the aquifer. Figs. 18 and 19 show the pressure induced permeability change and porosity change for Case 2 during 30 years' CO₂ injection period. The two figures only show the permeability and porosity change in the fault. Both the length and width of fault are 100 m. The



Fig. 8. Saturation contour profile of the supercritical CO₂ gas in the target saline aquifer for Case 1 during 30 years' injection period: (a) 1 year, (b) 3 years, (c) 5 years, (d) 10 years, (e) 20 years and (f) 30 years.

permeability and porosity ration are displayed within the range of 100 m. The stress weakness is induced with the fault, which causes the mean stress increase significantly. This phenomenon can be

observed from the mean stress profile in Figs. 12 and 13. The permeability is proportional to the effective mean stress. Therefore, the permeability change in the fault domain is significant. The



Fig. 9. Spread of the supercritical CO₂ gas in the target saline aquifer for Case 1 during 30 years injection period (curves from inward to outward: 1 year, 3 years, 5 years, 10 years, 20 years and 30 years).

permeability has increased by a factor of 325 and the porosity has increased by a factor of about 1.84.

4.4. Phase equilibrium and chemical equilibrium: solubility trapping

Within a long term storage time, the dissolved CO₂ in aqueous phase is consumed by the geochemical reaction between aquifer water and rock mineral, especially for the dissolution/precipitation of the carbonate minerals. The aqueous CO_2 continues to be consumed in aqueous phase, and the CO₂ gas phase continues to be dissolved into aqueous phase. The CO₂ gas saturation continues to decrease in the area of two phase mixture. The area near wellbore is occupied by two phase mixture. Fig. 20 shows the spatial distribution of CO₂ gas saturation during 10,000 years' storage period. Majority of the CO₂ gas accumulates under the middle caprock, which can be observed from Fig. 20 (a-c). After 5000 years, majority of the supercritical CO₂ gas escapes the barrier of middle cparock, and penetrates into the upper caprock, which can be observed from Fig. 20 (d-f). The CO_2 gas is accumulates in the area with a width of 30,000 m and a length of 300 m. The amount of CO₂ gas starts to decrease and some of CO₂ gas continues to move upwards at the same time. After 10,000 years, the CO₂ gas saturation decrease to 0.1 because of the chemical reaction.

Dissolution of the free phase CO₂ in aquifer water is caused by the geochemical reaction between water and CO₂. This chemical reaction is believed as the fastest reaction and always set as equilibrium condition. It generates the aqueous chemical species of H⁺, H_2CO_3 , HCO_3^- , and CO_3^{2-} . The chemical species H^+ acidizes the aqueous environment and decreases the pH value in the saline aquifer. After the dissolution of free phase CO₂, the two phase mixture area become acidized region, where the pH is less than 7.0. Fig. 21 shows the spatial distribution of pH value during the 10,000 years' CO₂ storage period. The pH value in the plume of CO₂ gas is 4.8 after 30 years' CO₂ injection in Fig. 21 (a). The acidized area by CO₂ dissolution continues to spread with CO₂ moving upwards during CO₂ storage period. After 5000 years, some of the CO₂ gas has already been consumed under the middle caprock. The pH value in the area under the middle caprock is above 7.0 and become alkalized, which is obvious in Fig. 21 (d-f).

4.5. Mineral dissolution and precipitation: mineral trapping

There are seven primary rock minerals and six secondary minerals present in this numerical model. The formation type is sandstone, which is always composed of large amount of quartz, small amount of carbonate minerals, plagioclase feldspar minerals and clay minerals, and minor components. For the geochemical composition in this model, the most common minerals in the potential CO_2 sequestration site from the literature are taken into account. Calcite represents the carbonate minerals. Oligolcase represents the plagioclase feldspar minerals. Chlorite represents the clay minerals. The volume fraction change profiles of the primary and secondary minerals during 3000 years are illustrated in Figs. 22–29.

Dissolution and precipitation of primary minerals: it is obvious to observe the dissolutions of oligoclase, chlorite and calcite in the order of magnitude, and the precipitation of smectite and quartz. Figs. 22-26 show the volume fraction evolutions of these rock minerals during 10,000 years' storage period. The dissolution happens in two areas in saline aquifer and in upper caprock. The reactivity in the middle caprock is not significant due to the small porosity and permeability of the middle caprock. Fig. 22 shows the dissolution of the oligocalse during the storage period. The maximum volume fraction decrease of oligoclase is 1.15 percent after 500 years (Fig. 22 (a)), 1.95 percent after 1000 years (Fig. 22 (b)), 2.90 percent after 3000 years (Fig. 22 (c)), and 3.95 percent after 5000 years (Fig. 22 (d)), 5.35 percent after 8000 years (Fig. 22 (e)), and 7.45 percent after 10,000 years (Fig. 22 (f)). The dissolution of oligoclase releases large amounts of chemical species (Ca^{2+}). $SiO_2(aq)$, AlO_2^- and Na^+), which supply the chemical species to precipitate albite (NaAlSi₃O₈), dawsonite (NaAlCO₃(OH)₂), and smectite-Na (Na_{0.29} Mg_{0.26} Al_{1.77} Si_{3.97} O₁₀(OH)₂). Fig. 23 shows the dissolution of the chlorite during the storage period. The maximum volume fraction decrease of chlorite is less than 0.1 percent after 500 years (Fig. 23 (a)), 0.62 percent after 1000 years (Fig. 23 (b)), 0.82 percent after 3000 years (Fig. 23 (c)), and 1.12 percent after 5000 years (Fig. 23 (d)), 1.72 percent after 8000 years (Fig. 23 (e)), and 2.12 percent after 10,000 years (Fig. 23 (f)). The dissolution of chlorite releases large amounts of chemical species (Fe²⁺, Mg²⁺, $SiO_2(aq)$, and AlO_2^-), which supply the chemical species to precipitate siderite (FeCO₃) and ankerite (CaMg_{0.3} Fe_{0.7}(CO₃)₂).

Fig. 24 shows the dissolution and precipitation of calcite during the long storage period. It is dissolved in the acidized area and precipitated in the alkalized area under the middle caprock. The volume fraction change of calcite reaches the maximum amounts till 10,000 years (Fig. 24 (e)). The maximum volume fraction increase of calcite is 0.5 percent in the alkalized zone, and the maximum volume fraction decrease is 0.8 percent at the acidized zone. Because the abundance of the chemical species of Mg^{2+} , $SiO_2(aq)$, AlO_2^- and Na^+ released by the dissolutions of oligoclase and chlorite, the smectite is precipitated into rock minerals. Fig. 25 shows the precipitation of smectite-Na during the storage period. The maximum volume fraction increase of smectite-Na is 0.52 percent after 500 years (Fig. 25 (a)), 1.70 percent after 1000 years (Fig. 25 (b)), 2.20 percent after 3000 years (Fig. 25 (c)), and 3.75 percent after 5000 years (Fig. 25 (d)), 5.20 percent after 8000 years (Fig. 25 (e)), and 6.70 percent after 10,000 years (Fig. 25 (f)). Fig. 26 shows the precipitation of quartz during the storage period. Quartz is precipitated with the largest amount in the acidized area under middle caprock during the total storage period of 10,000 years (Fig. 26). The dissolution of primary rock minerals releases large amounts of $SiO_2(aq)$, which make the chemical species $SiO_2(aq)$ supersaturated in the aquifer water, then precipitated into the rock. Quartz continues to precipitate into the mineral phase during 10,000 years' storage time, and the maximum amount of volume



Fig. 10. Saturation contour profile of the supercritical CO₂ gas in the target saline aquifer for Case 2 during 30 years' injection period: (a) 1 year, (b) 3 years, (c) 5 years, (d) 10 years, (e) 20 years and (f) 30 years.

fraction increase is 1.0 percent (Fig. 26 (f)).

Precipitation of secondary minerals: the order of volume fraction increase for secondary minerals are albite, ankerite and dawsonite. Majority of the potential secondary minerals are carbonate minerals except for albite. The precipitation of the secondary rock minerals mainly happens in aquifer and the upper caprock.



Fig. 11. Spread of the supercritical CO₂ gas in the target saline aquifer for Case 2 during 30 years injection period: (curves from inward to outward: 1 year, 3 years, 5 years, 10 years, 20 years and 30 years).

Fig. 27 shows the precipitation of albite during the storage period. The precipitation of albite can be observed after 3000 years. The maximum volume fraction increase of aibite is 1.5 percent after 5000 years (Fig. 27 (d)), 2.75 percent after 8000 years (Fig. 27 (e)), and 4.25 percent after 10,000 years (Fig. 27 (f)). Fig. 28 shows the precipitation of ankerite during the storage period. The majority of the ankerite precipitation occurs in the middle of the CO₂ plume. The maximum volume fraction increase of ankerite is 0.62 percent after 500 years (Fig. 28 (a)), 0.70 percent after 1000 years (Fig. 28 (b)), 0.88 percent after 3000 years (Fig. 28 (c)), and 1.12 percent after 5000 years (Fig. 28 (d)), 1.85 percent after 8000 years (Fig. 28 (e)), and 2.23 percent after 10,000 years (Fig. 28 (f)). Fig. 29 shows the precipitation of dawsonite during the storage period. The majority of the ankerite precipitation occurs in the middle of the CO₂ plume and the upper caprock. The precipitation of albite after 1000 vears. The maximum volume fraction increase of dawsonite is 0.38 percent after 1000 years (Fig. 29 (b)), 0.42 percent after 3000 years (Fig. 29 (c)), and 0.52 percent after 5000 years (Fig. 29 (d)), 0.87 percent after 8000 years (Fig. 29 (e)), and 1.22 percent after 10,000 years (Fig. 29 (f)).

It is indicated that, chlorite and oligoclase play an role important role as primary minerals to permanently trapped CO_2 in the aquifer rock, and the secondary carbonate minerals directly lead to the mineral trapping of injected CO_2 , such as ankerite and dawsonite, especially for long term storage period. Thus, dawsonite and ankerite are the most important minerals for mineral trapping of injected CO_2 . Ca^{2+} , $SiO_2(aq)$, AlO_2^- and Na^+ are the essential chemical species of the secondary silicate and carbonate minerals (i.e., ankerite, smectite-Na, dawsonite and albite) for the mineral trapping of supercritical CO_2 , are released from the dissolution of oligoclase and chlorite.

4.6. Contributions of mineral trapping mechanism

With time increasing, the mineral trapping become dominated and determines the fate of supercritical CO_2 in saline aquifer. As the efficacy is discussed in the previous cases, only the mass of CO_2 sequestrated in rock mineral is shown in this model to locate the places, where CO_2 mineralization occurs in layered formation.

The amounts of CO₂ permanently trapped into mineral phase (i.e., precipitation of the primary and secondary carbonate

minerals) in the saline aquifer are shown in Fig. 30. As time increasing, the mass of CO_2 permanently trapped in mineral phase increases continuously in the acidized area and reaches the maximum amounts in the aquifer and upper caprock due to precipitation of the secondary silicate and carbonate minerals, such as ankerite, dawsonite and albite. The maximum amount of CO_2 stored by mineral trapping is about 20.0 kg/m³ rock after 10,000 years (Fig. 30 (d)).

It is indicated that the precipitated new minerals are mainly in the CO₂ plume of target aquifer and in the upper caprock. The mineral trapping of CO₂ is not significant in the middle caprock compared with the saline aquifer and upper caprock. The permeability and porosity of middle caprock is 0.3×10^{-17} and 0.0094, there is only a small amount of saline water saturated in the middle caprock and CO₂ gas trapped in the pore space. The possibility of chemical reactions is reduced due to the small permeability and porosity. In addition, the CO₂ migrates into upper caprock during long term storage period. The mineralogical composition of the upper rock determines the long term fate of supercritical CO₂ in subsurface. It is obvious that the mineralization of CO₂ gas occurs at the bottom of the upper caprock.

Fig. 31 indicates the temporal changes of the mass fraction of CO₂ trapped by the three mechanisms: structural trapping, solubility trapping and mineral trapping. The fraction of structural trapping starts at 81.7 percent at the beginning of storage period, and then decreases gradually to 54.96 percent after the chemical reaction become dominant with time increasing. The fraction of solubility trapping starts at the maximum 18.34 percent at the beginning of the storage time. The pressure rises up rapidly during the 30 years injection period, then the partial pressure of CO_2 in the aqueous phase increases accordingly, which drives more CO₂ dissolve into the aqueous phase. When the injection stops, long term storage period begins and pressure buildup releases rapidly. The total pressure around the injection area starts to decrease, thus the CO₂ partial pressure decreases successively. A small amount of dissolved CO₂ is released into the gaseous phase again, and a certain amount of dissolved CO₂ is consumed by the mineralization, the contribution of solubility trapping decreases to 9.98 percent till 10,000 years. Finally, the mineral trapping become dominant in the long term storage time, which is shown in the black line of 31. In particular, the fraction of mineral trapping increases slowly at the first 100 years' storage period, and then it is increasing rapidly till 10,000 years. At the beginning of the storage time, various chemical species (i.e., Fe²⁺, Mg²⁺, Ca²⁺, etc.) release into the aqueous phase, the previous established chemical equilibrium state is broke. Alternations of rock minerals become dominated after these chemical species become supersaturated in the aqueous phase. A new stable state is achieved when the supply of aqueous CO₂ is sufficient for the kinetic reactions in the acidized area, then the fraction of mineral trapping increases stably to 35 percent. In the previous literature, the researcher has presented a general sketch of the evolution of trapping mechanisms over time (IPCC 2005). Fig. 31 gives a quantitative view of the contribution of the three mechanisms. The area under the black line represents the contribution of mineral trapping, the middle area between the black and red lines is the contribution of solubility trapping, and the top area is the contribution of structural and residual trapping. It is indicated that the chemical reaction is the most dominated trapping mechanism in the long term storage period.

4.7. Effects of oligoclase and chlorite presences on mineral trapping

We investigate the effects of volume fraction changes of oligoclase and chlorite on the mineral trapping of CO₂. Based on the mineral compositions in the model, three additional cases are run



Fig. 12. Pressure, mean stress and volumetric strain contour profile for Case 1 after 10 years' injection period: (a) pressure contour; (b) iso-pressure line; (c) mean stress contour; (d) iso-stress line; (e) strain contour; (f) iso-strain line.

to study the sensitivity of oligoclase fraction. The volume fraction of oligoclase is increased by 5 percent in each case, and the volume fraction of quartz is decreased by 5 percent. The sensitivity study of chlorite has the same scenario with oligoclase. The temporal

changes of the CO_2 trapped by the mineralization in terms of the volume fraction changes of oligoclase and chlorite are shown in Figs. 32 and 33. Fig. 32 shows that the contribution of mineral trapping increases to 53.21 percent due to the abundance of



Fig. 13. Pressure, mean stress and volumetric strain contour profile for Case 2 after 10 years' injection period: (a) pressure contour; (b) iso-pressure line; (c) mean stress contour; (d) iso-stress line; (e) strain contour; (f) iso-strain line.

oligoclase (25.662%). When the volume fraction of oligoclase increases by 5 percent, the contribution of mineral trapping increases by about 6 percent. Because of sufficient Na^+ , $SiO_2(aq)$, and AlO_2^-

releasing in to aqueous phase at the late of storage period, the gaseous CO_2 continues to be trapped by the alternation of rock minerals. Fig. 33 shows that the contribution of mineral trapping



Fig. 14. The vertical displacement of the ground surface caused by 30 years' CO_2 injection for Case 1.



Fig. 15. The vertical displacement of the ground surface caused by 30 years' CO_2 injection for Case 2.

increases to 45.53 percent due to the abundance of chlorite (25.031%). When the volume fraction of chlorite increases by 5 percent, the contribution of mineral trapping increases by about 3 percent. Because of sufficient Mg^{2+} , Fe^{2+} , $SiO_2(aq)$, and AlO_2^- releasing in to aqueous phase at the late of storage period, the gaseous CO₂ continues to be trapped by the alternation of rock minerals. It is indicated from the simulation results that the chemical reactions dominate the long term storage of CO₂, and the rock mineral compositions play an important role for trapping free phase CO₂ in saline aquifer. The volume fractions of oligoclase and chlorite present in the rock have significant impact on the trapping contribution of the three mechanisms.

5. Concluding marks

The significance of THMC process interactions during CO_2 geosequestration has been well recognized in the perspectives of field scale and pore scale. Chemical reaction is the most complex process among the THMC processes. The rock minerals, which play a major key role in the trapping mechanisms, are identified. A novel mathematical model of the THMC processes is developed. A computational framework, sequentially coupled, is proposed and used to simulate reactive transport of supercritical CO₂ in subsurface formation with geo-mechanics. The novel frameworks are designed to keep a generalized computational structure, which can be easily applied for the numerical simulation of other THMC processes. Finally, a 2D reactive transport model is presented to analyze the THMC processes quantitatively, especially the coupled effects of geo-chemical reactions and geo-mechanics on CO₂ geo-sequestration, the long term fate of CO₂ and its sensitivity mineralogical compositions with respect to key minerals. The numerical simulation results have indicated that.

- For the formation with heterogeneous domains (upper caprock, middle caprock, saline aquifer and lower bedrock), pore pressure and mean stress increase significantly under the middle caprock, that may lead to rock failure. The upward migration of supercritical CO₂ speeds up through permeable faults, created by geomechanical permeability and porosity increase. The mineral trapping of supercritical CO₂ mainly occurs in upper caprock saline aquifer. The possibility of chemical reaction is reduced due to the small permeability and porosity of middle caprock and the small amounts of saturated water in middle caprock.
- Important geochemical reactions leading to favorable mineral trapping of CO_2 include dissolution of plagioclase feldspar and chlorite minerals, which release large amounts of chemical species Fe^{2+} , Mg^{2+} , Na^+ , AlO_2^- and $SiO_2(aq)$, the precipitations of carbonate and silicate minerals, such as dawsonite, albite and ankerite, which combine metal ions with bicarbonate together to consume more supercritical CO_2 gas. The long term fate of supercritical CO_2 under the subsurface is to be sequestrated in the rock mineral permanently in the forms of carbonate minerals.
- In terms of the efficacy for the trapping mechanisms, structural trapping is the dominated mechanism during supercritical CO₂ injection period, and mineral trapping dominates during long term storage period. In a typical sandstone formation, with 60 percent quartz, 20 percent plagioclase feldspar minerals, 10 percent chlorite minerals, and 10 percent clay minerals, the efficacy of solubility trapping is 18.34 percent at the early injection period, which decreases to 9.98 percent after 10,000 years; the efficacy of mineral trapping is zero percent at early injection period, which increases to 35 percent after 10,000 years.
- Rock mineral compositions of the potential formation of CO₂ geo-sequestration play a significant role on the geochemical behavior of supercritical CO₂, trapping mechanism and their efficacies. Oligoclase and chlorite are two key rock minerals as representatives of plagioclase feldspar minerals and chlorite minerals, which are the common rock forming minerals in sandstone. The efficacies of mineral trapping increases with the increasing volume fractions of oligoclase and chlorite. In sandstone aquifer, the efficacy of mineral trapping increases by 5 percent when the volume fraction of oligoclase increases by 5 percent. The contribution of mineral trapping increases to 53.21 percent due to the abundance of oligoclase (25.662%) When the volume fraction of chlorite increases by 5 percent, the contribution of mineral trapping increases by about 3 percent. The contribution of mineral trapping increases to 45.53 percent due to the abundance of chlorite (25.031%)
- The limitations of this simulator are as follows: it does not have the capability to simulation non-aqueous chemical reactions, i.e. the geochemical reactions between supercritical CO₂ and rock minerals. It does not have the capability to solve the shear stress,



Fig. 16. Permeability change ratio profile for Case 1 after 30 years' injection period: (a) 1 year; (b) 3 years; (c) 5 years; (d) 10 years; (e) 20 years; (f) 30 years.

since a simplified mean stress equation is taken in account in this paper. Vertical displacement can be obtained as the results of the mean stress calculation. Stress failure cannot be predicted. Furthermore, it may require much more runtime for a certain simulation case, since the chemical reaction is coupled together with geomechanics in the same simulator.



Fig. 17. Porosity change ratio profile for Case 1 after 30 years' injection period: (a) 1 year; (b) 3 years; (c) 5 years; (d) 10 years; (e) 20 years; (f) 30 years.



Fig. 18. Permeability change ratio profile for Case 2 after 30 years' injection period: (a) 1 year; (b) 3 years; (c) 5 years; (d) 10 years; (e) 20 years; (f) 30 years.



Fig. 19. Porosity change ratio profile for Case 2 after 30 years' injection period: (a) 1 year; (b) 3 years; (c) 5 years; (d) 10 years; (e) 20 years; (f) 30 years.

Fig. 20. CO2 gas saturation profile during 10,000 years' storage period: (a) 100 years; (b) 500 years; (c) 3000 years; (d) 5000 years; (e) 8000 years; (f) 10,000 years.

Fig. 21. The pH value profile during 10,000 years' storage period: (a) 30 years; (b) 500 years; (c) 1000 years; (d) 5000 years; (e) 8000 years; (f) 10,000 years.

Fig. 22. The volume fraction change of oligoclase during 10,000 years' storage period: (a) 500 years; (b) 1000 years; (c) 3000 years; (d) 5000 years; (e) 8000 years; (f) 10,000 years.

Fig. 23. The volume fraction change of chlorite during 10,000 years' storage period: (a) 500 years; (b) 1000 years; (c) 3000 years; (d) 5000 years; (e) 8000 years; (f) 10,000 years.

Fig. 24. The volume fraction change of calcite during 10,000 years' storage period: (a) 30 years; (b) 1000 years; (c) 3000 years; (d) 5000 years; (e) 8000 years; (f) 10,000 years.

Fig. 25. The volume fraction change of smectite-Na during 10,000 years' storage period: (a) 500 years; (b) 1000 years; (c) 3000 years; (d) 5000 years; (e) 8000 years; (f) 10,000 years.

Fig. 26. The volume fraction change of quartz during 10,000 years' storage period: (a) 500 years; (b) 1000 years; (c) 3000 years; (d) 5000 years; (e) 8000 years; (f) 10,000 years.

Fig. 27. The volume fraction change of albite during 10,000 years' storage period: (a) 500 years; (b) 1000 years; (c) 3000 years; (d) 5000 years; (e) 8000 years; (f) 10,000 years.

Fig. 28. The volume fraction change of ankerite during 10,000 years' storage period: (a) 500 years; (b) 1000 years; (c) 3000 years; (d) 5000 years; (e) 8000 years; (f) 10,000 years.

Fig. 29. The volume fraction change of dawsonite during 10,000 years' storage period: (a) 500 years; (b) 1000 years; (c) 3000 years; (d) 5000 years; (e) 8000 years; (f) 10,000 years.

Fig. 30. The amount of CO₂ sequestrated in rock mineral during 10,000 years' storage period: (a) 500 year; (b) 1000 years; (c) 3000 years; (d) 5000 years; (e) 8000 years; (f) 10,000 years.

Fig. 31. Trapping contribution of CO₂(gas) during 10,000 years' CO₂ storage period.

Fig. 32. Mineral trapping contribution of $CO_2(gas)$ relative to the volume fraction of oligoclase during 10,000 years' CO_2 storage period.

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References

- Ague, J.J., Brimhall, G.H., 1989. Geochemical modeling of steady state fluid flow and chemical reaction during supergene enrichment of porphyry copper deposits. Econ. Geol. 84 (3), 506–528. http://economicgeology.org/content/84/3/506. abstract.
- Appelo, C.A.J., 1994. Cation and proton exchange, ph variations, and carbonate reactions in a freshening aquifer. Water Resour. Res. 30 (10), 2793–2805. http:// dx.doi.org/10.1029/94WR01048.

Fig. 33. Mineral trapping contribution of CO₂(gas) relative to the volume fraction of chlorite during 10,000 years' CO₂ storage period.

- Audigane, P., Gaus, I., Czernichowski-Lauriol, I., Pruess, K., Xu, T., 2007. Twodimensional reactive transport modeling of co_2 injection in a saline aquifer at the Sleipner site, North Sea. Am. J. Sci. 307 (7), 974–1008.
- Balashov, V.N., Guthrie, G.D., Hakala, J.A., Lopano, C.L., Rimstidt, J.D., Brantley, S.L., 2013. Predictive modeling of co₂ sequestration in deep saline sandstone reservoirs: impacts of geochemical kinetics. Appl. Geochem. 30, 41–56.
- Bethke, C.M., 2002. The Geochemists Workbench Release 4.0: a Users Guide to Rxn, Act2, Tact, React, and Gtplot.
- Cederberg, G.A., Street, R.L., Leckie, J.O., 1985. A groundwater mass transport and equilibrium chemistry model for multicomponent systems. Water Resour. Res. 21 (8), 1095–1104. http://dx.doi.org/10.1029/WR021i008p01095.
- Davies, J.P., Davies, D.K., 2001. Stress-dependent permeability: characterization and modeling. SPE J. 6 (2), 224–235.
- Delshad, M., Pope, G.A., Sepehrnoori, K., 1996. A compositional simulator for modeling surfactant enhanced aquifer remediation, 1 formulation. J. Contam. Hydrol. 23 (4), 303–327. http://www.sciencedirect.com/science/article/pii/ 0169772295001069.
- Engesgaard, P., Kipp, K.L., 1992. A geochemical transport model for redox-controlled movement of mineral fronts in groundwater flow systems: a case of nitrate removal by oxidation of pyrite. Water Resour. Res. 28 (10), 2829–2843. http:// dx.doi.org/10.1029/92WR01264.
- Feely, R.A., Sabine, C.L., Lee, K., Berelson, W., Kleypas, J., Fabry, V.J., Millero, F.J., 2004. Impact of anthropogenic CO₂ on the CaCO₃ system in the oceans. Science 305 (5682), 362–366. http://www.sciencemag.org/content/305/5682/362.abstract.
- Gaus, I., Azaroual, M., Czernichowski-Lauriol, I., 2005. Reactive transport modelling of the impact of CO₂ injection on the clayey cap rock at Sleipner (North Sea). Chem. Geol. 217 (34), 319–337. http://www.sciencedirect.com/science/article/ pii/S0009254105000197.
- Gunter, W.D., Perkins, E.H., Hutcheon, I., 2000. Aquifer disposal of acid gases: modelling of water – rock reactions for trapping of acid wastes. Appl. Geochem. 15 (8), 1085–1095.
- Hitchon, B., 1996. Aquifer Disposal of Carbon Dioxide: Hydrodynamic and Mineral Trapping: Proof of Concept. Geoscience Pub.
- IPCC, 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Cambridge University Press, New York, NY, USA.
- IPCC, 2007. Climate Change 2007: the Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Johnson, J.W., Nitao, J.J., Knauss, K.G., 2001. Reactive transport modeling of CO₂ storage in saline aquifers to elucidate fundamental processes, trapping mechanisms and sequestration partitioning. In: The First National Conference on Carbon Sequestration, May 14–17, 2001, Washington, DC.
- Ketzer, J.M., Iglesias, R., Einloft, S., Dullius, J., Ligabue, R., De Lima, V., 2009. Waterrock-CO₂ interactions in saline aquifers aimed for carbon dioxide storage: experimental and numerical modeling studies of the rio bonito formation (permian), southern Brazil. Appl. Geochem. 24 (5), 760–767.
- Kharaka, Y.K., Gunter, W.D., Aggarwal, P.K., Perkins, E.H., DeBraal, J.D., 1989. SOL-MINEQ. 88: a Computer Program for Geochemical Modeling of Water-rock Interactions. US Geological Survey Menlo Park, California.
- Kihm, J., Kim, J., Wang, S., Xu, T., 2012. Hydrogeochemical numerical simulation of impacts of mineralogical compositions and convective fluid flow on trapping mechanisms and efficiency of carbon dioxide injected into deep saline sandstone aquifers. J. Geophys. Res. Solid Earth (1978–2012) 117 (B6).

- Knauss, K.G., Johnson, J.W., Steefel, C.I., 2005. Evaluation of the impact of CO₂, cocontaminant gas, aqueous fluid and reservoir rock interactions on the geologic sequestration of CO₂. Chem. Geol. 217 (3), 339–350.
- Kohl, T., Evansi, K., Hopkirk, R., Rybach, L., 1995. Coupled hydraulic, thermal and mechanical considerations for the simulation of hot dry rock reservoirs. Geothermics 24 (3), 345–359.
- Lasaga, A.C., 1984. Chemical kinetics of water-rock interactions. J. Geophys. Res. 89 (B6), 4009–4025.
- Lasaga, A.C., Soler, J.M., Ganor, J., Burch, T.E., Nagy, K.L., 1994. Chemical weathering rate laws and global geochemical cycles. Geochim. Cosmochim. Acta 58 (10), 2361–2386.
- Liu, C.W., Narasimhan, T.N., 1989. Redox-controlled multiple-species reactive chemical transport: 1. model development. Water Resour. Res. 25 (5), 869–882. http://dx.doi.org/10.1029/WR025i005p00869.
- Liu, F., Lu, P., Zhu, C., Xiao, Y., 2011. Coupled reactive flow and transport modeling of CO₂ sequestration in the Mt. Simon sandstone formation, midwest USA. Int. J. Greenh. Gas Control 5 (2), 294–307.
- Longuemare, P., Mainguy, M., Lemonnier, P., Onaisi, A., Gérard, C., Koutsabeloulis, N., 2002. Geomechanics in reservoir simulation: overview of coupling methods and field case study. Oil Gas Sci. Technol. 57 (5), 471–483.
- McKee, C.R., Bumb, A.C., Koenig, R.A., 1988. Stress-dependent permeability and porosity of coal and other geologic formations. SPE Form. Eval. 3 (1), 81–91.
- Millero, F.J., 1995. Thermodynamics of the carbon dioxide system in the oceans. Geochim. Cosmochim. Acta 59 (4), 661–677. http://www.sciencedirect.com/ science/article/pii/0016703794003540.
- Minkoff, S.E., Stone, C.M., Bryant, S., Peszynska, M., Wheeler, M.F., 2003. Coupled fluid flow and geomechanical deformation modeling. J. Petrol. Sci. Eng. 38 (1), 37–56.
- Mito, S., Xue, Z., Ohsumi, T., 2008. Case study of geochemical reactions at the nagaoka CO₂ injection site, Japan. Int. J. Greenh. Gas Control 2 (3), 309–318.
- Najafabadi, N.F., Han, C., Delshad, M., Sepehrnoori, K., 2009. Development of a three phase, fully implicit, parallel chemical flood simulator. In: SPE 119002, SPE Reservoir Simulation Symposium, 2–4 February 2009. The Woodlands, Texas. Nguyen, T., 1996. Description of the computer code fracon. Dev. Geotechn. Eng. 79,
- 539–544. Nogrichad L. Tsang, C. Witherspeen, P. 1094. Coupled thermal hydraulic
- Noorishad, J., Tsang, C., Witherspoon, P., 1984. Coupled thermal-hydraulicmechanical phenomena in saturated fractured porous rocks: numerical approach. J. Geophys. Res. Solid Earth (1978–2012) 89 (B12), 10365–10373.
- Orr, J.C., Fabry, V.J., Aumont, O., Bopp, L., Doney, S.C., Feely, R.A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Key, R.M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R.G., Plattner, G.K., Rodgers, K.B., Sabine, C.L., Sarmiento, J.L., Schlitzer, R., Slater, R.D., Totterdell, I.J., Weirig, M.F., Yamanaka, Y., Yool, A., 2005. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437 (7059), 681–686.
- Ostensen, R.W., 1986. The effect of stress-dependent permeability on gas production and well testing. SPE Form. Eval. 1 (3), 227–235.
- Palandri, J.L., Kharaka, Y.K., 2004. A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. Tech. rep., no. OPEN-FILE-2004-1068. In: Geological Survey, Menlo Park, California.
- Parkhurst, D.L., Appelo, C.A.J., et al., 1999. User's Guide to PHREEQC (Version 2): a Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations.
- Parkhurst, D.L., Thorstenson, D.C., Plummer, L.N., 1991. Phreeque: a computer program for geochemical calculations—us geological survey. Water Resour. Invest. 80–90.
- Raistrick, M., Hutcheon, I., Shevalier, M., Nightingale, M., Johnson, G., Taylor, S., Mayer, B., Durocher, K., Perkins, E., Gunter, B., 2009. Carbon dioxide-watersilicate mineral reactions enhance CO₂ storage; evidence from produced fluid measurements and geochemical modeling at the iea weyburn-midale project. Energy Proc. 1 (1), 3149–3155.
- Rutqvist, J., Tsang, C., 2002. A study of caprock hydromechanical changes associated with CO₂-injection into a brine formation. Environ. Geol. 42 (2–3), 296–305.
- Rutqvist, J., Wu, Y.-S., Tsang, C.-F., Bodvarsson, G., 2002. A modeling approach for analysis of coupled multiphase fluid flow, heat transfer, and deformation in fractured porous rock. Int. J. Rock Mech. Min. Sci. 39 (4), 429–442.
- Samier, P., Onaisi, A., de Gennaro, S., et al., 2008. A practical iterative scheme for coupling geomechanics with reservoir simulation. SPE Reserv. Eval. Eng. 11 (05), 892–901.
- Settari, A., Walters, D.A., et al., 2001. Advances in coupled geomechanical and reservoir modeling with applications to reservoir compaction. SPE J. 6 (03), 334–342.
- Šimůnek, J., Suarez, D.L., 1994. Two-dimensional transport model for variably saturated porous media with major ion chemistry. Water Resour. Res. 30 (4), 1115–1133. http://dx.doi.org/10.1029/93WR03347.
- Steefel, C.I., Lasaga, A.C., 1994. A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. Am. J. Sci. 294 (5), 529–592.

- Tran, D., Settari, A., Nghiem, L., et al., 2004. New iterative coupling between a reservoir simulator and a geomechanics module. SPE J. 9 (03), 362–369.
- Walter, A.L., Frind, E.O., Blowes, D.W., Ptacek, C.J., Molson, J.W., 1994. Modeling of multicomponent reactive transport in groundwater: 2. metal mobility in aquifers impacted by acidic mine tailings discharge. Water Resour. Res. 30 (11), 3149–3158. http://dx.doi.org/10.1029/94WR00954.
- Wang, W., Kolditz, O., 2007. Object-oriented finite element analysis of thermohydro-mechanical (THM) problems in porous media. Int. J. Numer. Methods Eng. 69 (1), 162–201.
- Wei, L., 2012. Sequential coupling of geochemical reactions with reservoir simulations for waterflood and EOR studies. SPE J. 30 (6), 469–484.
- White, S.P., Allis, R.G., Moore, J., Chidsey, T., Morgan, C., Gwynn, W., Adams, M., 2005. Simulation of reactive transport of injected CO₂ on the colorado plateau, utah, USA. Chem. Geol. 217 (3–4), 387–405.
- Wigand, M., Carey, J.W., Schütt, H., Spangenberg, E., Erzinger, J., 2008. Geochemical effects of CO₂ sequestration in sandstones under simulated in situ conditions of deep saline aquifers. Appl. Geochem. 23 (9), 2735–2745.
 Winterfeld, P.H., Wu, Y., 2012. A novel fully coupled geomechanical model for co₂
- Winterfeld, P.H., Wu, Y., 2012. A novel fully coupled geomechanical model for co₂ sequestration in fractured and porous brine aquifers. In: XIX International Conference on Water Resources CMWR, pp. 17–22.
- Winterfeld, P.H., Wu, Y., Pruess, K., Oldenburg, C., 2012. Development of an advanced thermal-hydraulic-mechanical model for co₂ storage in porous and fractured saline aquifers. In: Proceedings, TOUGH Symposium 2012 Lawrence Berkeley National Laboratory, Berkeley, California, September 17–19, 2012.
- Wolery, T.J., 1992. EQ3/6: a Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide (Version 7.0). Lawrence Livermore National Laboratory, Livermore, CA.
- Wu, Y.-S., Chen, Z., Kazemi, H., Yin, X., Pruess, K., Oldenburg, C., Winterfeld, P., Zhang, R., 2014. Simulation of Coupled Processes of Flow, Transport, and Storage of CO₂ in Saline Aquifers. Tech. rep.. Trustees Of The Colorado School Of Mines http://www.osti.gov/scitech/servlets/purl/1167349.
- Xiong, Y., Fakcharoenphol, P., Winterfeld, P.H., Zhang, R., Wu, Y.-S., 2013. Coupled geomechanical and reactive geochemical model for fluid and heat flow: application for enhanced geothermal reservoir. In: SPE Reservoir Characterization and Simulation Conference and Exhibition, 16–18 September. UAE. SPE, Abu Dhabi.
- Xu, T., 1996. Modeling Non-isothermal Multicomponent Reactive Solute Transport through Variably Saturated Porous Media. Ph.D. thesis. Civil Engineering School, University of La Coruña, Coruña, Spain.
- Xu, T., Apps, J.A., Pruess, K., 2003. Reactive geochemical transport simulation to study mineral trapping for CO₂ disposal in deep arenaceous formations. J. Geophys. Res. Solid Earth (1978–2012) 108 (B2).
- Xu, T., Apps, J.A., Pruess, K., 2004a. Numerical simulation of co₂ disposal by mineral trapping in deep aquifers. Appl. Geochem. 19 (6), 917–936.
- Xu, T., Apps, J.A., Pruess, K., 2005. Mineral sequestration of carbon dioxide in a sandstone shale system. Chem. Geol. 217 (3-4), 295-318.
- Xu, T., Apps, J.A., Pruess, K., Yamamoto, H., 2007. Numerical modeling of injection and mineral trapping of CO₂ with h₂s and so₂ in a sandstone formation. Chem. Geol. 242 (3), 319–346.
- Xu, T., Gérard, F., Pruess, K., Brimhall, G., 1997. Modeling Non-isothermal Multiphase Multi-species Reactive Chemical Transport in Geologic Media. Tech. rep., Lawrence Livermore National Lab., CA, United States.
- Xu, T., Ontoy, Y., Molling, P., Spycher, N., Parini, M., Pruess, K., 2004b. Reactive transport modeling of injection well scaling and acidizing at tiwi field, philippines. Geothermics 33 (4), 477–491.
- Xu, T., Sonnenthal, E., Spycher, N., K, P., 2004c. Toughreact Users Guide: a Simulation Program for Nonisothermal Multiphase Reactive Geochemical Transport in Variably Saturated Geologic Media. Lawrence Berkeley National Laboratory, Berkeley, California.
- Yeh, G.T., Tripathi, V.S., 1991. A model for simulating transport of reactive multispecies components: model development and demonstration. Water Resour. Res. 27 (12), 3075–3094. http://dx.doi.org/10.1029/91WR02028.
- Zerai, B., Saylor, B.Z., Matisoff, G., 2006. Computer simulation of CO₂ trapped through mineral precipitation in the rose run sandstone, ohio. Appl. Geochem. 21 (2), 223–240.
- Zhang, R., 2013. Numerical simulation of thermal hydrological mechanical chemical processes during CO₂ geological sequestration. Ph.D. thesis. Colorado School of Mines.
- Zhang, R., Yin, X., Winterfeld, P.H., Wu, Y.-S., 2012a. A fully coupled model of nonisothermal multiphase flow, geomechanics, and chemistry during CO₂ sequestration in brine aquifers. Proc. TOUGH Symp. 838–848.
- Zhang, R., Yin, X., Wu, Y.-S., Winterfeld, P.H., 2012b. A fully coupled model of nonisothermal multiphase flow, solute transport and reactive chemistry in porous media. In: SPE Annual Technical Conference and Exhibition, 8–10 October, San Antonio, Texas, USA.
- Zysset, A., Stauffer, F., Dracos, T., 1994. Modeling of reactive groundwater transport governed by biodegradation. Water Resour. Res. 30 (8), 2423–2434. http:// dx.doi.org/10.1029/94WR01045.